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Understanding pH Effects on Trichloroethylene and Perchloroethylene Adsorption to Iron in Permeable Reactive Barriers for Groundwater Remediation

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Abstract

Metallic iron filings are becoming increasingly used in permeable reactive barriers for remediating groundwater contaminated by chlorinated solvents. Understanding solution pH effects on rates of reductive dechlorination in permeable reactive barriers is essential for designing remediation systems that can meet treatment objectives under conditions of varying groundwater properties. The objective of this research was to investigate how the solution pH value affects adsorption of trichloroethylene (TCE) and perchloroethylene (PCE) on metallic iron surfaces. Because adsorption is first required before reductive dechlorination can occur, pH effects on halocarbon adsorption energies may explain pH effects on dechlorination rates. Adsorption energies for TCE and PCE were calculated via molecular mechanics simulations using the Universal force field and a self-consistent reaction field charge equilibration scheme. A range in solution pH values was simulated by varying the amount of atomic hydrogen adsorbed on the iron. The potential energies associated with TCE and PCE complexes were dominated by electrostatic interactions, and complex formation with the surface was found to result in significant electron transfer from the iron to the adsorbed halocarbons. Adsorbed atomic hydrogen was found to lower the energies of TCE complexes more than those for PCE. Attractions between atomic hydrogen and iron atoms were more favorable when TCE versus PCE was adsorbed to the iron surface. These two findings are consistent with the experimental observation that changes in solution pH affect TCE reaction rates more than those for PCE.

Keywords

groundwater; molecular mechanics; reductive dechlorination; tetrachloroethylene; trichloroethylene; Universal force field; zerovalent iron

Introduction

Zerovalent iron has been widely used as a chemical reducing agent for removing chlorinated solvents from contaminated groundwaters (Gillham and Hanesin, 1994; Orth and Gillham, 1996; Cundy *et al.*, 2008). Although reaction rates and chemical intermediates have been measured for most commonly encountered chlorinated solvents, the reaction mechanisms themselves have not been fully resolved. These reaction mechanisms may involve either

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physical (Noubactep, 2011) or chemical adsorption (Zhang, *et al.*, 2008), and may occur via outer-sphere electron tunneling, inner-sphere electron transfer, or via reduction by atomic hydrogen produced from proton reduction (Matheson and Tratnyek, 1994; Li and Farrell, 2001; Jiao, *et al.*, 2009; Noubactep, 2010; Ghauch, *et al.*, 2011).

Several studies have reported that the relative reaction rates of homologous chloroethenes with zerovalent iron depend on the reaction conditions (Wust *et al.*, 1999; Wang and Farrell, 2003). For example, Wust *et al.* reported that the relative rates of TCE and cis-dichloroethene (DCE) reduction varied between batch and column reactors. This unusual behavior was hypothesized to result from differences in TCE and DCE adsorption to reactive sites in the batch and column reactors. Other investigators have reported that the relative rates of TCE versus PCE dechlorination were dependent on the solution pH value (Wang and Farrell, 2003). The mechanism responsible for this unexpected pH effect may involve complex adsorption interactions between the halocarbons and adsorbed atomic hydrogen produced from proton reduction.

Chloroethene reductive dechlorination by iron first requires either physical or chemical adsorption of the reactant to the surface. There is indirect experimental evidence that chloroethenes form di-sigma complexes with zerovalent iron (Arnold and Roberts, 2000). However, the amount of chloroethene adsorption to reactive sites on the iron surface cannot be directly measured due to the reactions that ensue upon adsorption, and because of interference by adsorption to non-reactive iron oxides coating the surface (Burris *et al.*, 1995; Gotpagar *et al.*, 1998; Noubactep, 2011). This inability to experimentally measure reactant adsorption complicates interpretation of experimental data.

