Sorption of Chlorobenzene Vapors on Styrene−Divinylbenzene Polymer

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Headspace gas chromatography was used to measure sorption equilibra between XAD-2, a styrene−divinylbenzene copolymer, and gaseous 1,2-dichlorobenzene (1,2-DiCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) and hexachlorobenzene (HCB) at temperatures above 40 °C. From the measurements, the sorption isotherms were constructed for the systems 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2. It is shown that (a) capillary condensation within the mesopore structure of XAD-2 occurs at higher partial pressures; (b) the equilibrium data at relatively low partial pressures can be fitted to Freundlich isotherms; and (c) the sorption isotherms for the three compounds of interest are linear at very low partial pressures. Sorption coefficients at low partial pressures and 20 °C, extrapolated from the slopes of the linear isotherms obtained in the temperature range 90 °C to 130 °C, were (1.2×10^{-6}, 1.5×10^{-5}, and 1.6×10^{-2}) $\mathrm{mol{\cdot}m^{-2}{\cdot}Pa^{-1}}$ for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2, respectively. This is in good agreement with values predicted using empirical models proposed in the literature.

Introduction

Static headspace gas chromatography (HS-GC) is routinely used for determining the phase distribution of volatile compounds in gas/liquid or gas/solid systems. This technique is based on the equilibrium partitioning of the compounds between a liquid or solid sample and the gas phase followed by a transfer of this gas phase to a gas chromatograph for separation and quantitative analysis. In particular, this technique has been employed for characterizing sorption equilibria between vapors and polymeric sorbents.[1,2] Porous polymers, in particular styrene−divinylbenzene copolymers, are widely used as stationary phases for gas and liquid chromatography[3−5] and sorbents for the separation of organic compounds from air[6−8] and water.[9−11] The main reason for being very popular as separating media lies in their hydrophobic behavior, high retention, inertness, and excellent performance in handling a wide range of organic compounds. Porous polymers have also been found to separate most of the inorganic gases efficiently.[12]

The need for quantitative information about the uptake of organic vapors in polymers arises in many investigations, for example, when there is a need to know the application limit of a sorbent for air sampling purposes. Attempts thus have been made to characterize and quantify the sorption of organic compounds by porous polymers. Gallant and coworkers characterized XAD-2 and Tenax-GC sorbents with a variety of organic probe compounds,[13] whereas Pankow and co-workers investigated gas/solid retention volumes of organic compounds on styrene−divinylbenzene and ethylvinylbenzene−divinylbenzene copolymer sorbents.[14] Both studies employed inverse gas chromatography and were thus limited to relatively volatile organic compounds. Using experimental retention volumes reported in the literature, Poole and Poole characterized the sorption properties of some styrene−divinylbenzene porous polymer sorbents using linear solvation energy relationships.[15]

In this work we report the results of a study on the sorption of 1,2-dichlorobenzene (1,2-DiCB), 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB), and hexachlorobenzene (HCB) on Amberlite XAD-2, one of the mostly commonly used styrene−divinylbenzene copolymers. Isotherms of sorption at different partial pressures are measured and discussed. Sorption coefficients at low partial pressures are determined and evaluated by comparison with estimated values.

Experimental Section

Materials. 1,2-DiCB (99%) and HCB (ex (Cl) 100 ± 0.5%) were purchased from BDH Chemicals Ltd.; 1,2,4,5-TeCB (98%) was purchased from Aldrich Chemical Co. Inc. The nonionic styrene−divinylbenzene polymer Amberlite XAD-2 (20−60 mesh, 350 m^2/g surface area, 9 nm pore diameter) was obtained from Supelco Inc. The resin was washed with Milli-Q water, methanol, acetonitrile, and dichloromethane, and dried with nitrogen prior to use.

Instrumentation. The experiments were performed on a Hewlett-Packard HP-7694 automatic headspace sampler connected to a HP-5890 series II gas chromatograph. A flame ionization detector (250 °C) was used when quantifying the vapor concentrations of 1,2-DiCB and 1,2,4,5-TeCB, whereas an electron capture detector (300 °C, argon/methane as make-up gas) served to detect HCB. A fused-silica, open-tubular column (DB-5, 25 m, 0.32 mm i.d., 0.25 μm film thickness, J&W Scientific, Folsom, CA) was used. The carrier gas was helium. The volume of the headspace (HS) vials V_{tot} was determined gravimetrically to be 22.02 ± 0.18 mL.

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When analyzing for 1,2-DiCB, the column and injector were kept at temperatures of 100 °C and 180 °C, respectively. Depending on the amount of 1,2-DiCB in the HS vials, the split ratio varied between 100:1 and 25:1. For the analysis of 1,2,4,5-TeCB, the column was kept at 110 °C, the injector temperature was 250 °C, and the split ratio was 15:1. For the HCB, the GC oven was kept at 50 °C for 4 min and then raised to 160 °C at 25 $°C\cdot min^{-1}$ and held at that temperature for a further 10 min; the injector had a temperature of 250 °C and was operated with a split ratio of 25:1.

