

The Pseudophase Approach to Assessing Chemical Partitioning in Air–Water–Cyclodextrin Systems

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Henry's Law constants (HLCs) of several common, subsurface hydrophobic organic pollutants (HOPs) including trichloroethylene (TCE), perchloroethylene (PCE) and benzene, toluene, ethylbenzene, and *o*-xylene (BTEX), were measured using a static headspace phase ratio (SHPR) method over a range of temperatures (35, 45, 55, and 65 °C) and experimentally and operationally relevant cyclodextrin (CD) concentrations (0, 10, 20, 50, and 100 g L⁻¹). In aqueous CD solutions, HLC values decrease according to a power law relationship with increasing CD concentration due to an apparent solubility enhancement caused by HOP partitioning to the hydrophobic cavity of CD molecules. The temperature dependence of air–water partitioning under the influence of CD was well described by the van't Hoff equation for all HOPs tested. A three-phase equilibrium model was used to interpret air–water–CD partitioning data, treating CD as a pseudophase. Our results show that HOP CD–water partition coefficients decrease linearly with increasing temperature. CD–water partition coefficients were generally independent of CD concentration, with a few exceptions. Comparison of our results for hydroxypropyl- β -CD and TCE to those from another study showed several major discrepancies, which were attributed to differences in the experimental methods employed. Our attempt to correlate CD–water partition coefficients with HOP chemical properties indicates that correlations based on individual chemical descriptors (e.g., aqueous solubility, octanol–water partition coefficient, molecular volume or E_T (30) polarity index) will not be sufficient to obtain accurate estimates of HOP CD–water partition coefficients for other compounds with differing chemical structures.

Introduction

Cyclodextrin (CD) molecules are cyclic glucose oligomers derived from starch that have a toroidal shape with a hydrophobic cavity into which hydrophobic organic pollutants (HOPs) can partition and a hydrophilic exterior that makes CD water-soluble (1, 2). This combination of hydrophobic and hydrophilic regions gives CD molecules surfac-

tant-like properties, but without the limitation of a critical micelle concentration (CMC). By associating with CD cavities, HOP molecules can significantly increase their apparent aqueous solubility (3). The association of HOP and CD molecules can be modeled using reaction equilibrium (1, 2, 4) or chemical partitioning arguments. In this study, we have chosen the latter approach and treat the CD cavity as a pseudophase in the same way previous studies have treated the interior of surfactant micelles (5, 6).

Several studies have applied the modified equilibrium partitioning in closed systems (EPICs) method (7) or another static headspace phase ratio (SHPR) method (8) to examine air–water partitioning in the presence of solubilizing agents, including alcohols (9), surfactants (5, 6), and CD (4, 10, 11). The same method can also be used to examine Henry's Law constant (HLC) enhancement at high salinity (12, 13). Addition of CD or other solubilizing agents to the aqueous phase causes a reduction in the apparent HLC of HOPs due to the removal of chemical from the dissolved phase. This effect can be used to extract information on the interaction of HOPs and solubilizing agents in solution. In the case of micellar or CD pseudophases, measurements performed with and without the solubilizing agent can be used to estimate the concentration of pseudophase-associated HOP in solution, from which pseudophase–water partition coefficients or solubility enhancement factors (14) can be calculated.

In general, models of interphase chemical exchange for air–water–CD systems are based on the assumption that the dissolved concentration is linearly related to the concentration in the air and the amount of CD-complexed chemical. It is further assumed that the ratio of gas to dissolved phase concentrations is aptly described by standard HLCs for air–water systems, requiring that the distribution of chemical between the air and dissolved phases be independent of the presence of CD. Among the SHPR studies of HOPs and CD, there are two approaches used to describe the phase interactions. Kashiwama and Boving (4) and Misawa et al. (10) base their approach on a system where there are two exchange processes: HOPs can move between the gas and dissolved phases and between the dissolved and CD-complexed phases. Lantz et al. (11) proposed a third exchange process between air and CD. At equilibrium, only two partition coefficients are needed to fully define the system and therefore either approach will provide a complete account of the chemical distribution. It seems reasonable to assume that there is no direct transfer of HOP molecules between the air and CD in solution such that the HOP partial pressure in air is solely a function of the dissolved HOP concentration. Based on these assumptions, partition coefficients between CD and water can be determined from a mass balance on the HOP using HLCs measured with and without CD.

