

Solubility Enhancement Effect of Cyclodextrin on Groundwater Pollutants

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Abstract

Cyclodextrin (CD) molecules are polycyclic glucose oligomers that have a hydrophilic exterior and a hydrophobic cavity. This structure provides CD the characteristic of enhancing the solubility of groundwater pollutants. The degree to which CD increases the apparent aqueous solubility of certain chemicals has been defined as the solubility enhancement factor (SEF). In this study, a novel and experimentally simple method has been developed to determine the SEF, which can be mathematically obtained by ratio of apparent and traditional Henry's law constants. The effects of temperature and CD concentration on the SEFs and CD cavity occupation have been investigated. Our results show that SEF values are inversely related to temperature for most examined chemicals, which is consistent with the assertion that the CD-chemical complexes are less stable at higher temperatures. The exception is toluene that shows the least SEF fluctuation within the temperature range studied (5 to 65 °C). This may indicate that the toluene-CD complex is particularly stable. As the definition of SEF predicted, linear relationships were found between the SEFs and CD concentrations for all the subject chemicals. The CD cavity occupation fraction at 5 °C were 3.14, 2.55, 2.04, 1.60, and 1.67 times greater than the values at 65 °C for of trichloroethylene, perchloroethylene, benzene, ethylbenzene, and *o*-xylene, respectively. The fraction of CD cavities occupied was found to be inversely related to the CD concentration for all tested chemicals when pollutant mass are held constant. This study provides important information to accurately evaluate the performance of CD when used for aquifer remediation.

Introduction

Hydrophobic organic pollutants such as chlorinated solvents, polycyclic aromatic hydrocarbons, and certain pesticides have been identified as a common cause of aquifer contamination (Domenico and Schwartz 1990;

Mercer and Cohen 1990; Pankow and Cherry 1996). Organic pollutants can enter subsurface as a result of accidental chemical spill and normally present as nonaqueous phase liquid phase (NAPL) or sorbed to the porous media. Pump-and-treat, which relies on the dissolution of NAPLs, is one of conventional techniques to remediate those contaminated sites. However, due to the low solubility of organic pollutants, the effectiveness of this method is limited and the life span of NAPLs in the subsurface is expected to be decades (MacKay and Cherry 1989; Mercer et al. 1991; West and Harwell 1992; Bizzigotti et al. 1997; Ko et al. 1999; McCray et al. 2000; Tick et al. 2003). The generally poor performance of pump-and-treat schemes has led to research and application of innovative in situ chemically enhanced-flushing remediation methods.

Chemically enhanced-flushing technologies are based on flushing contaminated sites with chemical agents to

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enhance contaminant dissolution and concomitantly the mass removal rate (Pennell et al. 1994; Martel et al. 1998a, 1998b; Jawitz et al. 2000; Gupta and Mohanty 2001; Taylor et al. 2001). Unfortunately, however, the commonly used additives such as cosolvents and surfactants have many disadvantages (Fountain et al. 1991; Jafvert and Heath 1991; Palmer and Fish 1992; Wang and Brusseau 1993). In recent years, a growing body of evidence suggests that cyclodextrins (CD) can be one of the most effective solubilizing agents for chemically enhanced-flushing technology (Bizzigotti et al. 1997; McCray and Brusseau 1998; Blanford et al. 2000; Boving and Brusseau 2000; Tick et al. 2003; Boving et al. 2006). In their studies, the effectiveness of CD flushing was evaluated by comparison of the aqueous concentration of organic compounds in extraction wells during both CD flushing and water flushing. Their study found that the degree to which the extraction rate of the 12 compounds was improved by CD over water ranged from a 100-fold increase to 20,000 times. Cost assessment has been performed by other researchers (Boving et al. 2004). They found that CD is cost-competitive compared to other remediation techniques.