The HS parameters for all three systems were 0.50 min pressurization time, 0.01 min loop fill time, 0.20 min loop equilibration time, and 0.05 min injection time. The equilibration temperatures varied within the range 40 °C to 130 °C.

Sorption Experiments. The primary data obtained from the HS-GC measurements are the peak area of the test compound, which is a function of the amount of the compound passing the detector. To obtain an isotherm at a given temperature, the partial pressure of the gaseous compound has to be determined from the peak area. In this study, the vapor phase calibration (VPC) method was used,[16] which determines the partial pressure of the test compound in the gas phase by external standard calibration. The concentration in the sorbent at equilibrium is then derived from the difference between the total amount added into the vial and that present in the gas phase. The following equations were applied for calculation of the partial pressure of the test compound in the gas phase and its concentration in the sorbent:

$$C_g = m_g/V_g = fA_g \tag{1}$$

$$V_g = V_{tot} - V_s \tag{2}$$

$$P = C_gRT = fA_gRT \tag{3}$$

$$C_s = (m_{tot} - m_g)/(MS) = (m_{tot} - fA_gV_g)/(MS) \tag{4}$$

where $C_g/mol\cdot m^{-3}$ and $C_s/mol\cdot m^{-2}$ are the respective concentrations of the test compound in the gas phase and the sorbent; m_{tot}/mol and m_g/mol are the total amount in the vial and the amount in the gas phase; M/g is the mass of sorbent added into the vial; $S/m^2\cdot g^{-1}$ is the specific surface area of the sorbent; V_{tot}, V_g, and V_s are the total volume of the vial and the volumes of the gas phase and the sorbent, respectively; P/Pa is the partial pressure of the test compound; R is the gas constant; T/K is the temperature; A_g is the peak area for the test compound in an aliquot of the headspace; and f is the proportionality constant.

In this work, the calibration curve was obtained by analyzing HS vials that contained appropriate amounts of the test compounds and had been thermostated at 120 °C. Stock solutions were made by dissolving the chlorobenzenes in hexane. The aliquots of the stock solutions were injected into the HS vials and totally evaporated at 120 °C. For the determination of sorption isotherms, accurately known masses of XAD-2 and an appropriate amount of a chlorobenzene were placed into the HS vials. After sealing and thermostating at a certain temperature for equilibration, the test compounds in the gas phase were transferred to the gas chromatograph for analysis. The time required to establish sorption equilibrium was estimated by analyzing a series of HS vials containing the sorbates and XAD-2 at a certain temperature. With increasing equilibration time, the detector signals decreased to a minimum constant value. The partial pressures in the gas phase and the concentrations present in XAD-2 were calculated using eqs 1−4, and then used to construct the isotherms. The sorption coefficients for the systems 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2 were obtained from the slopes of the linear sorption isotherms that were obtained at very low partial pressures.

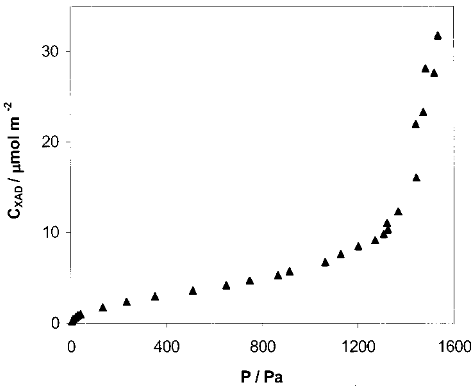

Figure 1. Sorption isotherm of 1,2-DiCB/XAD-2 at 70 °C.

Results and Discussion

Determination of Equilibration Time. The equilibration time refers to the time necessary to reach the minimum partial pressure of the test compound in the gas phase. For the systems of interest, the equilibration time was found to increase with decreasing temperature. In particular, the following thermostating times were found to be sufficient to ensure an equilibrium distribution of the chlorobenzenes in the HS vials: 120 min at 40 °C to 70 °C; 90 min at 90 °C to 110 °C; and 60 min at 120 °C to 130 °C.

A sorption isotherm is the quantitative relationship between the amount of gas sorbed by the sorbent and the partial pressure of the gas at a given temperature. Sorption isotherms were obtained within different ranges of gas partial pressure.