Partitioning behavior in three phase systems of air, water and hydroxypropyl- β -cyclodextrin (HP β CD) has been evaluated for six environmentally relevant HOPs, including the chlorinated solvents trichloroethylene (TCE) and perchloroethylene (PCE) and the monoaromatic hydrocarbons benzene, toluene, ethylbenzene, and *o*-xylene (BTEX), over a range of CD concentrations and temperatures. The objectives of this study were to (1) obtain quantitative descriptions of the effects of temperature and CD concentration on HOP air–water partitioning, (2) determine the effects of CD concentration and temperature on CD–water partitioning, and (3) determine if a correlation between CD–water partition coefficients can be found with a commonly reported chemical property such as aqueous solubility at 25 °C,

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molecular volume, octanol–water partition coefficient (K_{OW}) or the E_T (30) solvatochromic polarity scale. To our knowledge, only one other study has examined CD-influenced HOP air–water partitioning varying both temperature and CD concentration (4). Information on air–water–CD partitioning has several applications. Because CD significantly affects the air–water partitioning behavior of HOPs, data describing the effects of CD on HLCs are needed in order to properly design and operate air stripping systems for postextraction treatment of CD flushing solutions used in groundwater remediation. It is also useful to understand how HOPs distribute between the aqueous and gas phases during CD-enhanced flushing for contaminant transport modeling of soil and unsaturated aquifer remediation using CD. It may also be possible to use CD–water partition coefficients as reference parameters to describe pollutant partitioning to various environmental sorbents in the same way that K_{OW} is currently applied.

Materials and Methods

Methanol, TCE, PCE, benzene, ethylbenzene, and *o*-xylene were purchased from Sigma-Aldrich (>99.5% purity). Toluene was purchased from EMD Chemicals (99.5% purity). HP β CD (degree of substitution = 4.98, average MW 1424 g mol⁻¹) was donated by Cargill and used as received (purity wt/wt: moisture content 5.0%; unmodified β CD <0.1%; propylene glycol 0.4%; ash 2.0%; HP β CD 92.6%). High purity deionized water was generated by a US Filter water purification system (Siemens, Warrendale, PA) to 18.2 M Ω and was disinfected by ultraviolet irradiation. Headspace vials (20.16 \pm 0.11 mL) and magnetic screw caps with silicone/PTFE-faced septa were purchased from Microliter Analytical Supplies (Suwannee, GA).

Aqueous HP β CD solutions with concentrations of 10, 20, 50, and 100 g L⁻¹ (concentrations not adjusted for CD purity) were prepared by addition of HP β CD powder to high purity water. A concentrated solution of each HOP (TCE 12.60 g L⁻¹; PCE 2.872 g L⁻¹; BTEX 2.516 g L⁻¹) was prepared in a methanol–water solution (20% methanol, *v/v*). Sample solutions were prepared by adding HOP stock solution to 142 mL bottles containing aqueous HP β CD solution (no headspace). Concentrations of TCE, PCE, and BTEX in all HP β CD solutions were 47.03, 10.72, and 9.39 mg L⁻¹, respectively; these concentrations are less than 5% of each compound's aqueous solubility at 25 °C. These solutions were allowed to equilibrate overnight prior to addition to the headspace vials. Liquid volumes in the headspace vials were 2, 5, and 10 mL for TCE and BTEX and 3, 5, and 10 mL for PCE. For each of the different air-to-solution volume ratios, samples were prepared in triplicate, so each HLC measurement for a particular HOP, temperature, and HP β CD concentration is calculated from nine data points. Vials were sealed immediately after filling and allowed to equilibrate at room temperature for between 1.5 and 13 h (waiting in the autosampler rack) prior to incubation at the desired temperature and headspace sample analysis by gas chromatography (GC) with mass selective detection (MSD). For quality assurance purposes, all volumetric measurements were verified gravimetrically. Methanol volume fractions (*v/v*) were kept below 0.005 in all HP β CD solutions, and it has been shown in a previous study (7) that small quantities of methanol (<0.05 *v/v*) have no discernible effect on HOP air–water partitioning.

A static headspace autosampler equipped with a temperature-stabilized shaking incubator (Combi PAL, Leap Technologies, Carrboro, NC), was used to equilibrate sample vials and obtain headspace samples for GC injection using a gas syringe. The temperature range employed was from 35 to 65 °C in 10° increments. Lower temperatures were not

studied due to limitations of the incubator. Vials were incubated at the temperature of interest and shaken at 250 RPM for 30 min. To prevent condensation prior to injection, the syringe was heated to 2 °C above the incubation temperature. Carryover was prevented by a 120 s helium flush between analyses and lack of carryover was confirmed by analysis of blanks (every 10th vial). Headspace samples were analyzed using an Agilent 6890 GC (Santa Clara, CA) equipped with an Agilent 5973N MSD and fitted with a HP-5MS column (30 m long, 250 μ m diameter) (see the Supporting Information for GC method details).