CD molecules are polycyclic glucose oligomers derived from starch that have a toroidal shape (Bender and Komiyama 1978; Saenger and Steiner 1998) (Figure 1). These glucose-based molecules have a hydrophilic exterior and a hydrophobic interior (Connors 1997; Kashiyama and Boving 2004). Low-polarity organic pollutants can partition into the CD cavity due to hydrophobic influences, while the polar exterior makes CD soluble in water (Figure 1). These characteristics allow CD molecules to carry organic pollutants (either presented as NAPLs or sorbed to porous media) and dissolve in water, which greatly enhance the apparent aqueous solubility. Typically, CD molecules are described as α , β , and γ -CD where the Greek letter denotes the number of glucose units ($\alpha = 6$, $\beta = 7$, and $\gamma = 8$, respectively) (McCray et al. 2000). Among the many derivatives of CDs, 2-hydroxypropyl- β -cyclodextrin (HPCD) has been determined to have the most potential remediation agent due to its favorable characteristics (e.g., water solubility, flow properties, relative cost) (Wang and Brusseau 1993; Boving and Brusseau 2000).

Solubility enhancement factor (SEF), which is defined as the ratio of the apparent solubility in presence of CD to the water solubility in the absence of CD, is an important parameter to evaluate the performance of CD. There are two historical methods to determine SEF, excess solute exposure, and generator column. The former approach involves exposing an excess amount of the solute to water and measuring the supernatant concentration after equilibrium (McCray et al. 2000). The primary disadvantages of this method are the relatively long exposure time required to fully saturate the solution and the presence of CD molecules and micro-sized NAPLs that might interfere with the concentration measurement.

Generator column method (Wang and Brusseau 1993; Boving et al. 1999) is another common method used to

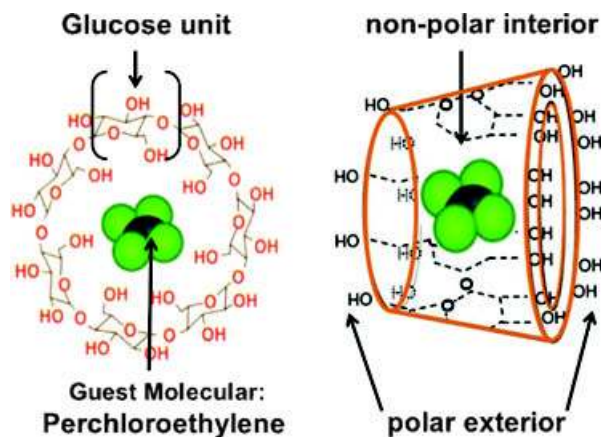


Figure 1. Structure of CD host-guest complexation: plane view (left) and three-dimensional view (right).

determine the SEF, especially for those compounds with low water solubility. In this approach, a glass distillation column was packed with diatomaceous earth coated with excess chemicals, through which a CD solution is recirculated to create a pollutant-saturated CD solution. The generator column method requires less time to reach equilibrium, but also has similar problems related to concentration measurement. Hence, there is an unmet need to explore an experimentally simple method to calculate the SEFs that can accurately forecast the performance of CD.

In this study, a novel and experimentally simple method is developed to determine SEF, in which neither longer exposure time nor a generator column is needed. This method involves first measuring the apparent Henry's law constant in presence and absence of CD. The SEF is then mathematically obtained by ratio of apparent and traditional Henry's law constants. The objectives of this study were to (1) obtain quantitative data of CD enhancement behavior by using the new method; (2) determine the effect of CD concentration and temperature on the SEF; and (3) evaluate the fraction of CD cavities occupied with chemicals (CD cavity occupation percentage) as a function of CD concentration and temperature. This study provides important information to accurately measure the performance of CD when used for aquifer remediation. The occupation percentage data are useful to understand how the CD molecule is occupied, and might be a guide for designing experiments in a mixed system. It may also be possible to use the SEFs over a range of CD concentrations as reference parameters to conduct a future field study for the purpose of investigating chemical flushes at contaminated sites.