Sorption of 1,2-DiCB at High Partial Pressures. Figure 1 shows the isotherm obtained at 70 °C for the sorption of 1,2-DiCB on XAD-2 across a large partial pressure range. The isotherm obtained was found to be made up of three parts: concave to the pressure axis in the low pressure region; convex in the relatively high pressure region; and approximately linear in the middle region. A sharp point indicating the completion of monolayer coverage did not appear. This isotherm is consistent with the characteristic shapes exhibited by mesoporous solids with pore widths in the range (2 to 50) nm. According to Sing,[17] the isotherm on a mesoporous sorbent in the monolayer region follows the same pathway as the isotherm on the nonporous sorbent with the same surface area. However, at relatively high partial pressures, for example, above 1300 Pa for 1,2-DiCB, a mesoporous sorbent can sorb more vapors than a nonporous sorbent, which is the direct result of capillary condensation occurring within the mesopore structure at pressures well below the saturation vapor pressure of the compound, which is above 2600 Pa for 1,2-DiCB at 70 °C.[18] Therefore, capillary condensation can play an important secondary role in the sorption of vapors by mesoporous sorbents.

Sorption of 1,2-DiCB at Relatively Low Partial Pressures. Figure 2 shows the measured isotherms of 1,2-DiCB on XAD-2 at 40 °C to 70 °C in the $P/P°$ range 0.05 to 0.30, where $P°$ refers to the saturation vapor pressure at a

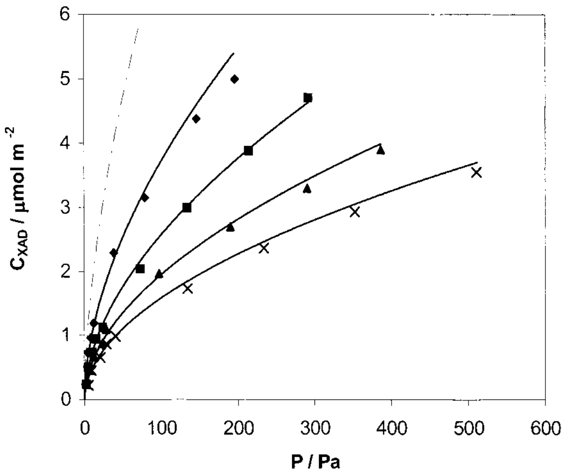

Figure 2. Sorption isotherms of 1,2-DiCB/XAD-2 at (◆) 40 °C, (■) 50 °C, (▲) 60 °C, (×) 70 °C, and 20 °C (calculated, dashed line).

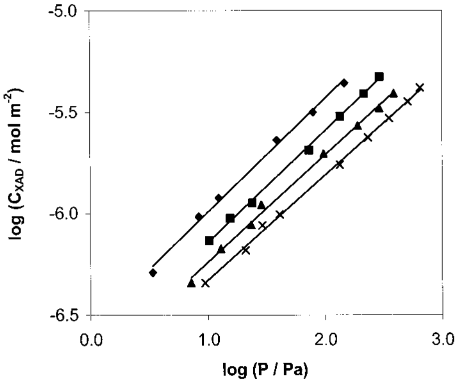

Figure 3. Freundlich isotherms of 1,2-DiCB/XAD-2 at (◆) 40 °C, (■) 50 °C, (▲) 60 °C, and (×) 70 °C.

Table 1. Regression Parameters of Freundlich Isotherms on XAD-2 for 1,2-DiCB

t/°C	log K_F	*n*	r^2
40	−6.55 ± 0.03	1.79 ± 0.06	0.995
50	−6.69 ± 0.01	1.82 ± 0.03	0.999
60	−6.77 ± 0.02	1.89 ± 0.04	0.997
70	−6.84 ± 0.02	1.92 ± 0.04	0.998

given temperature. The experimental data are quite well described by a Freundlich isotherm:

$$C_s = K_F P^{1/n} \tag{5}$$

where K_F is an indicator of sorption capacity and *n*, which is usually greater than unity, is a measure of the nonlinearity of the sorption isotherm. The larger *n*, the more nonlinear the sorption isotherm. K_F and *n* are temperature-dependent parameters and can be obtained by plotting log C_s against log *P*:

$$\log(C_s/\text{mol}\cdot\text{m}^{-2}) = \log(K_F/\text{mol}\cdot\text{m}^{-2}\cdot\text{Pa}^{-(1/n)}) + (1/n)\log(P/\text{Pa}) \tag{6}$$

yielding a straight line with a slope of 1/*n* and an intercept of log K_F. Figure 3 shows such Freundlich plots for the data displayed in Figure 2. The regression parameters for the Freundlich isotherms for 1,2-DiCB/XAD-2 are listed in Table 1. High regression coefficients r^2 suggest that the Freundlich equation is obeyed. Freundlich isotherms were also observed by Xu[19] for the systems of naphthalene derivatives/XAD-2 and Sarzanini[11] for PAN/XAD-2 and TAN/XAD-2.