HLCs were determined from GC area response values using the phase ratio method (8). Briefly, this approach allows for determination of HLCs by comparing the GC area response from the headspace of a set of samples with the same total volume and solution composition prepared with different air-to-solution volume ratios. Plotting the reciprocal of the GC area response (ordinate) against the air–solution ratio (abscissa) generates a line and the ratio of the slope to the *y*-intercept gives the HLC.

Data Analysis. Using HLCs determined from solutions with and without HP β CD, a CD–water partition coefficient can be determined for a particular HOP and temperature. The following treatment was developed based on differentiation of the dissolved and CD-complexed chemical present in the aqueous phase. A similar method has been applied to describe micelle–water partition coefficients for surfactants (6). The traditional HLC for air and water is

$$K_{A12} = \frac{C_{A1}}{C_{A2}} \quad (1)$$

where K_{A12} is the HLC (dimensionless), C_{A1} is the concentration of HOP (*A*) in air (phase 1, mg L⁻¹) and C_{A2} is the HOP concentration dissolved in water (phase 2, mg L⁻¹). For air in contact with CD solutions, the apparent HLC is defined as

$$K'_{A12} = \frac{C_{A1}}{C_{A2} + C'_{A2}} \quad (2)$$

where K'_{A12} is the apparent HLC (dimensionless) and C'_{A2} is the HOP concentration in water complexed with CD (mg L⁻¹). K_{A12} and K'_{A12} are determined experimentally as described above and can be used to determine the HOP concentrations in the air, dissolved and CD-complexed phases using a mass balance approach

$$V_2 C_{A20} = V_1 C_{A1} + V_2 C_{A2} + V_2 C'_{A2} \quad (3)$$

where V_2 is the volume of water or CD-solution (L), C_{A20} is the initial HOP concentration in solution prior to equilibration with air and CD (mg L⁻¹) and V_1 is the volume of air in a particular sample (L). Combining eq 2 and 3 and rearranging allows for calculation of the air phase concentration

$$C_{A1} = \frac{C_{A20}}{\frac{V_1}{V_2} + \frac{1}{K'_{A12}}} \quad (4)$$

which can then be used with eq 1 to calculate the dissolved concentration (C_{A2}) and finally eq 3 can be rearranged and solved for C'_{A2} using the results from eqs 4 and 1. It should be noted that this treatment depends on the assumption that the only effect CD has on the HOP distribution between air and water is to remove a fraction of HOP mass from being available for air–water partitioning. The ratio of the CD-complexed and HOP dissolved concentrations in CD solutions can be used to determine a CD–water partition coefficient

$$K'_{AC2} = \frac{C_{A2}}{C_{A2}} = K_{AC2} C_{C2} \quad (5)$$

where K'_{AC2} is the dimensionless CD–water partition coefficient (subscript C denotes the CD pseudophase), K_{AC2} is the CD-normalized partition coefficient (L kg^{-1}), and C_{C2} is the concentration of HP β CD in solution (kg L^{-1} , adjusted for CD purity). The solubility enhancement factor described in other CD studies (12, 15, 16) can be calculated by adding one to K'_{AC2} . The CD-normalized partition coefficient can be determined directly from K_{A12} and K'_{A12} using a relationship derived from eqs 1, 2, and 5

$$K_{AC2} = \frac{\left(\frac{K_{A12}}{K'_{A12}} - 1\right)}{C_{C2}} \quad (6)$$

where all terms have been defined previously.

It is well-known that HLCs vary with temperature. For systems where pressure differences are small, HLC temperature dependence can be described using the van't Hoff equation (4, 5, 7, 8, 17–21)

$$\ln K_{A12} = -\frac{A}{T} + B \quad (7)$$

where T is temperature (K) and A (K) and B are constants for a particular HOP and CD concentration.

Results and Discussion

Henry's Law Constants. Measured values of the traditional (K_{A12}) and apparent (K'_{A12}) HLCs are listed in Table 1. Dimensionless K_{A12} values for TCE, PCE, and BTEX presented here are consistent with those reported in a wide range of published studies (4–8, 12, 13, 19–26) and were in good agreement with HLCs calculated using vapor pressure and aqueous solubility data (22, 27). Examination of replicate samples showed that the average coefficient of variation (COV = standard deviation/mean) for K_{A12} and K'_{A12} values determined in this study was 0.049 ($n = 120$; 6 HOPs, four

temperatures, five CD concentrations). Only 13% of the HLCs had COVs higher than 0.1 ($n = 16$; max COV = 0.207 for ethylbenzene, no CD, 65 °C) and more than one-third of those were in the ethylbenzene data set ($n = 6$).