Molecular mechanics modeling can be used to gain information on aspects of a system that are not experimentally accessible. Molecular mechanics simulations employing the Universal force field (UFF) (Rappé *et al.*, 1992) have been used to investigate the structure of chemical intermediates bonded to metal catalysts (Castonguay and Rappé, 1992; Rappé *et al.*, 2000), and have been found to model organometallic complexes (Rappé *et al.* 1993; White and Douglas, 2001) and chlorinated hydrocarbons (Casewit and Rappé, 1992) with reasonable accuracy. However, because it is applicable to the entire periodic table, in some cases it is not as accurate as force fields developed for specific classes of molecules (Casewit and Rappé, 1992). The UFF is a rule-based force field whose parameters depend on the element, its hybridization and connectivity. Structural-electronic effects, that include: electronegativity, resonance, metal-ligand π bonding, and metal-ligand π back-bonding are accounted for using bond order and electronegativity corrections. Molecular mechanics simulations with the UFF can be used to predict bond distances, bond angles, atomic charge distributions, and atomic interaction energies.

The total system energy (U) in the UFF is composed of bonded (U_b) and nonbonded (U_{nb}) potential energies according to:

$$U = \underbrace{E_B + E_A + E_T + E_I}_{U_b} + \underbrace{E_{vdW} + E_{elec}}_{U_{nb}} \quad (1)$$

The bonded energy (U_b) includes bond stretching energy (E_B), bond angle bending and distortion energy (E_A), dihedral angle torsion energy (E_T), and inversion energy (E_I). The nonbonded energy (U_{nb}) includes van der Waals (E_{vdW}) and electrostatic (E_{elec}) energies. Energies associated with bond stretching or compression from the natural bond length (r_{ij}) are described by a harmonic oscillator:

$$E_B = \frac{k_{ij}}{2}(r - r_{ij})^2 \quad (2)$$

where r is the bond length and k_{ij} is a force constant for the i - j bond. The natural bond length is assumed to be the sum of atom-type specific single bond radii (r_i & r_j), a bond order correction, and an electronegativity correction. The bond order correction is of the Pauling (1960) type, and the electronegativity correction is of the O'Keeffe and Brese (1991) type. Fourier cosine expansions are employed to describe all angular and torsional displacements away from their minimum energy values. A Lennard-Jones-type 6–12 potential is used to describe van der Waals interactions and electrostatic interactions are described by Coulomb's law. For the bonded interactions, the energy reference values are the natural bond lengths and bond angles; while for the nonbonded interactions, infinite separation between atoms is assigned an energy value of zero. With mixed reference states for bonded and nonbonded interactions, energy comparisons can only be made between systems with the same bonds between all atoms.

The UFF models charge transfer and induced polarization interactions by allowing the partial atomic charges to respond to the electrostatic environment using the *QEq* charge equilibration method of Rappé and Goddard (1991). The *QEq* method is a scheme that calculates self-consistent reaction-field partial atomic charges by equalizing the electronic chemical potential on each atom. The core electrons are fixed while the valence electrons are allowed to shift centers. Experimentally measured ionization potentials, electronegativities, and atomic radii, along with shielded electrostatic interactions between all charges, are used to construct the electronic chemical potential for each atom. This approach results in atomic charge distributions that depend on both the bonding between atoms and the system geometry.

The goal of this study was to determine how solution pH values affect adsorption of TCE and PCE on iron surfaces. Typically, changes in observed reaction rates with solution pH values have been used to infer that protons are involved in a rate-controlling step in the reaction pathway. However, impedance spectroscopy evidence indicates that the rate-limiting step for both TCE and PCE dechlorination at neutral pH is the transfer of the second electron (Wang and Farrell, 2003). This finding makes it difficult to understand why the reaction rate for TCE is more sensitive to pH than the reaction rate for PCE. The hypothesis behind this work is that solution pH values affect TCE adsorption more than that for PCE. This mechanism may explain why PCE reacts faster at neutral pH values while TCE reacts faster at low pH values (Wang and Farrell, 2003). Towards that end, molecular mechanics simulations using the UFF and *QEq* charge equilibration scheme were performed to determine how the energies of chemisorbed TCE and PCE complexes are affected by the atomic hydrogen surface coverage (θ_H), which is known to increase with decreasing solution pH values (Bockris, 1970; Wang and Farrell, 2006).