Materials and Methods

Chemicals

HPCD was donated by Wacker Chemie AG (Adrian, Michigan) with the following characteristics: degree of substitution = 4.98, average molecular weight = 1424 g/mol; moisture content 5.0% (wt/wt); HP β CD

92.6%(wt/wt); unmodified β CD <0.1%(wt/wt); propylene glycol 0.4%(wt/wt); ash 2.0%. Trichloroethylene (TCE), perchloroethylene (PCE), benzene, ethylbenzene, and *o*-xylene were purchased from Sigma-Aldrich (>99.5% purity; St. Louis, Missouri). Toluene was purchased from EMD Chemicals (99.5% purity; Gibbstown, New Jersey).

SEF Development

Several previous researchers have reported that the apparent solubility of organic compounds (S_A) in aqueous solution containing CD increasing linearly with the CD concentration (Wang and Brusseau 1993; Bizzigotti et al. 1997). In order to fully understand solubility enhancement behavior, a linear partition model for the solubility enhancement can be used to represent the interaction between the solutes and the solubilizing agents (Kile and Chiou 1989). The magnitude of partition-like interaction for an organic solute with respect to the solubilizing agents can be expressed as:

$$S_A = S_W + C_{CD} \cdot C_{HOP}, \quad (1)$$

where S_A is the apparent solute solubility in water containing CD (mg/L), S_W is the solubility in pure water (mg/L), C_{CD} is the concentration of CD in water phase (g/L), and C_{HOP} is the mass of solute partitioned into a unit mass of CD (mg/g).

An expression of the relationship between the water solubility S_W and the solute amount partitioned into CD cavity (C_{HOP}) is defined as the partition coefficient between S_A and pure water:

$$K_{HOP-CD} = \frac{C_{HOP}}{S_W}. \quad (2)$$

Therefore the apparent solubility (S_A) can be rearranged by combining Equations 1 and 2 to give:

$$\begin{aligned} S_A &= S_W + C_{CD} \cdot K_{HOP-CD} \cdot S_W \\ &= S_W(1 + C_{CD} \cdot K_{HOP-CD}) \\ &= S_W \cdot E \end{aligned} \quad (3)$$

The SEF (E) is defined as the ratio of apparent solubility in the presence of CD and the solubility in pure water, which is equivalent to:

$$E = 1 + C_{CD} \cdot K_{HOP-CD}. \quad (4)$$

Previous researchers (Gao et al. 2009) reported that K_{HOP-CD} can be calculated by Equation 5:

$$K_{HOP-CD} = \frac{\frac{K_{A12}}{K'_{A12}} - 1}{C_{CD}}, \quad (5)$$

where K_{A12} and K'_{A12} are the Henry's law constants in the absence and presence of CD. A new method to calculate

E (Equation 6) can be obtained by substitution Equation 5 into Equation 4:

$$E = 1 + \left(\frac{\frac{K_{A12}}{K'_{A12}} - 1}{C_{CD}} \right) \cdot C_{CD} = \frac{K_{A12}}{K'_{A12}}. \quad (6)$$

The K_{A12} and K'_{A12} were obtained from a previous study (Gao et al. 2009) using the static headspace phase ratio method (Robbins 1993). Briefly, in the static headspace phase ratio method, the gas chromatograph area responses of the headspaces in a set of CD-chemical solutions with different air-to-liquid volume ratios were measured. A straight line was then generated by plotting the reciprocal of the area response (ordinate) against the air-liquid ratio (abscissa) and Henry's constants can be calculated from the ratio of the slope to the y-intercept (Gao et al. 2009). Because their Henry's constants were measured at the temperature range of 35 through 65 °C, additional data were obtained in this study by applying the well-known van't Hoff equation (Equation 7) (Gossett 1987; Vane and Giroux 2000; Kashiya and Boving 2004; Gao et al. 2009) to extrapolate the Henry's law constants at 5, 10, and 25 °C. The SEFs were then calculated using the projected K_{A12} and K'_{A12} . The A and B values in Equation 7 were listed in Table 1 (Gao et al. 2009):

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

The CD cavity occupation percentage was obtained by first calculating the moles of pollutants in each phase using a mass balance approach described in previous research (Gao et al. 2009), then calculating the mole of CD occupied using the host: guest stoichiometry ratio of 1:1, finally dividing the occupied CD moles by the total moles of CD added to each system.