Values of K_{A12} and K'_{A12} increased exponentially with increasing temperature in accordance with and were well described by the van't Hoff equation ($R^2 \geq 0.95$, see Supporting Information Table S2 for details). Though the specific values of the van't Hoff parameters may not represent true thermodynamic quantities, they can be useful for estimating K_{A12} and K'_{A12} values at other temperatures. Values of the van't Hoff parameters for the air–water systems (K_{A12}) of all six HOPs were similar to values calculated using HLCs reported elsewhere over a similar temperature range (8). K'_{A12} values decreased with increasing HP β CD concentration according to a power law relationship (see Supporting Information Table S3 for details). At higher temperatures, larger relative increases were observed for K'_{A12} compared to K_{A12} , indicating that the CD-HOP interaction is less stable at higher temperatures. The destabilization of CD-complexes is further influenced by increasing HOP aqueous solubility and vapor pressure with increasing temperature. The effects of CD concentration on HLCs were very similar among all six HOPs. Measured K_{A12} values were between 30 and 70% lower than K_{A12} at the same temperature in 10 g L^{-1} HP β CD solutions and between 1 and 2 orders of magnitude lower in 100 g L^{-1} solutions. These significant decreases in HLC values are consistent with those reported elsewhere for TCE in HP β CD solutions over comparable temperature and CD concentration ranges (4).

To illustrate how the HOP mass distribution in air–water–CD systems changes with temperature and CD concentration, ternary phase diagrams (Figure 1) showing the total HOP mass fraction present in each phase were constructed using the mass balance treatment described previously (eqs 1–4). The plots represent systems with equal volumes of air and water. As CD concentration increases, the fraction of HOP mass present in CD-complexes proportionally rises. As temperature increases, the HOP mass fraction present in CD-complexes decreases, with most of

TABLE 1. Dimensionless Henry's Law Constants for TCE, PCE, and BTEX (K_{A12} , K'_{A12}) Determined at Different Temperatures and CD Concentrations

| compound | K_{A12} | | K'_{A12} | | | |
|------------------|-----------|--------|-------------------------|-------------------------|-------------------------|--------------------------|
| | temp (°C) | no CD | 10 g L^{-1} CD | 20 g L^{-1} CD | 50 g L^{-1} CD | 100 g L^{-1} CD |
| TCE | 35 | 0.6220 | 0.4401 | 0.2981 | 0.1456 | 0.0588 |
| | 45 | 0.9796 | 0.6953 | 0.4352 | 0.2387 | 0.1141 |
| | 55 | 1.2464 | 0.8786 | 0.5931 | 0.3337 | 0.1733 |
| | 65 | 1.5271 | 1.1562 | 0.8562 | 0.4757 | 0.2427 |
| PCE | 35 | 1.0787 | 0.3189 | 0.1974 | 0.0903 | 0.0416 |
| | 45 | 1.3122 | 0.4916 | 0.2942 | 0.1423 | 0.0644 |
| | 55 | 1.7415 | 0.6027 | 0.4217 | 0.2117 | 0.0953 |
| | 65 | 2.6252 | 0.8421 | 0.5442 | 0.2512 | 0.1364 |
| benzene | 35 | 0.3581 | 0.1735 | 0.1261 | 0.0602 | 0.0337 |
| | 45 | 0.4446 | 0.2518 | 0.1747 | 0.0866 | 0.0484 |
| | 55 | 0.5863 | 0.3312 | 0.2423 | 0.1202 | 0.0690 |
| | 65 | 0.7433 | 0.4392 | 0.3115 | 0.1723 | 0.0962 |
| toluene | 35 | 0.4052 | 0.1812 | 0.1222 | 0.0590 | 0.0316 |
| | 45 | 0.5934 | 0.2746 | 0.1786 | 0.0874 | 0.0469 |
| | 55 | 0.8486 | 0.3873 | 0.2529 | 0.1249 | 0.0648 |
| | 65 | 1.1541 | 0.5135 | 0.3501 | 0.1700 | 0.0923 |
| ethylbenzene | 35 | 0.4882 | 0.1325 | 0.0677 | 0.0314 | 0.0136 |
| | 45 | 0.6416 | 0.1958 | 0.1173 | 0.0532 | 0.0198 |
| | 55 | 1.0979 | 0.3184 | 0.1826 | 0.0784 | 0.0393 |
| | 65 | 1.2190 | 0.4125 | 0.2356 | 0.1120 | 0.0629 |
| <i>o</i> -xylene | 35 | 0.3048 | 0.1151 | 0.0706 | 0.0363 | 0.0202 |
| | 45 | 0.4623 | 0.1788 | 0.1126 | 0.0550 | 0.0323 |
| | 55 | 0.6400 | 0.2609 | 0.1660 | 0.0808 | 0.0418 |
| | 65 | 0.8153 | 0.3623 | 0.2426 | 0.1173 | 0.0641 |