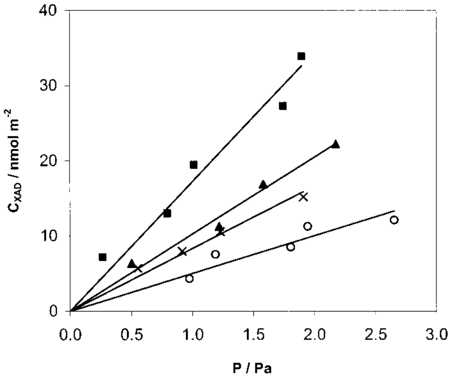

Figure 4. Sorption isotherms of 1,2-DiCB/XAD-2 at (■) 100 °C, (▲) 110 °C, (×) 120 °C, and (○) 130 °C.

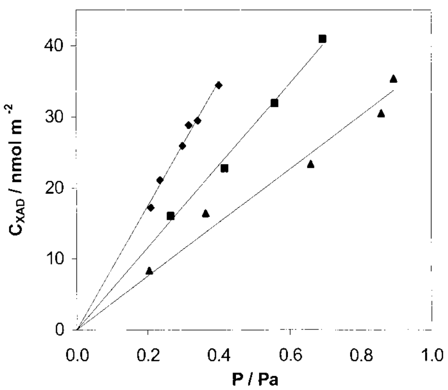

Figure 5. Sorption isotherms of 1,2,4,5-TeCB/XAD-2 at (◆) 110 °C, (■) 120 °C, and (▲) 130 °C.

To extrapolate the sorption isotherms for 1,2-DiCB/XAD-2 to lower temperatures, we regressed log K_F and *n* against reciprocal absolute temperature:

$$\log(K_F/\text{mol}\cdot\text{m}^{-2}\cdot\text{Pa}^{-(1/n)}) = (1025 \pm 106)/(T/\text{K}) - (9.84 \pm 0.32) \quad r^2 = 0.979 \tag{7}$$

$$n = -(516 \pm 55)/(T/\text{K}) - (3.43 \pm 0.17) \quad r^2 = 0.978 \tag{8}$$

Using these equations, it is possible to estimate a K_F of 4.5×10^{-7} and an *n* of 1.67 for the sorption of 1,2-DiCB onto XAD-2 at 20 °C. The isotherms at 20 °C constructed from these extrapolated parameters are included in Figure 2.

Sorption of 1,2-DiCB, 1,2,4,5-TeCB, and HCB at Very Low Partial Pressures. When using XDA-2 as a sorbent for the sampling of organic vapors from air, information on the uptake capacity of XAD-2 in a very low partial pressure range is required for designing experiments and interpreting results. Isotherms at very low partial pressures were investigated for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2. As shown in Figures 4−6, the concentrations of the test compounds in XAD-2 increase linearly with increasing partial pressures. This allows sorption coefficients *K* for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2 to be derived from the slopes of the linear isotherms. Table 2 lists the measured sorption coefficients *K* at different temperatures.

The logarithm of the *K* values in Table 2 was regressed against reciprocal absolute temperature (see Figure 7),

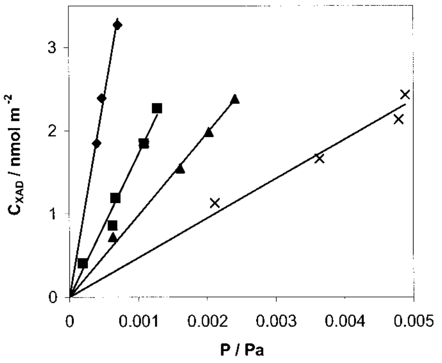

Figure 6. Sorption isotherms of HCB/XAD-2 at (◆) 90 °C, (■) 100 °C, (▲) 110 °C, and (×) 120 °C.

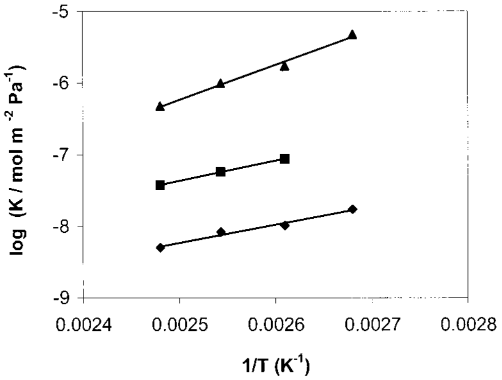

Figure 7. Relationship between logarithm of *K* and reciprocal absolute temperature for (◆) 1,2-DiCB/XAD-2, (■) 1,2,4,5-TeCB/XAD-2, and (▲) HCB/XAD-2.