Table 1
van't Hoff Parameters for Henry's Constants
in Water and CD Solutions¹

Compound	Parameter	No CD	1% CD	2% CD	5% CD	10% CD
TCE	A	3074	3273	3619	4056	4888
	B	9.6	9.8	10.5	11.3	13.1
PCE	A	3060	3252	3553	3630	4122
	B	9.9	9.4	9.9	9.4	10.2
Benzene	A	2568	3194	3171	3626	3649
	B	7.3	8.6	8.2	9.0	8.4
Toluene	A	3648	3620	3655	3687	3688
	B	10.9	10.1	9.8	9.1	8.5
Ethylbenzene	A	3429	4063	4378	4384	5490
	B	10.4	11.2	11.6	10.8	13.5
<i>o</i> -Xylene	A	3424	3982	4266	4066	3880
	B	10.0	10.8	11.2	9.9	8.7

¹ Values were obtained from Gao et al. (2009).

Table 2
SEFs of Six Compounds at 0 ~ 65 °C

CD Concentration		5 °C	10 °C	25 °C	35 °C	45 °C	55 °C	65 °C	23 °C ¹
TCE	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	NA
	1% CD	1.67	1.65	1.60	1.41	2.25	1.42	1.32	NA
	2% CD	2.89	2.79	2.53	2.09	2.25	2.1	1.78	NA
	5% CD	6.24	5.86	4.92	4.27	4.1	3.74	3.21	NA
	10% CD	20.55	18.31	13.27	10.58	8.59	7.19	6.29	13.30 ¹ (6.5 ² ; 6.04 ³ ; 9.5 ⁴ ; 8.7 ⁵ ; 13.51 ⁶)
PCE	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	NA
	1% CD	3.29	3.25	3.14	3.38	2.67	2.89	2.19	NA
	2% CD	5.89	5.71	5.23	5.46	4.46	4.13	3.98	NA
	5% CD	12.8	12.35	11.16	11.95	9.22	8.23	8.64	NA
	10% CD	33.74	31.54	26.12	25.93	20.38	18.27	17.28	28.09 ¹ (8.9 ² ; 20.66 ⁵ ; 36 ⁴)
Benzene	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	NA
	1% CD	2.59	2.49	2.23	2.06	1.77	1.77	1.69	NA
	2% CD	3.55	3.42	3.07	2.84	2.54	2.42	2.39	NA
	5% CD	8.2	7.67	6.35	5.95	5.13	4.88	4.31	NA
Toluene	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	NA
	1% CD	2.01	2.02	2.03	2.24	2.16	2.19	2.25	NA
	2% CD	3.08	3.08	3.08	3.32	3.32	3.36	3.3	NA
	5% CD	6.96	6.94	6.9	6.87	6.79	6.79	6.79	NA
Ethylbenzene	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	12.62 ¹ (9.6 ²)
	1% CD	4.39	4.22	3.77	3.68	3.28	3.45	2.96	NA
	2% CD	9.14	8.6	7.27	7.21	5.47	6.01	5.17	NA
	5% CD	20.78	19.56	16.5	15.55	12.06	14	10.88	NA
	10% CD	74.52	65.37	45.32	35.9	32.4	27.94	19.38	47.43 ¹ (24.9 ²)
<i>o</i> -Xylene	0% CD	1.00	1.00	1.00	1.00	1.00	1.00	1.00	NA
	1% CD	3.34	3.23	2.92	2.65	2.59	2.45	2.25	NA
	2% CD	6.22	5.9	5.08	4.32	4.11	3.86	3.36	NA
	5% CD	11.12	10.67	9.52	8.4	8.41	7.92	6.95	NA
	10% CD	18.91	18.37	16.94	15.09	14.31	15.31	12.72	17.11 ¹ (16.11 ²)

¹ Values calculated using the method developed in this study and van't Hoff equation for comparison purpose.

² Reported by McCray et al. (2000).

³ Derived from Wang and Brusseau (1993).

⁴ Reported by Boving et al. (1999).

⁵ Derived from Liang et al. (2007).

⁶ Derived from Kashiyama and Boving (2004).