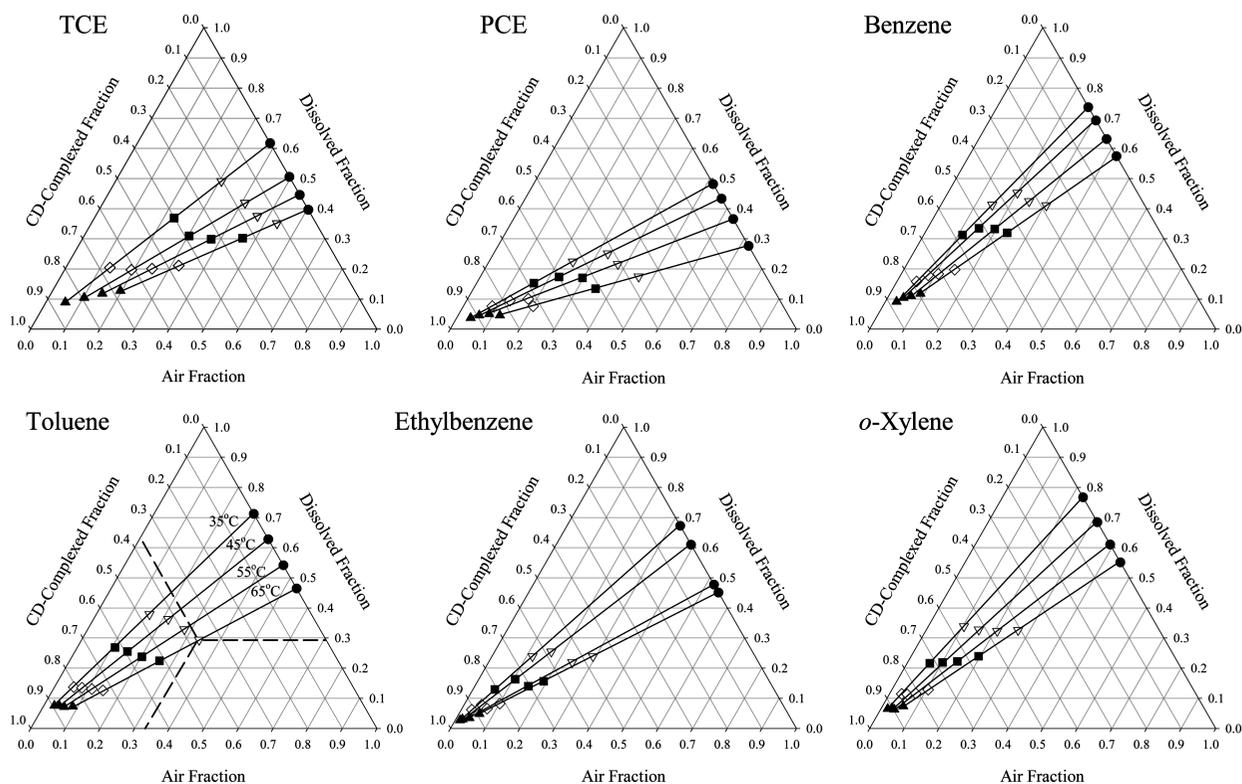


FIGURE 1. Ternary diagrams of HOP mass distribution in air–water–CD systems with equal volumes of air and water (10 mL): no CD (●), 10 g L⁻¹ CD (▽), 20 g L⁻¹ CD (■), 50 g L⁻¹ CD (◇) and 100 g L⁻¹ CD (▲). The toluene plot provides guidance for reading the mass fractions (dashed lines for CD conc. Ten g L⁻¹ at 65 °C: air = 0.29, dissolved = 0.34, CD-complexed = 0.37) and indicates isotherms for 35 – 65 °C (solid lines).