Table 2. *K* Values for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2 at Different Temperatures

	K/mol·m^{-2}·Pa^{-1}		
t/°C	1,2-DiCB	1,2,4,5-TeCB	HCB
100	$(1.72 \pm 0.08) \times 10^{-8}$		$(4.73 \pm 0.13) \times 10^{-6}$
110	$(1.02 \pm 0.04) \times 10^{-8}$	$(8.69 \pm 0.11) \times 10^{-8}$	$(1.72 \pm 0.06) \times 10^{-6}$
120	$(8.31 \pm 0.32) \times 10^{-9}$	$(5.78 \pm 0.11) \times 10^{-8}$	$(9.84 \pm 0.17) \times 10^{-7}$
130	$(5.00 \pm 0.32) \times 10^{-9}$	$(3.77 \pm 0.14) \times 10^{-8}$	$(4.74 \pm 0.16) \times 10^{-7}$

yielding the following linear regression equations:

1,2-DiCB:

$$\log(K/\text{mol·m}^{-2}\text{·Pa}^{-1}) = (2555 \pm 287)/(T/\text{K}) - (14.62 \pm 0.74)\quad r^2 = 0.975 \qquad (9)$$

1,2,4,5-TeCB:

$$\log(K/\text{mol·m}^{-2}\text{·Pa}^{-1}) = (2800 \pm 79)/(T/\text{K}) - (14.36 \pm 0.20)\quad r^2 = 0.999 \qquad (10)$$

HCB:

$$\log(K/\text{mol·m}^{-2}\text{·Pa}^{-1}) = (4881 \pm 356)/(T/\text{K}) - (18.44 \pm 0.92)\quad r^2 = 0.989 \qquad (11)$$

These relationships allow the estimation of *K* at lower temperatures. In particular, sorption coefficients of 1.2 × 10^{-6}, 1.5 × 10^{-5}, and 1.6 × 10^{-2} mol·m^{-2}·Pa^{-1} at 20 °C can be deduced for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HCB/XAD-2, respectively.

Comparison of *K* Values at 20 °C with Values Predicted Using Empirical Equations Suggested in the Literature. Various relationships have been proposed to estimate sorption properties of organic compounds onto styrene−divinylbenzene copolymers from more readily available parameters. Specifically, Pankow et al. presented a model based on vapor pressure and another one based on boiling point,[14] whereas Poole and Poole suggested linear solvation energy relationships.[15]

To predict the specific retention volume $V_{g,20}$/L·g^{-1} of a wide range of organic compounds on styrene−divinylbenzene and ethylvinylbenzene−divinylbenzene sorbents at 20 °C, Pankow et al.[14] proposed the following general equations:

$$\log(V_{g,20}/\text{L·g}^{-1}) = -1.16\log(P_L/\text{Pa}) + 1.05 \qquad (12)$$

$$\log(V_{g,20}/\text{L·g}^{-1}) = 0.0227\log(T_b/\text{K}) - 6.60 \qquad (13)$$

On 3M(a) (350 m^2·g^{-1}) sorbent, sorption properties of compounds can be predicted using

$$\log(V_{g,20}/\text{L·g}^{-1}) = -0.99\log(P_L/\text{Pa}) + 0.936 \qquad (14)$$

$$\log(V_{g,20}/\text{L·g}^{-1}) = 0.0175\log(T_b/\text{K}) - 4.97 \qquad (15)$$

where P_L/Pa and T_b/K are the liquid vapor pressure and standard boiling point of a compound, respectively. To obtain the P_L value of 1,2-DiCB at 20 °C, the Wagner-type equation with the parameters given by Roháč et al. was used.[20] For 1,2,4,5-TeCB and HCB, the solid vapor pressure P_S values at 20 °C were first derived from regression of the logarithm of P_S against reciprocal absolute temperature. The P_S data at different temperatures were taken from the compilation by Shiu and Ma.[18] The P_S values at 20 °C were then converted to P_L using the entropy of fusion $\Delta_{fus}S$/J·mol^{-1}·K^{-1} at the melting point T_m/K:[21]

$$\ln(P_S/P_L) = -\Delta_{fus}S/R(T_m/293.15\ \text{K} - 1) \qquad (16)$$

The $\Delta_{fus}S$ values for 1,2,4,5-TeCB and HCB are 60.4 and 50.2 J·mol^{-1}·K^{-1}, respectively.[22] All melting point and boiling point temperatures were obtained from the *CRC Handbook of Chemistry and Physics*[23] and are listed in Table 3, together with the obtained P_L values.

LSERs are used to correlate a solubility-related property SP, such as a specific retention volume or a distribution coefficient, with a number of solute descriptors:[24]

$$\log \text{SP} = c + rR_2 + s\pi_2^{\text{H}} + a\sum\alpha_2^{\text{H}} + b\sum\beta_2^{\text{H}} + l\log L^{16} \qquad (17)$$

where R_2 is an excess molar refraction; π_2^{H} is a combined dipolarity−polarizability descriptor; $\Sigma\alpha_2^{\text{H}}$ and $\Sigma\beta_2^{\text{H}}$ are the overall solute hydrogen-bond acidity and solute hydrogen-bond basicity; and L^{16} is the solute gas−hexadecane partition coefficient at 298 K. All five descriptors are assumed to be independent of temperature.[25] The set of coefficients *c, r, s, a, b,* and *l* characterizes the system in which the SP is measured. Poole and Poole derived the coefficients *c, r, s, a, b,* and *l* to predict the sorption properties of organic compounds onto some styrene−divinylbenzene copolymers.[15] The retention volumes on 3M-(a) (350 m^2·g^{-1}), a styrene−divinylbenzene copolymer, can be described with the following equation:

