Temperature Dependence of Infinite Dilution Activity Coefficients in Octanol and Octanol/Water Partition Coefficients of Some Volatile Halogenated Organic Compounds

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Infinite dilution activity coefficients and Henry's law coefficients have been measured for 11 halogenated C_1 to C_3 compounds in 1-octanol above room temperature using a gas–liquid chromatographic measurement method. Then, using our earlier data for these substances in water and a correlation relating the limiting activity coefficients of a substance in pure water and in pure 1-octanol to their octanol/water partition coefficients, these latter quantities have been computed. One conclusion from these measurements is that the limiting activity coefficients in octanol and the octanol/water partition coefficients of the halogenated compounds studied are only weakly dependent on temperature over the range from 25 to 50 °C. Also, from these and our earlier data, we have estimated the infinite dilution partial molar excess enthalpies and excess entropies of these compounds in both 1-octanol and water.

Introduction

The study of the fate and transport of volatile halogenated organic compounds in the environment is of interest as these chemicals, many of which have been classified as pollutants, are widely used as industrial solvents and are now appearing in water supplies. Some of these compounds have been demonstrated to have carcinogenic and/or mutagenic potential.

One property that is useful for analyzing the fate and transport of a pollutant in the environment is its activity coefficient, γ_i, defined by

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

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 pollutants in the environment are generally at very small concentrations, an important parameter is the infinite dilution activity coefficient, γ_i^∞ defined by

$$\lim_{x_i \to 0} \gamma_i(x_i) = \gamma_i^\infty \qquad (2)$$

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, H_i, can be computed from

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

where P_i^{sat} (T) is the pure component vapor pressure. The Henry's law constant is useful for designing separation and purification equipment, and for predicting the air/water distribution of a chemical. Infinite dilution activity coefficient measurements made by techniques such as ebulliometry or the static cell are slow. By using gas–liquid chromatography, accurate measurements can be made rapidly using extremely small amounts of the chemical of interest (Orbey and Sandler, 1991).

Another property useful for the characterization of pollutant behavior in the environment is the octanol/water partition coefficient for species i, $K_{\mathrm{OW},i}$, defined to be

$$K_{\mathrm{ow},i} = C_i^{\mathrm{op}}/C_i^{\mathrm{w}} \qquad (4)$$

where C_i^{op} and C_i^{w} are the concentrations (g/L) of the species in the octanol-rich and water-rich phases, respectively, when 1-octanol, water, and a small amount of the species are allowed to come to equilibrium. At 25 °C the octanol-rich phase in octanol/water partitioning is a mixture of 1-octanol and water (79.3 mol % 1-octanol) (Sorenson and Arlt, 1979); the water-rich phase is essentially pure water (99.99 mol % water).

The determination of Henry's law and octanol/water partition coefficients by traditional methods can be tedious and difficult. For example, the octanol/water partition coefficient of a hydrophobic compound is usually determined by allowing a long equilibration time with slow stirring (Organization of Economic Cooperation and Development, 1981) so that emulsions or microemulsions do not form, followed by a difficult analysis of a hydrophobic chemical that is very dilute and may adsorb on surfaces during sampling and analysis. Here we use a fast, accurate technique for the determination of the Henry's law and octanol/water partition coefficients based on a relative gas chromatographic method.

Relative Gas–Liquid Chromatographic Technique

As before (Tse et al., 1992) we use the relative gas–liquid chromatographic technique of Orbey and Sandler (1991) for the determination of the infinite dilution activity coefficient of a solute species in a solvent that has been loaded on a packed column. In this method a solute is injected into the column simultaneously with another species (the standard) whose infinite dilution activity coefficient in the solvent is known. One then measures the net retention time ratio, α_{BA}, defined by

$$\alpha_{\mathrm{BA}} = \frac{t_{\mathrm{B}} - t_{\mathrm{ref}}}{t_{\mathrm{A}} - t_{\mathrm{ref}}} \qquad (5)$$

where t denotes the retention times (mins) of the solute (A) whose infinite dilution coefficient is to be determined, the standard (B), and a reference chemical (ref) that does not interact with either the solvent loaded on the column or the column packing. Previously we have shown (Orbey

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and Sandler, 1991) that when the gas chromatograph is operated at low pressure, the net retention time ratio is related to the infinite dilution activity coefficients of the solute and the standard components in the solvent as follows:

$$\frac{\gamma_A^\infty}{\gamma_B^\infty} = (P_B^{sat}/P_A^{sat})\alpha_{AB} \qquad (6)$$

where P_i^{sat} is the species saturation pressure at the column operating temperature. Thus, from the known infinite dilution activity coefficient of species B in a given solvent, the limiting activity coefficient of species A can be determined on the basis of the knowledge of the saturation pressures and the relative net retention times of the substances through a column loaded with that solvent. Further, even if the vapor pressure of component A is not known, from eqs 3 and 6 its Henry's law coefficient can still be found from

$$H_A = \gamma_A^\infty P_A^{sat} = \gamma_B^\infty P_B^{sat}\alpha_{BA} = H_B\alpha_{BA} \qquad (7)$$

Previous work (Orbey and Sandler, 1991; Tse et al., 1992; Tse and Sandler, 1994) has shown that this relative gas chromatographic technique is very rapid and accurate when either water or 1-octanol is the solvent loaded on the column.