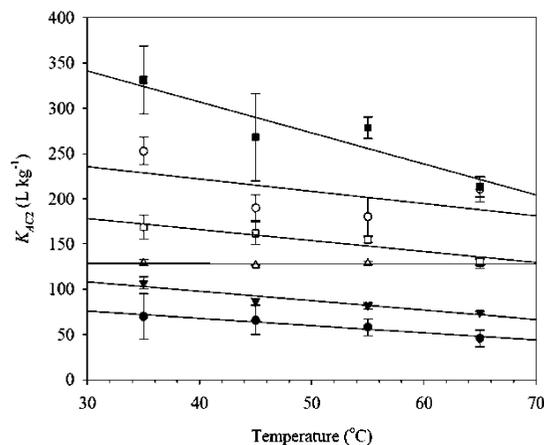


FIGURE 2. CD–water partition coefficients (K_{AC2} , L kg⁻¹) as a function of temperature: TCE (●), PCE (○), benzene (▼), toluene (△), ethylbenzene (■) and *o*-xylene (□). Trend lines shown for reference.

the displaced mass moving to the air phase. At the highest CD concentration, 65% or more of the total mass of each HOP was present in CD-complexes across the entire temperature range. The CD concentration required for $\geq 50\%$ of the total HOP mass to be present in CD-complexes at 35 °C followed the trend: TCE > benzene > toluene > *o*-xylene \approx PCE > ethylbenzene. A slightly different trend was observed for 65 °C: TCE > benzene > toluene \approx PCE > *o*-xylene > ethylbenzene. This difference is attributed to the stronger temperature dependence of PCE vapor pressure relative to *o*-xylene and ethylbenzene (22, 27).

CD Pseudophase–Water Partitioning. Values of K_{AC2} for the four CD concentrations tested were calculated using eq 6 and the averages and standard deviations (error bars) are shown in Figure 2. Increasing temperature led to a decrease

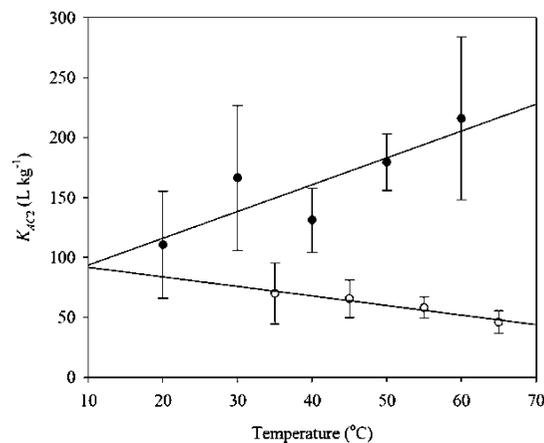


FIGURE 3. Comparison of CD–water partition coefficients (K_{AC2} , L kg⁻¹) as a function of temperature for TCE: Kashiyama and Boving (ref 4) (●) and this study (○).

in K_{AC2} , as indicated by the slopes of the trend lines: TCE, -0.80 L kg⁻¹ °C⁻¹; PCE, -1.36 L kg⁻¹ °C⁻¹; benzene, -1.04 L kg⁻¹ °C⁻¹; toluene, -0.01 L kg⁻¹ °C⁻¹; ethylbenzene, -3.42 L kg⁻¹ °C⁻¹; and *o*-xylene, -1.21 L kg⁻¹ °C⁻¹. The decrease in K_{AC2} with increasing temperature is indicative of decreasing CD–HOP complex stability at higher temperatures. The K_{AC2} values for toluene appeared to be almost independent of temperature over the range tested, possibly indicating that complexes formed between HP β CD and toluene are particularly stable over the temperature range examined. K_{AC2} was higher for the more hydrophobic HOPs. The chlorinated solvents had lower K_{AC2} values than comparable BTEX compounds despite having higher K_{OW} values. This may be due to the greater effect increasing temperature has on the vapor pressure of chlorinated solvents compared to BTEX compounds with similar solubilities (22, 27).