$$\log(V_{g,20}/\text{L·g}^{-1}) = -1.92 - 0.70R_2 + 0.54\sum\alpha_2^{\text{H}} + 0.85\sum\beta_2^{\text{H}} + 1.21\log L^{16} \qquad (18)$$

where *s* equals zero, indicating that interactions of a dipole type are not significant for styrene−divinylbenzene sorbents. On XAD-2 (364 m^2·g^{-1}), the retention volumes at

Table 3. Solute Descriptors of 1,2-DiCB, 1,2,4,5-TeCB, and HCB[a]

				LSER descriptors				
compound	$P_{L,20}$/Pa	t_b/°C	t_m/°C	R_2	π_2^H	$\Sigma\alpha_2^H$	$\Sigma\beta_2^H$	log L^{16}
1,2-DiCB	133.6	80.5	−17	0.872	0.78	0.00	0.04	4.518
1,2,4,5-TeCB	13.22	243−6	139−40	1.160	0.86	0.00	0.00	5.926
HCB	0.1156	322	230	1.466	1.37	0.00	0.07	7.888

[a] For sources, see text.

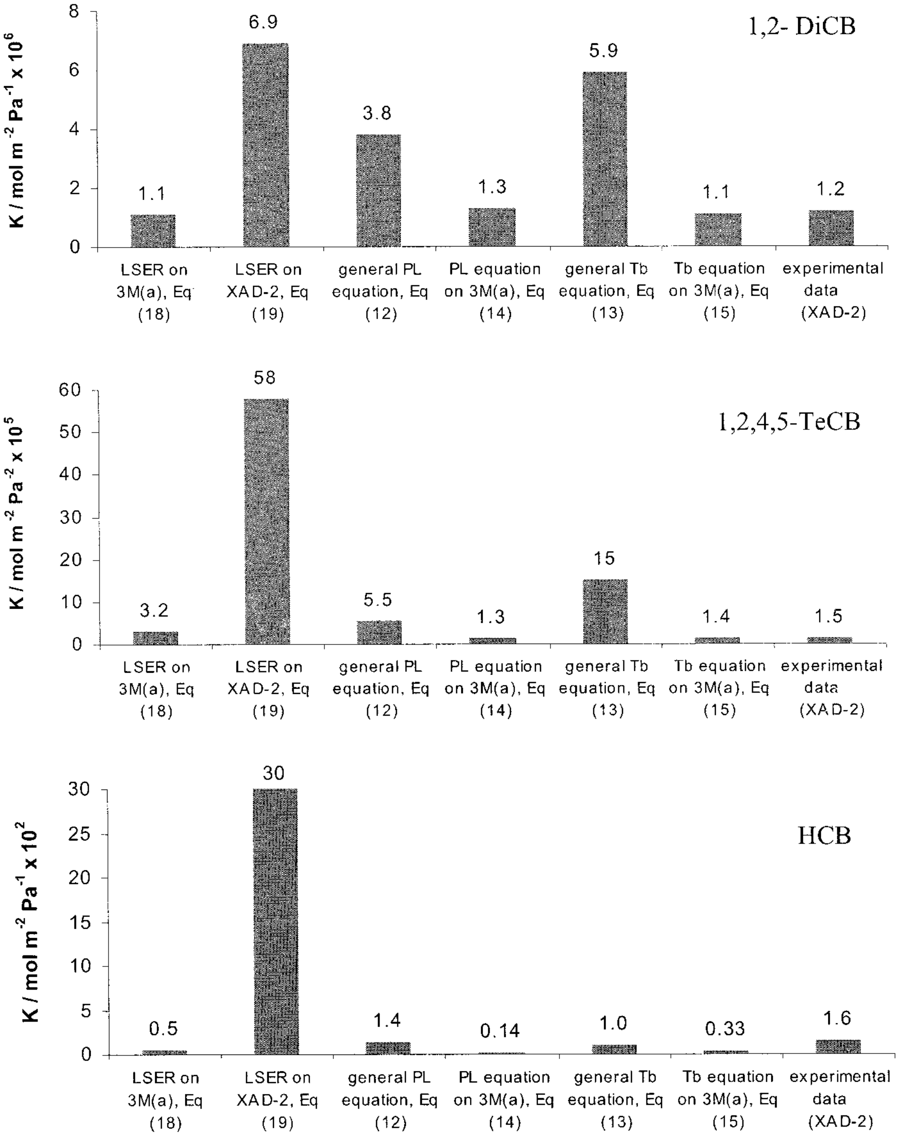

Figure 8. Comparison of the distribution coefficients at 20 °C for 1,2-DiCB/XAD-2, 1,2,4,5-TeCB/XAD-2, and HxCB/XAD-2 with values predicted using empirical equations.