Results and Discussion

Quantitative Analysis of SEF

The SEFs of six common chemicals in aqueous solution of HPCD were determined by Equation 6. The results of these determinations are summarized in Table 2. Little comparable data exists in the literature for this type of CD, these chemicals and this range of CD concentrations and temperatures. There are a few studies (Wang and Brusseau 1993; Boving et al. 1999; McCray et al. 2000; Liang et al. 2007) which reported the SEFs on limited type of pollutants of one CD concentration (10%) but at one different temperature, 23 ± 1 °C. Their SEFs were obtained using saturation/generator column methods and the values were listed in the parentheses of Table 1. In order to compare our results their value, SEFs at 23 °C was extrapolated using our method and van't Hoff equation (Equation 7).

As can be seen in Table 2, SEFs of TCE, PCE, toluene, and *o*-xylene at 23 °C presented here are close to those published values obtained using saturation/generator column methods. There is a difference between the ethylbenzene's SEF proposed by McCray et al. (2000) (SEF = 24.9) and this study (SEF = 47.43). The discrepancy is either due to the differences in the quantitative methods applied in the two studies, or the different CD impurity/substitution used.

The average degree of substitution and the level of impurities of CD are known to affect performance of CD (Loftsson and Brewster 1996; Müller and Brauns 2006; Schönbeck et al. 2010), but unfortunately many authors fail to report these basic values. Overall, the method developed in this study has the advantage of not requiring long equilibrium time to reach saturation, which is experimentally simple. In addition, the static headspace phase ratio method (Robbins 1993) and autosampler used

to determine Henry's constants provide reproducible measurements during equilibrium, which is beneficial to avoid system error. Therefore, it is reasonable to believe that the proposed method gives accurate results.

Dependence of SEFs on CD Concentration and Temperature

During application of CD enhanced flushing for groundwater remediation, temperature fluctuation in nature may significantly change the CD's enhancement level. Therefore, it is beneficial to know how SEFs changes at different temperatures. In order to gain a better understanding of the temperature effect, CD normalized SEFs are obtained by dividing the apparent SEFs by the CD concentration. The results are shown in Figure 2. As can be seen, the SEFs decrease with increasing temperature for most of the chemicals examined in this study. This is consistent with the assertion that the CD-chemical complexes are less stable at higher temperatures. Toluene (green dotted line) shows the least SEFs fluctuation during the temperature change, which might indicate the toluene-CD complex is particularly stable over the temperature range examined.

As the definition of SEF ($E = 1 + C_{CD} \cdot K_{HOP-CD}$) predicted, linear relationships (R^2 above 0.90) between the SEFs and CD concentrations were found for all tested chemical within the temperature range (Table 3). The intercepts of all regression lines are close to 1, which is expected. The intercept physically represents the SEF of a CD-free solution, "pure water" in this study, and therefore the SEF should be a constant value, 1, when CD is absent in solutions. This finding confirms the accuracy of the measurement of SEFs in this study. The slopes of the regression lines are indicators of the partitioning coefficients of chemicals between CD and water; it also indicates thermodynamic stability of the chemicals-CD complex. As can be seen from Figure 3, the slopes in each group increase as temperatures increase

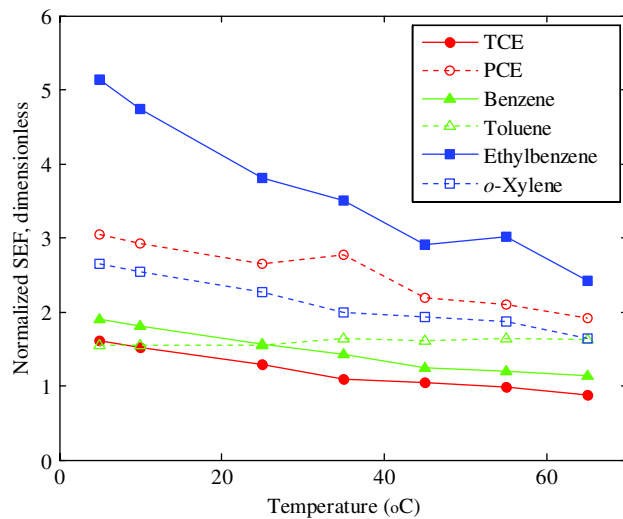


Figure 2. Dependence of CD concentration normalized SEF on temperature.