Experimental Method

To determine the net retention times of solutes through the column, either a 1 or 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. An HP 5890A gas–liquid chromatograph with a flame ionization detector (FID) was used with a 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 the set points (30, 35, 40, and 50 °C) using the thermostat in the gas chromatograph. 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. (1986) to be 2.81 at 25 °C. The value of the infinite dilution activity coefficient of hexane in 1-octanol at 40 °C was reported to be 2.77 by extrapolating VLE data measured by Heintz et al. (1986) to infinite dilution. Activity coefficients at 30, 35, and 50 °C were then determined using the two-constant relation

$$\ln \gamma_i^\infty(T) = \frac{\bar{G}_i^{E,\infty}}{RT} = \frac{\bar{H}_i^{E,\infty}}{RT} - \frac{\bar{S}_i^{E,\infty}}{R} \qquad (8)$$

where $\bar{G}_i^{E,\infty}$, $\bar{H}_i^{E,\infty}$, and $\bar{S}_i^{E,\infty}$ are the partial molar excess Gibbs free energy, enthalpy, and entropy, respectively, at infinite dilution. For the small temperature intervals of interest here, these last two quantities have been assumed to be constant. In the measurements here, hexane was used as the standard, and was injected into the column simultaneously with each of the solutes being studied. However, for 1,1-dichloroethane, *n*-heptane was used as the standard, since the retention time of 1,1-dichloroethane was too close to that of hexane to have an adequate separation of the components in the gas chromatograph. Also, since hexane had a very short retention time on the 1 ft column used for the 1,1,2-trichloroethane measurements, heptane was used as the reference for that substance as well. The infinite dilution activity coefficients of heptane in 1-octanol were also determined here using hexane as the standard. Consequently, the errors in the infinite dilution activity coefficients for 1,1-dichloroethane and 1,1,2-trichloroethane include the errors for both their measurements and that for heptane, and are about twice that of the other chemicals studied.

The measurement procedure involved first completely loading the column with the 1-octanol. The loaded column was then installed in the chromatograph, and after stable operating conditions were attained, approximately 75 mL of methane was injected to determine the reference retention time, t_{ref}. Then, approximately 0.04 mL samples which consisted of the solute and the hexane standard were injected. Periodically methane reference gas was injected between analyses to account for variations in t_{ref} as a result of the small amount of 1-octanol being continually, but very slowly, stripped off the column.

Infinite Dilution Activity Coefficients in 1-Octanol

The vapor pressures needed for the calculation in eq 7 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) (1995) or from correlations in the literature (Ohe, 1976). 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, and the measured net retention time ratio α_{BA}. There are no other data for the infinite dilution activity coefficients of these chemicals in 1-octanol at these temperatures to compare with.

We have used eq 8, the equation

$$\frac{\partial}{\partial T}\left(\frac{\bar{G}_i^{E,\infty}}{RT}\right) = \left(\frac{\partial \ln \gamma_i^\infty}{\partial T}\right) = -\frac{\bar{H}_i^{E,\infty}}{RT^2} \qquad (9)$$

the data we report in Table 1, and infinite dilution activity coefficient data for the same components in water reported earlier (Tse et al, 1992; Wright et al., 1992) to compute average values of their excess partial molar enthalpies and entropies at infinite dilution in water and in octanol. These values are given in Table 2. Because of the small temperature range studied, and the limited number of data points, we estimate these values to be accurate only to about ±25%, and therefore of only qualitative accuracy. The main observation to be made from the values reported in Table 2 is that the partial molar excess entropies at infinite dilution for these components are very large and negative in water, and smaller in magnitude and generallly positive in 1-octanol. Also, with few exceptions, excess enthalpies of these components are similar in both water and 1-octanol.

Previously (Tse and Sandler, 1992) we have shown that the following relation exists between the octanol/water partition coefficient of a species and its infinite dilution activity coefficients in pure water and in pure 1-octanol:

$$\log K_{ow} = 0.10 + 0.91 \log(0.1508(\gamma_i^{\infty,w}/\gamma_i^{\infty,o})) \qquad (10a)$$

or equivalently

$$\log K_{ow,i} = 0.65 + 0.91 \log(\gamma_i^{\infty,w}) - 0.91 \log(\gamma_i^{\infty,o}) \qquad (10b)$$

This correlation is valid for a wide range of hydrophobicities. Using this simple correlation, the octanol/water partition coefficients were calculated for the chemicals studied here, and the values also appear in Table 1.