20 °C can be calculated using

$$\log(V_{g,20}/\mathrm{L \cdot g^{-1}}) = -2.46 + 0.44R_2 + 0.85\sum\alpha_2^{H} + 0.65\sum\beta_2^{H} + 1.29 \log L^{16} \quad (19)$$

Table 3 lists the solute descriptors of 1,2-DiCB and 1,2,4,5-TeCB from the database provided by Abraham et al.[24] and those of HCB calculated using a group contribution approach.[26]

Equations 12−15, 18, and 19 were used to predict the specific retention volumes $V_{g,20}$ for the three chlorobenzenes at 20 °C. $V_{g,20}$ is related with the sorption coefficient K used in this study through the following equation:[13]

$$K = V_g/(SRT) \quad (20)$$

The predicted K values at 20 °C are shown in Figure 8 together with the experimental results. In general, the predicted K values are in reasonable agreement with our experimental results. All of the K values predicted from P_L and T_b show good agreement, but the predictions resulting from eqs 14 and 15 are even better and in the case of 1,2-DiCB and 1,2,4,5-TeCB almost identical with the experimental value. This is consistent with the conclusion made by Pankow et al. that P_L and T_b are equally useful for predicting sorption onto styrene–divinylbenzene sorbents.[14] Among the two LSER equations, eq 18 performs much better than eq 19, which tends to overestimate the sorption coefficient, sometimes by as much as an order of magnitude. Poole and Poole derived eq 18 from measured retention volumes by Pankow et al. and eq 19 from data by Gallant et al. The deviation of the results predicted by these two equations confirms the statement of Poole and Poole that the data by Pankow et al. are more useful for predicting sorption onto styrene–divinylbenzene sorbents.

Equations 14, 15, and 18, which are specific for the sorbent 3M(a) (350 $m^2 \cdot g^{-1}$), proved superior to eqs 12, 13, and 19. This might be due to the fact that 3M(a) has the same specific surface area as that of the XAD-2 used in this study. These three equations are likely to provide the most reliable prediction of the sorption coefficients of the chlorobenzenes and other semivolatile nonpolar organic substances onto Amberlite XAD-2.

The results of this study allow the estimation of appropriate sampling volumes when XAD-2 is used for sampling organic compounds from air. Equation 20 relates the reported K values with retention volumes V_g. For example, the specific retention volumes at 20 °C, $V_{g,20}$, of XAD-2 for 1,2-DiCB, 1,2,4,5-TeCB, and HCB are 1 $m^3 \cdot g^{-1}$, 10 $m^3 \cdot g^{-1}$, and 10^4 $m^3 \cdot g^{-1}$, respectively. For compounds less volatile than the chlorobenzenes, the retention volumes are larger than 10^4 $m^3 \cdot g^{-1}$. Knowledge of the retention volume can guide the selection of safe sampling volumes and helps to prevent sample loss by breakthrough.