Table 3
Regression Parameters of Correlation Between SEFs (Y) and CD Concentration (X)

	TCE	PCE	Benzene	Toluene	Ethylbenzene	o-Xylene
5 °C	$Y = 1.74X + 1$ ($R^2 = 0.92$)	$Y = 3.07X + 1$ ($R^2 = 0.92$)	$Y = 1.50X + 1$ ($R^2 = 1.00$)	$Y = 1.17X + 1$ ($R^2 = 1.00$)	$Y = 6.57X + 1$ ($R^2 = 0.93$)	$Y = 1.87X + 1$ ($R^2 = 0.98$)
10 °C	$Y = 1.55X + 1$ ($R^2 = 0.93$)	$Y = 2.88X + 1$ ($R^2 = 0.98$)	$Y = 1.39X + 1$ ($R^2 = 1.00$)	$Y = 1.17X + 1$ ($R^2 = 1.00$)	$Y = 5.81X + 1$ ($R^2 = 0.94$)	$Y = 1.63X + 1$ ($R^2 = 0.99$)
25 °C	$Y = 1.12X + 1$ ($R^2 = 0.95$)	$Y = 2.40X + 1$ ($R^2 = 0.99$)	$Y = 1.13X + 1$ ($R^2 = 1.00$)	$Y = 1.16X + 1$ ($R^2 = 1.00$)	$Y = 4.12X + 1$ ($R^2 = 0.97$)	$Y = 1.43X + 1$ ($R^2 = 0.92$)
35 °C	$Y = 0.88X + 1$ ($R^2 = 0.96$)	$Y = 2.42X + 1$ ($R^2 = 1.00$)	$Y = 0.97X + 1$ ($R^2 = 1.00$)	$Y = 1.18X + 1$ ($R^2 = 1.00$)	$Y = 3.36X + 1$ ($R^2 = 0.99$)	$Y = 1.95X + 1$ ($R^2 = 1.00$)
45 °C	$Y = 0.73X + 1$ ($R^2 = 0.99$)	$Y = 1.87X + 1$ ($R^2 = 0.99$)	$Y = 0.81X + 1$ ($R^2 = 1.00$)	$Y = 1.16X + 1$ ($R^2 = 1.00$)	$Y = 2.93X + 1$ ($R^2 = 0.97$)	$Y = 1.37X + 1$ ($R^2 = 0.99$)
55 °C	$Y = 0.60X + 1$ ($R^2 = 0.99$)	$Y = 1.67X + 1$ ($R^2 = 0.99$)	$Y = 0.75X + 1$ ($R^2 = 1.00$)	$Y = 1.20X + 1$ ($R^2 = 1.00$)	$Y = 2.67X + 1$ ($R^2 = 1.00$)	$Y = 1.42X + 1$ ($R^2 = 1.00$)
65 °C	$Y = 0.51X + 1$ ($R^2 = 0.99$)	$Y = 1.60X + 1$ ($R^2 = 1.00$)	$Y = 0.67X + 1$ ($R^2 = 1.00$)	$Y = 1.15X + 1$ ($R^2 = 1.00$)	$Y = 1.87X + 1$ ($R^2 = 1.00$)	$Y = 1.18X + 1$ ($R^2 = 1.00$)