Materials and Methods

Molecular mechanics simulations were performed using the Cerius2 modeling suite (Molecular Simulations, Inc. 2000) and the Materials Studio Forcite module (Accelrys, Inc. 2003) with the UFF version 1.02 (Rappé *et al.*, 1992). The UFF force field was selected because it has been validated for all the atoms of interest, and because it is the only widely used force field that incorporates charge transfer effects (Young, 2001). Simulations were performed with a four-layer thick iron slab with 90 iron atoms on its surface. The iron slab was generated by cutting a body centered cubic iron crystal through its (100) plane. To simplify interpretation of the modeling results, the (100) face was chosen for study since all

Fe atoms on that face are equivalent. Because the molecular mechanics approach does not allow bond breaking or forming, the simulations were started with either TCE or PCE chemisorbed to the iron surface in the di-sigma complexes previously proposed by Arnold and Roberts (2000). This approach will not allow the calculation of binding energies for TCE and PCE, but this is not important here since the chemisorption reaction is not the rate-limiting step for their dechlorination (Wang and Farrell, 2003). However, the approach used

here will allow energy changes due to variations in θ_H (*i.e.*, $\frac{dU}{d\theta_H}$) to be compared for TCE and PCE complexes. Although the energy calculations in this study will not be as accurate as those produced by quantum mechanical simulations, they are expected to be at least qualitatively accurate.

Solution pH values will affect the amount of atomic hydrogen adsorbed on the iron surface, which in turn will affect the energetics of TCE and PCE adsorption. Changes in solution pH values were simulated by varying the atomic hydrogen surface coverage on the iron surface. Simulations were performed for systems with 0 to 54 H atoms under conditions where the H atoms were free to move on the iron surface, and under the constraint of fixed positions of the H atoms. All simulations were performed with no constraints on the iron atoms. The fraction of the surface covered by adsorbed atomic hydrogen (θ_H) was calculated by dividing the number of H atoms in each simulation by 90, which was the number of Fe atoms on the adsorption surface of the slab. A single TCE or PCE molecule was used for modeling each complex, and the reported energies were normalized to 1 mole of surface complexes.

Iterative energy minimization and charge equilibration were performed to investigate the energies associated with chemisorbed TCE and PCE complexes. Energies of the iron slab with adsorbed H atoms were subtracted from the energies calculated with the chemisorbed halocarbons. The *QEq* method (Rappé and Goddard, 1991) was used for charge equilibration and the energies were minimized using molecular mechanics simulations performed at 0 K. To avoid local minima and enable the structures to pass over potential energy barriers on the way to the global minimum, the temperature of the system was periodically increased to temperatures above 800 K. The partial atomic charges are expressed in multiples of the fundamental unit of charge, $|e|$, which is 1.602×10^{-19} C.

Results

Figure 1 shows the bond lengths and partial atomic charges for gas phase TCE and PCE determined with the UFF along with the experimentally measured bond lengths (Hellwege and Hellwege, 1976; Kisiel and Pszczolkowski, 1996). These charges and bond lengths will change upon TCE and PCE interaction with the iron surface. Figure 2 shows the structure of TCE chemisorbed to the iron surface and the partial atomic charges on each atom for the conditions of 0 and 6 H atoms. Energies (U) for the TCE-iron complexes as a function of θ_H are given in Figure 3. As shown in Figure 3a, the overall energy was dominated by the electrostatic component arising predominantly from attraction of the negatively charged Cl atoms with the positively charged Fe atoms. The partial charges on each atom in chemisorbed TCE are shown in Figure 2a, and the charges on the iron atoms are shown in Figure 4. Comparison of atomic charges in gas and adsorbed phase TCE shows that the Cl atoms in the adsorbed complex were more negatively charged, while the C atoms in the complex were more positively charged. Overall, there was a net charge transfer of $-1.375 |e|$ from the iron to TCE for the case of $\theta_H=0$.

Electron transfer from the iron resulted in both positively and negatively charged Fe atoms, as illustrated in Figure 4. The two Fe atoms involved in bond formation were the most

positively charged as a result of electron withdrawal by the TCE molecule. In the surface layer, charge transfer from the Fe atoms decreased with increasing distance away from the bonding atoms, and were diminished by more than 95% at a distance of 3 atoms from the C-Fe bond. Iron layers below the surface became both positively and negatively charged. The magnitude of the partial charges decreased rapidly with depth, and by the fourth layer, the maximum charge transferred was reduced to less than 6% of that in the surface layer.