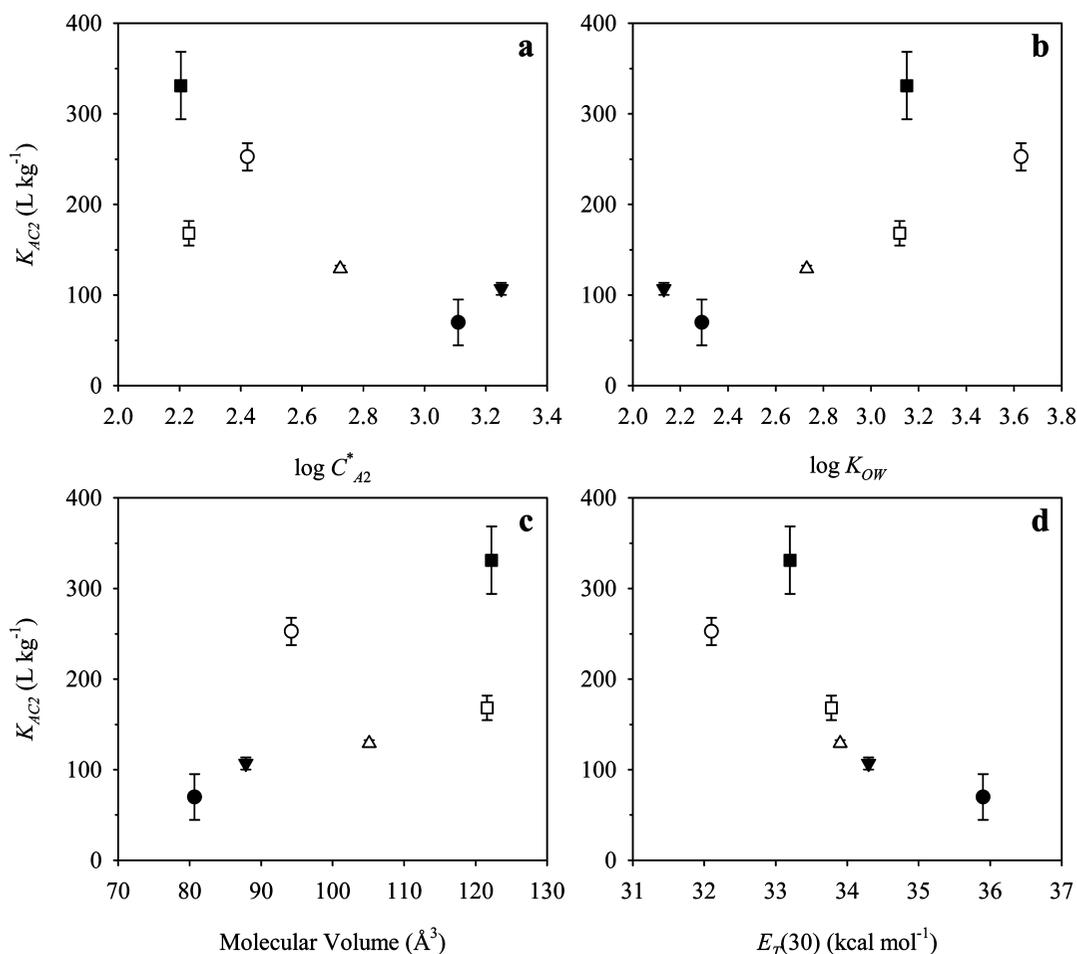


FIGURE 4. Comparison of K_{AC2} values at 35 °C to various chemical properties of chlorinated solvents TCE (●) and PCE (○) and BTEX compounds benzene (▼), toluene (Δ), ethylbenzene (■) and *o*-xylene (□): (a) $\log C^*_{A2}$ (aqueous solubility at 25 °C, mg L⁻¹), (b) $\log K_{OW}$, (c) molecular volume (Å³) and (d) solvatochromic polarity index $E_T(30)$ (kcal mol⁻¹).

A linear increase in HOP saturation in aqueous solutions with increasing CD concentration has been observed by others (1), indicating that K_{AC2} values should be independent of CD concentration. In general, this was true of the results presented here for experiments conducted at HOP concentrations which are several orders of magnitude below saturation. The exceptions were TCE and ethylbenzene, which in some cases showed increases in K_{AC2} with increasing CD concentration (see Supporting Information Figure S3). In the case of TCE at 55 °C and below, K_{AC2} nearly doubles as CD concentration increases from 10 to 100 g L⁻¹, whereas for ethylbenzene, this increase is only ~30% at 35 and 45 °C. It is not clear from their chemical structures or properties why TCE and ethylbenzene would behave differently from the other HOPs with regard to CD dependence of K_{AC2} , so it is possible that the effect is an artifact of the data.

The effects of HPβCD on TCE air–water partitioning were examined by Kashiyama and Boving (4) over the same CD concentration range and at similar temperatures. Using their HLC measurements, K_{AC2} values were calculated (eq 6) for comparison with those presented here. The results are shown in Figure 3. The plot illustrates three major differences in the two data sets: (1) the error bars (representing the standard deviation between K_{AC2} values determined at different CD concentrations) are much narrower in our data set; (2) the values of K_{AC2} determined from our HLC measurements are lower by a factor of 2 or more; and (3) the temperature trends determined for K_{AC2} in the two studies are contradictory. The first discrepancy relates to the variability of K_{AC2} in solutions of different CD concentrations. Examination of the results of the previous study revealed no consistent trend for K_{AC2}