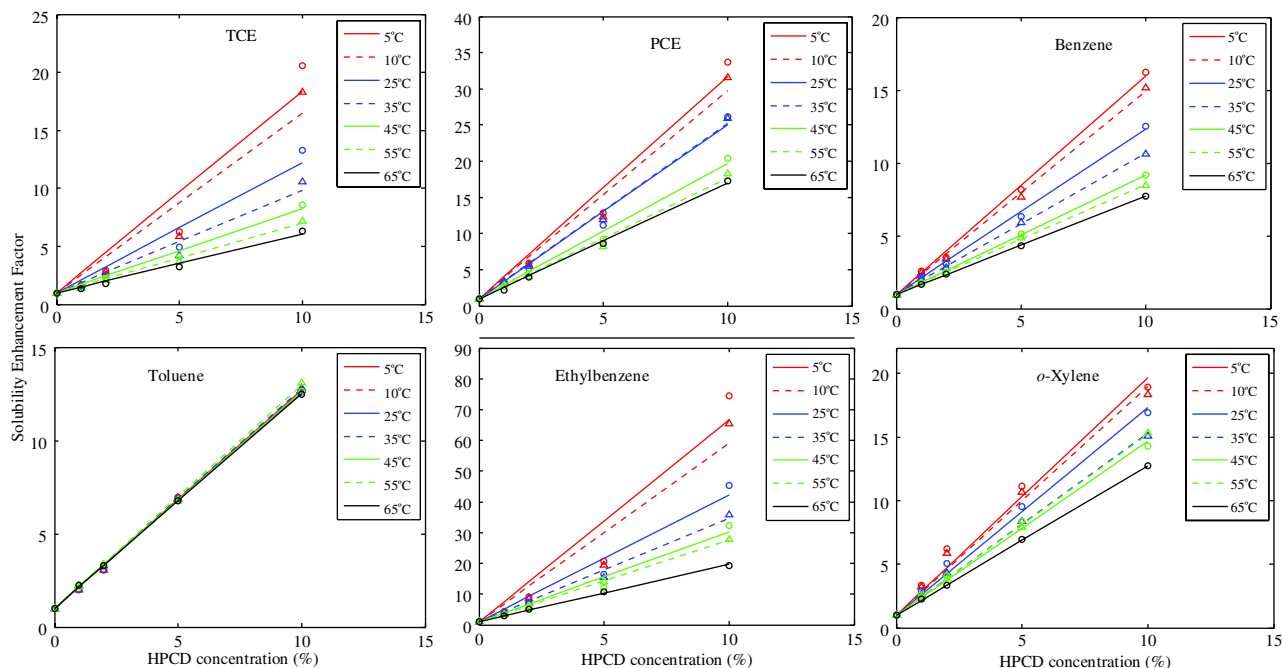


Figure 3. Correlations between SEFs and CD concentrations.

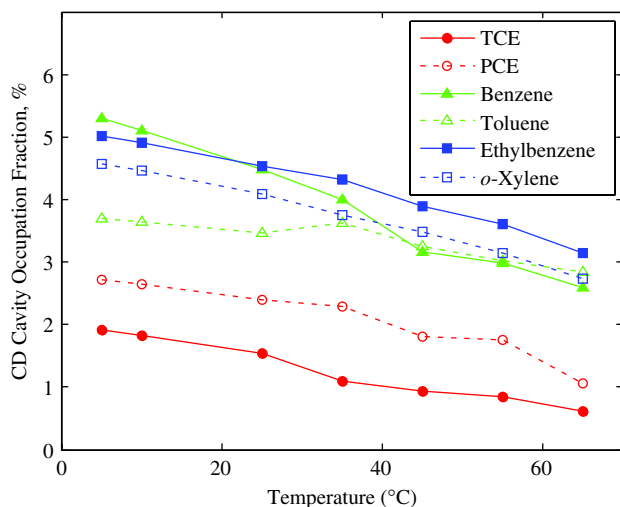


Figure 4. Effect of temperature on CD cavity occupation.

for all the tested compounds except toluene, likely because TCE, PCE, benzene, ethylbenzene, and *o*-xylene are less stable at higher temperatures while toluene is temperature tolerant. The SEFs over a range of CD concentrations at the range of temperature tested in this study can provide reference parameters to future field studies investigating chemical flushes of contaminated site. The finding of linear relationship between SEFs and CD concentrations has the potential to significantly reduce the effort required to accurately estimate SEFs data in a proposed application for groundwater remediation.