In contrast to the negative electrostatic energies between adsorbed TCE and the iron surface, the van der Waals energies associated with the TCE complex were positive, as shown in Figure 3a. The positive E_{vdW} values over the entire θ_H range indicate that atoms in chemisorbed TCE were sufficiently close to the iron surface to experience repulsions. The total bonded energies associated with the TCE complexes were also unfavorable, as indicated by the positive values for U_b in Figure 3a. The individual energies associated with bond bending, stretching and torsion were all positive, as illustrated in Figure 3b. Most of the unfavorable U_b can be attributed to the bond angle distortions associated with the C-Fe bonds.

Figure 3 also shows the effect of H atoms on the potential energies for the TCE-iron complexes. The increasingly negative U values with increasing θ_H values show that the presence of H atoms significantly enhanced the energetic favorability of the TCE complexes. This can be attributed to electrostatic effects arising from electron donation by hydrogen to atoms in TCE, and to attractions between TCE and the H atoms themselves. As illustrated in Figure 2b for the case of 6 H atoms, all but one of the H atoms surrounding TCE became positively charged. Electron donation by the H atoms resulted in an additional charge transfer of $-0.468 |e|$ to the TCE molecule. Hydrogen inducement of more negative charges on the Cl atoms in TCE resulted in greater electrostatic attraction to the positively charged Fe atoms in the surface layer.

The structure of chemisorbed PCE is shown in Figure 5 for the case of 0 and 6 H atoms, and the U values associated with the PCE-iron complexes are shown in Figure 6 as a function of θ_H . Similar to the case for TCE, there was a net charge transfer from the iron to PCE. The charge transfer was greatest for the two Cl atoms closest to the surface, and the overall charge transferred to PCE was greater than that for TCE at all θ_H values. The overall potential energy was also dominated by the electrostatic component, and the E_{vdW} and U_b were both positive. As with TCE, the presence of H made PCE adsorption more energetically favorable, as indicated by the decreasing U values with increasing θ_H values shown in Figure 6a.

Increasing θ_H values decreased the energies for both PCE and TCE complexes, but at low

θ_H values, the $\frac{dU}{d\theta_H}$ for TCE was greater than that for PCE, as shown in Figure 7. This can be attributed primarily to differences in charge transfer, rather than by differences in the positions of the H atoms, as simulations with H atoms in fixed positions yielded similar results. Figure 8 shows that the greater charge transfer to PCE versus TCE was relatively constant over the entire range of θ_H values. The greater charge transferred to PCE versus TCE came from both the Fe and H atoms. The positively charged Fe and H atoms experienced electrostatic repulsion, resulting in positive E_{elec} contributions to the total system energy. The repulsive Fe-H electrostatic interactions were greater for the PCE versus TCE system, due to more positively charged H and Fe atoms in the PCE system. Smaller electrostatic Fe-H repulsions in the TCE system explains why charge transfer from H atoms to the halocarbons lowered the energies for the TCE complexes more than those for PCE.

Discussion

There are several ways to interpret the modeling results that are consistent with published experimental data. Electrochemical impedance spectroscopy indicates that reduction of TCE and PCE may occur via direct electron transfer from the iron, or by atomic hydrogen adsorbed on the iron surface (Wang and Farrell, 2003). The mechanism involving reduction by atomic hydrogen becomes more important with decreasing pH values due to increasing θ_H as pH declines (Wang and Farrell, 2006). Results from the modeling indicate that adsorbed TCE and PCE both decrease the energetic favorability for atomic hydrogen adsorbed on the iron surface, as shown in Figure 9. For all θ_H values, the greater charge withdrawal by PCE versus TCE resulted in decreased attractions between Fe and H atoms for the PCE complex. This suggests that for a fixed pH value, iron surfaces with adsorbed PCE will have lower θ_H values than those with adsorbed TCE. Since the rate of halocarbon reduction by atomic hydrogen should be proportional to the θ_H value, reduction by atomic hydrogen may be more important for TCE versus PCE at low pH values. This hypothesis was proposed by Wang and Farrell (2003) to explain why decreasing pH values increased TCE reaction rates more than those for PCE.