Acknowledgment

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Literature Cited

(1) Kolb, B.; Ettre, L. S. *Static Headspace-Gas Chromatography: Theory and Practice*; Wiley-VCH: New York, 1997.
(2) Schoene, K.; Steinhanses, J.; König, A. Determination of the Solubility of Vapours in Polymers by Automated Headspace Gas Chromatography. *J. Chromatogr.* **1988**, *455*, 67–75.
(3) Gawdzik, B.; Gawdzik, J.; Czerwinska-Bil, U. Copolymer of Bis-(methacryloyloxymethyl) naphthalene and Divinylbenzene as a Column Packing for High-performance Liquid Chromatography. *Chromatographia* **1988**, *26*, 399–407.
(4) Jahangir, L. M.; Samuelson, O. Chromatography in Aqueous Solution on Styrene-Divinylbenzene Resins. *J. Chromatogr.* **1980**, *193*, 197–206.
(5) Jessen, E. B.; Taugboel, K. T. Separation and Purification of Organotin Halides. *J. Chromatogr.* **1979**, *168*, 139–142.
(6) Rexwinkel, G.; Heesink, B. B. M.; Van Swaajj, W. P. M. Adsorption of Halogenated Hydrocarbons from Gaseous Streams by Amberlite XAD-4 Resin and Activated Carbon: Equilibria. *J. Chem. Eng. Data* **1999**, *44*, 1146–1150.
(7) Podlesnyuk, V. V.; Hradil, J.; Kralova, E. Sorption of Organic Vapours by Macroporous and Hypercross-linked Polymeric Adsorbents. *React. Funct. Polym.* **1999**, *42*, 181–191.
(8) Hillery, B. R.; Basu, I.; Sweet, C. W.; Hites, R. A. Temporal and Spatial Trends in a Long-Term Study of Gas-Phase PCB Concentrations near the Great Lakes. *Environ. Sci. Technol.* **1997**, *31*, 1811–1816.
(9) Rexwinkel, G.; Heesink, B. B. M.; Van Swaajj, W. P. M. Adsorption of Halogenated Hydrocarbons from Aqueous Solutions by Hydrophobic and Hydrophilic Sorbent: Equilibria. *J. Chem. Eng. Data* **1999**, *44*, 1139–1145.
(10) Kuo, H.; Wang, J. Collection and Determunation of 4, 4′-Bipyridine Vapor Using XAD-2 resin. *Chemosphere* **1996**, *32*, 2057–2065.
(11) Sarzanini, C.; Porta, V.; Mentasti, E. Study of Adsorption of 1-(2′-pyridylazo)-2-Naphthol (PAN) and 1-(1′, 3′-thiazolyl-2′-azo)-2-Naphthol (TAN) onto Styrene-Divinylbenzene Polymers. *New J. Chem.* **1989**, *13*, 463–471.
(12) Castello, G.; D′Amato, G. Determination of Sulfur and Nitrogen Gases by Gas Chromatography on Polystyrene Porous Polymer Columns. *J. Chromatogr.* **1991**, *585*, 93–100.
(13) Gallant, R. F.; King, J. W.; Levins, P. L.; Piecewicz, J. F. *Characterization of Sorbent Resins for Use in Environmental Sampling*; EPA-600/7-78-054; U.S. Environmental Protection Agency: Washington, DC, 1978.
(14) Pankow, J. F.; Luo, W.; Isabelle, L. M.; Hart, K. M.; Hagen, D. F. Gas–solid Retention Volumes of Organic Compounds on Styrene-Divinylbenzene and Ethylvinylbenzene-Divinylvenzene Copolymer Sorbent Beads. *J. Chromatogr., A* **1996**, *732*, 317–326.
(15) Poole, S. K.; Poole, C. F. Sorption Properties of Styrene-Divinylbenzene Macroreticular Porous Polymers. *Anal. Commun.* **1996**, *33*, 353–356.
(16) Kolb, B.; Welter, C.; Bichler, C. Determination of Partition Coefficients by Automatic Equilibrium Headspace Gas Chromatography by Vapor Phase Calibration. *Chromatographia* **1992**, *34*, 235–240.
(17) Sing, K. S. W. In *Analysis of Physisorption Isotherms in Physical Adsorption: Experiment, Theory and Applications*; Fraissard, J., Ed.; Kluwer Academic Publishers: Boston, MA, 1997.
(18) Shiu, W. Y.; Ma, K. C. Temperature Dependence of Physical-Chemical Properities of Selected Chemicals of Environmental Interest. II. Chlorobenzenes, Polychlorinated Biphenyls, Polychlorinated Dibenzo-*p*-dioxins, and Dibenzofurans. *J. Phys. Chem. Ref. Data* **2000**, *29*, 387–462.
(19) Xu, Z.; Zhang, Q.; Wu, C.; Wang, L. Adsorption of Naphthalene Derivatives on Different Macroporous Polymeric Adsorbents. *Chemosphere* **1997**, *35*, 2269–2276.
(20) Roháč, V.; Růžička, V.; Růžička, K.; Aim, K. Measurements of Saturated Vapor Pressure above the Liquid Phase for Isomeric Dichlorobenzenes and 1,2,4-Trichlorobenzene. *J. Chem. Eng. Data* **1998**, *43*, 770–775.
(21) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*; Wiley: New York, 1993.
(22) Sabbah, R.; An, X. W. Thermodynamic Analysis of Chlorobenzenes. *Thermochim. Acta* **1991**, *179*, 81–88.
(23) *CRC Handbook of Chemistry and Physics*, 64th ed.; Weast, R. C., Astle, M. J., Beyer, W. H., Eds.; CRC Press: Boca Raton, FL, 1983–1984.
(24) Abraham, M. H.; Andonian-Haftvan, J.; Whiting, G. S.; Leo, A.; Taft, R. W. Hydrogen Bonding. Part 34. The Factors that Influence the Solubility of Gases and Vapours in Water at 298K, and a New Method for Its Determination. *J. Chem. Soc., Perkin Trans. 2* **1994**, 1777–1791.
(25) Abraham, M. H.; Poole, C. F.; Poole, S. K. Classification of Stationary Phases and Other Materials by Gas Chromatography. *J. Chromatogr., A* **1999**, *842*, 79–114.
(26) Platts, J. A.; Butina, D.; Abraham, M. H.; Hersey, A. Estimation of Molecular Linear Free Energy Relation Descriptors Using a Group Contribution Approach. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 835–845.

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