CD Cavity Occupation Percentage

The combination of hydrophilic exterior with hydrophobic cavity gives CD molecules surfactant-like

properties which can effectively enhance solubility of pollutants without the potential toxic limitations as common surfactants do (Wang and Brusseau 1993). However, it is important to understand how that occupied percentage changes as a function of CD concentration and temperature. This can be informative and applicable for calculating the CD loading for application CD to groundwater remediation.

Figure 4 shows the temperature effect on CD cavity occupation fraction in an air-CD-water system containing 1% CD with the ratio of liquid: headspace =1:1 and individual pollutant concentration of 50 ppm. As temperature increases, the CD cavity occupation percentage

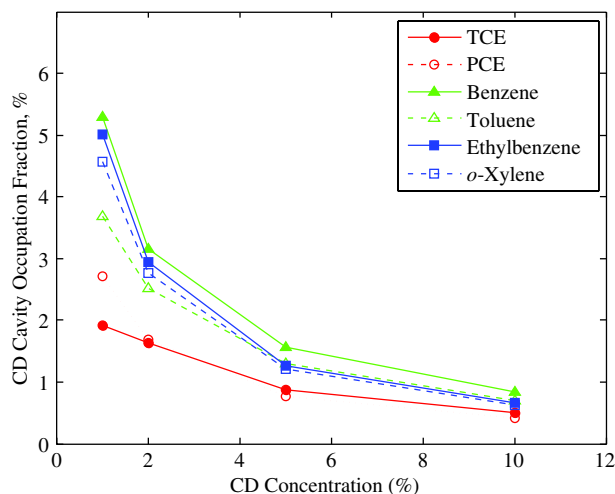


Figure 5. Effect of CD concentrations on CD cavity occupation.

shows a decreasing trend for most of the tested compounds. The occupation fractions at 5 °C were 3.14, 2.55, 2.04, 1.60, and 1.67 times greater than the values at 65 °C for TCE, PCE, benzene, ethylbenzene, and *o*-xylene, respectively. This can be explained as that higher temperature provides more motion energy for organic pollutants such that they are prone to “wiggling” out of CD cavities. Toluene did not show significant temperature dependence, possibly because the CD-toluene complex is thermodynamically stable. The temperature dependence phenomenon can be a benefit for CD-enhancement groundwater remediation. Because groundwater is commonly at lower temperatures, CD can be occupied at a higher percentage, indicating a more efficient CD usage, and therefore it might be possible to lower the CD loading and relevant cost.

Figure 5 shows the dependence of CD cavity occupation fraction on CD concentration in an air-CD-water system with the ratio of liquid: headspace =1:1 and individual pollutant concentration of 50 ppm. As can be seen, the CD occupation percentage increases when CD concentration decreases for all tested chemicals. This indicates that a lower CD concentration should provide more cavity fractions to complex the same amount of guest molecules because fewer cavities are available at lower concentrations, compared with higher concentrations. It is of interest to note that even though CD solutions show excellent solubility enhancement as described in this study, only a small fraction of cavities were occupied in this typical conditions. Thus, it is possible to complex even more contaminants, which is especially promising for engineering applications.

Conclusions

The SEF is an important parameter to evaluate the performance of CD. This study developed a novel method to determine the SEF without the limitation of longer exposure time. The SEF values of HPCD on six common organic pollutants were calculated over a range of CD concentrations (0 to 10% wt/vol) and temperatures (5 to 65 °C) in this study. In conclusion, SEF values are inversely related to temperature for most of the examined chemicals, which is consistent with the assertion that the CD-guest complexes are less stable at higher temperatures. As the definition of SEF predicted, linear relationships (R^2 above 0.90) were found between the SEFs and CD concentrations for all the subject chemicals within the examined temperature range. The CD cavity occupation fraction at 5 °C were 3.14, 2.55, 2.04, 1.60, and 1.67 times greater than the values at 65 °C for TCE, PCE, benzene, ethylbenzene, and *o*-xylene, respectively. The fraction of CD cavities occupied was found to be inversely related to the CD concentration for all tested chemicals when pollutant mass is held constant. This study provides important information to accurately evaluate the performance of CD when used for aquifer remediation.

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