An alternative or complementary interpretation of the modeling results involves the effect of atomic hydrogen on the equilibrium amounts of TCE and PCE adsorbed on the iron surface. The qualitative prediction of the modeling is that atomic hydrogen decreases the energy of TCE complexes more than those for PCE. Thus, adsorbed atomic hydrogen may increase the rate of TCE dechlorination more than that for PCE by increasing the equilibrium constant for TCE adsorption more than that for PCE.

The validity of these two interpretations of the modeling can be assessed using a simple mathematical model and experimental data. For surface mediated reactions that first require adsorption of the reactant (i), the overall reaction rate (R) may be expressed as:

$$R = k\theta_i \quad (3)$$

where k is the rate constant for the reaction, and θ_i is the fraction of the electroactive surface covered by adsorbed molecules of type i . If the reaction is not limited by the rate of adsorption, the adsorption reaction is in equilibrium under steady-state conditions (Fogler, 1999). Since past evidence has shown that TCE and PCE reaction rates on iron surfaces are limited by the transfer rate of the first two electrons (Wang and Farrell, 2003), rates of reactant adsorption (r_{ads}) and desorption (r_{des}) are in equilibrium and may be expressed as:

$$r_{ads} = k_{ads}(1 - \theta_i)C \quad (4)$$

$$r_{des} = k_{des}\theta_i \quad (5)$$

where C is the aqueous concentration of i in equilibrium with the surface, and k_{ads} and k_{des} are the adsorption and desorption rate constants, respectively. Because the adsorption reaction is in equilibrium under steady-state conditions, r_{ads} is equal to r_{des} , and equations 4 and 5 may be combined to yield:

$$\theta_i = \frac{K_{eq}C}{1 + K_{eq}C} \quad (6)$$

where $K_{eq} = k_{ads}/k_{des}$. Inserting equation 6 into equation 3 gives the rate expression for reaction of compound i as:

$$R = k \frac{K_{eq}C}{1 + K_{eq}C} \quad (7)$$

Equation 7 shows that the observed rate of reaction should depend on both the rate constant, k , and the adsorption equilibrium constant, K_{eq} .

The equation 7 model can be applied to published data for TCE and PCE dechlorination by polished iron wires at pH values of 3 and 7 (Wang and Farrell, 2003). The rate constants in Table 1 show that decreasing the pH value from 7 to 3 increased the k for TCE by a factor of 32 while only a factor of 23 increase was seen for PCE. For a reaction mechanism that involves reduction by atomic hydrogen, the greater increase in the TCE versus PCE reaction rate constant is consistent with higher levels of adsorbed atomic hydrogen when TCE versus PCE is adsorbed on the surface. Thus, the first interpretation of the modeling results is consistent with the experimental data.

The second interpretation of the modeling results can be tested by looking at the effect of pH on the adsorption equilibrium constants for TCE and PCE. Table 1 shows that decreasing the pH value from 7 to 3 increased the K_{eq} for TCE by a factor of 54 while only a factor of 15 increase was seen for PCE. Given that prior work has shown that θ_H values on iron are approximately 0.02 at neutral pH (Bockris *et al.*, 1987) and 0.08 at a pH value of 3 (Wang and Farrell, 2006), the trend in energies for the adsorbed TCE and PCE complexes is consistent with the trend in K_{eq} values over the relevant θ_H range.

The factor of 3.6 greater increase in the K_{eq} value for TCE versus PCE appears to be small

compared to the large differences in $\frac{dU}{d\theta_H}$ for TCE versus PCE at low θ_H values. Some of the disparity between the effect size in the experiment and that observed in the simulations can be attributed to disparities between the model and a real system. The two most obvious disparities include solvent effects and the heterogeneity of surfaces on real iron. Of these two possibilities, solvent effects are likely the dominating factor, since ignoring solvation effects for a polar solvent will lead to artificially high electrostatic interaction energies. Surface heterogeneity on real iron is likely a smaller factor, since there is considerable experimental evidence that halocarbon reactions occur primarily at cracks in the oxide where bare metal is exposed (Logue and Westall, 2003; Wang *et al.*, 2004), and reactions on other surfaces, such as magnetite (Danielson and Hayes, 2004) or other iron oxide phases (Odziemkowski and Simpraga, 2004), are much slower. The presence of crystal planes other than the (100) on real iron surfaces may also contribute to the disparity between the experimental and calculated effect size. However, this factor is likely to be small since the mechanism for the differences in TCE and PCE behavior, *i.e.*, greater charge withdrawal by PCE, would also be valid on other iron surface planes.