with CD concentration at any particular temperature, therefore the large error bars appear to be the result of experimental variability. The second discrepancy is attributed to the higher HOP affinity of the HPβCD used in the previous study (CAVASOL W7 MTL, Wacker Inc.) due to its lower degree of substitution ($DS = 1.6 - 1.9$) by hydroxypropyl groups. It has been shown that complex stability for HPβCD is reduced at higher DS (28). The third discrepancy indicates very different properties for CD–TCE partitioning. An increase in K_{AC2} with temperature would indicate that partitioning was in some way enhanced at higher temperatures, despite the concurrent increase in aqueous solubility and vapor pressure which would be expected to drive chemical out of the CD pseudophase. It seems unlikely that increasing temperature would enhance partitioning of HOPs to CD. All of the HOPs studied here showed trends of decreasing K_{AC2} with increasing temperature with the exception of toluene, which was neutral with respect to temperature under the conditions of this study. This leads us to conclude that the increase in K_{AC2} with temperature observed previously (4) is an experimental artifact, which may be due to the use of manual sampling and GC injection of headspace vapor samples.

Correlation of K_{AC2} with HOP Chemical Properties. As mentioned in a previous section, the K_{AC2} values determined in this study were not well correlated with K_{OW} for chlorinated solvents and BTEX. Figure 4 shows K_{AC2} plotted against four chemical properties, including HOP aqueous solubility at 25 °C (C^*_{A2} , mg L⁻¹, panel a) (23, 29, 30), K_{OW} (panel b) (31), molecular volume (Å³, panel c) (32) and the $E_T(30)$ index (kcal mol⁻¹, panel d) (33–35). Aqueous solubility and K_{OW} are commonly employed and readily available descriptors

of chemical hydrophobicity. Molecular volume has been shown to impact CD-complex stability in that larger compounds form more stable complexes, provided they can fit in the cavity (36). The E_T (30) index is an empirical polarity scale based on changes in electron transition energies (kcal mol⁻¹) due to the negative solvatochromism of a particular betaine dye in solvents of different polarity (33). E_T (30) values are larger in more polar solvents.

The results of these comparisons yielded no consistent trends when all six compounds were included as one or more outliers appeared in each comparison. It is apparent that chlorinated solvents and BTEX compounds exhibit similar relationships with each of the parameters, for example K_{AC2} decreases with increasing solubility for both chlorinated solvents and BTEX, but they do not follow the same trend lines. This indicates that chlorinated solvents and BTEX associate with CD cavities due to the combined effects of several chemical properties. By contrasting the chlorinated solvents with BTEX compounds exhibiting similar CD-water partitioning behavior, this can be illustrated. TCE has K_{AC2} values that are ~30% lower than benzene even though benzene is 30% more soluble and has a lower K_{OW} . However, benzene is also less polar and 10% larger than TCE. PCE has K_{AC2} values that are ~25% lower than ethylbenzene even though ethylbenzene has a K_{OW} that is 65% lower and is more polar than PCE. In contrast, ethylbenzene is 40% less soluble (though reported solubilities for these compounds vary considerably) and has a molecular volume that is 30% larger than PCE. The usefulness of K_{OW} in describing HOP CD affinity seems questionable considering that CD is chemically very different from *n*-octanol. It appears that a combination of polarity and molecular size may be used to describe the K_{AC2} trend observed. PCE is very apolar, which allows it to form very stable CD-complexes despite its relatively small molecular size. TCE is smaller and much more polar than the other compounds, which leads to weaker CD partitioning despite having a higher K_{OW} and lower aqueous solubility than benzene.

Ethylbenzene showed a divergence from the trends observed between the chemical properties and K_{AC2} values for the other BTEX compounds. As mentioned in previous sections, the ethylbenzene data had more variability than that of the other compounds studied, which could be taken as an indication that the high values of K_{AC2} determined in this study were an artifact. However, our CD-water partition coefficients for the BTEX compounds are consistent with CD association constants reported in several other studies conducted at ambient temperature (14, 37–39). Ethylbenzene has shown association constants that are 60–160% larger than those of toluene and 30–60% greater than those of *o*-xylene, which is consistent with our findings. This large increase in CD affinity going from methyl- to ethyl-substituted aromatic rings could be due to an interaction between the ethyl substituent with the narrow rim of the CD cavity (36). It is also possible that multiple types of interactions occur between HOPs and different parts of the CD molecule in addition to the cavity, which may be why correlations using single chemical properties appear to be inadequate for prediction of K_{AC2} .

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Supporting Information Available

Additional detail regarding experiments and additional tables and figures are presented. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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