Table 1. Measured Net Retention Time Ratios, Computed Infinite Dilution Activity Coefficients in Octanol, γ, Estimated Error in γ , $\delta\gamma$, Henry's Law Coefficients, H, and Octanol/Water Partition Coefficients, log K_{ow}, as a Function of Temperature

compound	P^{sat}/bar	t/°C	net retention time ratio	γ	error in $\pm\delta\gamma$	$10^4 H$/(m^3 atm mol^{-1})	log K_{ow}
dichloromethane	0.5840	25	1.61	1.57	0.26		1.35
	0.8498	35	1.56	1.58	0.34	1.65	1.34
	1.4394	50	1.41	1.45	0.33	2.57	1.37
dibromomethane	0.0603	25	0.227	2.15	0.36		1.70
	0.0953	35	0.263	2.36	0.51	0.277	1.65
	0.1826	50	0.277	2.25	0.49	0.506	1.64
chloroform	0.2620	25	0.465	1.02	0.18		2.00
	0.3985	35	0.481	1.03	0.22	0.507	2.01
	0.7017	50	0.508	1.07	0.24	0.928	2.00
carbon tetrachloride	0.1520	25	0.486	1.83	0.25		2.73
	0.1889	30	0.462	1.71	0.37	0.399	2.74
	0.2845	40	0.464	1.69	0.38	0.592	2.73
1,1 dichloroethane	0.3030	25		2.01	0.345	0.58	1.82
	0.4480	35	2.96	2.01	0.85	1.11	1.66
	0.7811	50	2.62	1.90	0.81	1.82	1.68
1,2 dichloroethane	0.1050	25	0.494	2.68	0.40		1.51
	0.1667	35	0.496	2.55	0.55	0.523	1.51
	0.3113	50	0.486	2.31	0.51	0.887	1.53
1,1,1-trichloroethane	0.1650	25	0.572	1.98	0.35		2.47
	0.2776	35	0.570	1.76	0.38	0.600	2.50
	0.5168	50	0.568	1.63	0.36	1.04	2.52
1,1,2-trichloroethane	0.03100	25		2.18	0.22		1.98
	0.04943	35	0.342	2.11	0.89	0.128	1.93
	0.10230	50	0.351	1.96	0.83	0.245	1.94
1,1,1,2-tetrachloroethane	0.02123	30	0.057	1.88	0.41	0.049	2.62
	0.03588	40	0.062	1.80	0.39	0.079	2.62
1,2-dichloropropane	0.0693	25	0.313	2.58	0.44		1.99
	0.1076	35	0.316	2.52	0.54	0.333	1.99
	0.2047	50	0.321	2.32	0.51	0.585	1.99
heptane	0.0607	25	0.325	3.05	0.59		
	0.0993	35	0.356	3.07	0.66	0.375	
	0.1901	50	0.382	2.97	0.65	0.696	

Table 2. Calculated Infinite Dilution Excess Enthalpies and Entropies in Octanol and in Water of the Chemicals Studied Here

	octanol		water	
compound	$\bar{H}^{E,\infty}$/ (J mol^{-1})	$\bar{S}^{E,\infty}$/ (J mol^{-1} K^{-1})	$\bar{H}^{E,\infty}$/ (J mol^{-1})	$\bar{S}^{E,\infty}$/ (J mol^{-1} K^{-1})
dichloromethane	2747	5.33	393	−44.33
dibromomethane	−1084	−10.25	3662	−43.54
chloroform	−1585	−5.45	−1534	−61.00
bromoform	21460	−32.46	5074	−52.34
carbon tetrachloride	3640	7.33	2052	−69.13
1,1-dichloroethane	1922	0.56	1075	−54.15
1,2-dichloroethane	4824	7.94	3139	−43.07
1,1,1-trichloroethane	6050	14.74	2011	−64.47
1,1,2-trichloroethane	3469	5.11	2987	−50.82
1,1,1,2-tetrachloroethane	3432	6.07	3403	−62.79
1,2 dichloropropane	3509	3.82	3123	−52.91
heptane	941	−6.18		

Conclusions

A relative gas chromatographic technique for the determination of infinite dilution activity coefficients presented earlier was used here over a limited range of temperatures with 11 halogenated C_1 to C_3 hydrocarbons as solutes and 1-octanol as the solvent. With the exception of bromoform, the infinite dilution activity coefficients were in the range from 1 to 2.5. Using these results, together with the aqueous infinite dilution activity coefficients for these same substances in the same temperature range we measured earlier, and a simple correlation, we have estimated the octanol/water partition coefficients for each of these halogenated hydrocarbons. Finally, from the measured infinite dilution activity coefficients in water and in 1-octanol as a function of temperature, we were able to compute the infinite dilution partial molar excess enthalpies and entropies of the halogenated hydrocarbons in each of these solvents. While the partial molar excess enthalpies of the solutes in water and in 1-octanol are similar, the excess entropies in water are much larger in magnitude than in 1-octanol and negative, demonstrating the role of these solutes as breakers of the intermolecular water structure.

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