This research employed a novel technique to investigate a factor impacting halocarbon dechlorination that would be impossible to study experimentally. Although the calculated energy values can only be considered qualitative, the trends identified in the molecular mechanics simulations suggest that solution pH values affect the adsorption behavior of TCE and PCE to different degrees. Although it lacks the accuracy required for quantitative predictions, this type of modeling is very useful for interpretation of experimental data and for identifying important factors in complex experimental systems.

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Fig. 1.

Bond lengths in units of Å computed using the UFF (1) and experimental bond lengths (2) for gas phase TCE (a) and PCE (b). Also shown are the partial atomic charges (3) in units of $|e|$ calculated with the *QEq* scheme

Fig. 2.

a) Structure of a TCE molecule chemisorbed to iron via di-sigma C-Fe bonds. Also shown are the partial atomic charges for chemisorbed TCE for the case of $\theta_H=0$. b) Structure and partial atomic charges for chemisorbed TCE for the case of 6 H atoms ($\theta_H=0.067$). Carbon is grey, chlorine is green, hydrogen is white, and iron is purple

Fig. 3.

a) Total potential energies (U) for TCE-iron complexes as function of the fractional iron surface coverage by atomic hydrogen. Also shown are the electrostatic (E_{Elec}), van der Waals (E_{vdW}), and total bonded (U_b) energy contributions to U . b) Bond length stretching (E_B), bond angle bending (E_A), and dihedral angle torsion (E_T) energy contributions to U_b as function of the fractional atomic hydrogen surface coverage

Fig. 4. Partial atomic charges on the iron atoms in units of $|e|$ for the TCE complex for $\theta_H=0$. Carbon atoms in TCE are bonded to iron atoms in row S5, columns 5 and 6 of layer 1

Fig. 5.

a) Structure of a PCE molecule chemisorbed to iron via di-sigma C-Fe bonds. Also shown are the partial atomic charges for chemisorbed PCE for the case of $\theta_H=0$. b) Structure and partial atomic charges for chemisorbed PCE for the case of 6 H atoms ($\theta_H=0.067$). Carbon is grey, chlorine is green, hydrogen is white, and iron is purple

Fig. 6.

a) Total potential energies (U) for PCE-iron complexes as function of the fractional iron surface coverage by atomic hydrogen. Also shown are the electrostatic (E_{Elec}), van der Waals (E_{vdW}), and total bonded (U_b) energy contributions to U . b) Bond length stretching (E_B), bond angle bending (E_A), and dihedral angle torsion (E_T) energy contributions to U_b as function of the fractional atomic hydrogen surface coverage

Fig. 7.

Comparison of the effect of θ_H on the potential energies (U) associated with chemisorbed TCE and PCE complexes. Note that because of different atomic bonding in the TCE and PCE complexes, the energies between TCE and PCE complexes cannot be directly

compared. Only comparisons between the $\frac{dU}{d\theta_H}$ for TCE and PCE are valid

Fig. 8. Charge transfer to TCE or PCE in units of $|e|$ as a function of the fractional atomic hydrogen surface coverage

Fig. 9.

Interaction energies for hydrogen and iron per mol of TCE or PCE as a function of the fractional atomic hydrogen surface coverage. Energies were determined by removing TCE or PCE from the geometry and charge optimized complexes and then calculating the pairwise interactions while keeping the atomic positions and partial atomic charges the same as those in the presence of TCE or PCE

Table 1

Equilibrium and rate constants determined by fitting equation 8 to published data for TCE and PCE dechlorination (Wang and Farrell, 2003).

	pH = 7		pH = 3	
	K_{eq}	k	K_{eq}	k
TCE	8.7×10^{-7}	3.4×10^{-9}	4.7×10^{-5}	1.1×10^{-7}
PCE	1.4×10^{-6}	5.9×10^{-9}	2.1×10^{-5}	1.4×10^{-7}