

## **Electrokinetically Enhanced Remediation of Hydrophobic Organic Compounds in Soils: A Review**

RICHARD E. SAICHEK and KRISHNA R. REDDY

*Department of Civil and Materials Engineering, University of Illinois at Chicago,  
Chicago, Illinois, USA*

*Electrokinetically enhanced remediation is an innovative technology that has the potential to remediate hydrophobic organic compound (HOC) contamination in soils and groundwater. A surfactant/cosolvent is used to increase HOC desorption and solubilization, and an applied electric potential facilitates contaminant transport primarily by electroosmosis and/or electrophoresis. Electroosmotic flow generally improves soil–solution–contaminant interaction, especially in zones of high organic content and/or low hydraulic conductivity. The electrokinetically enhanced remediation process is fairly simple to implement and operate, but the fundamental reactions that govern the remediation method are complex. An adequate knowledge of the contaminant transport mechanisms and the physical, chemical, and electrochemical processes is essential in order to optimize system performance. This article reviews previous research efforts on HOC remediation and the use of in situ flushing and electrokinetics for organic contaminants. In addition, to gain a better understanding of the individual components and the complexities of the electrokinetically enhanced in situ flushing process, this article presents background information on HOCs and surfactants/cosolvents, as well as the basic parameters that affect the performance of in situ flushing and electrokinetic technologies. Since the success or failure of electrokinetic remediation for HOC pollutants in low permeability soils largely depends*

---

This study was partly supported by the National Science Foundation Grant, CMS number 0100073. The financial support of this agency is gratefully acknowledged.

Address correspondence to Krishna R. Reddy, Department of Civil and Materials Engineering, University of Illinois at Chicago, 2095 Engineering Research Facility, 842 West Taylor Street, Chicago, IL 60565, USA. E-mail: kreddy@uic.edu

*on electroosmotic advection and/or electrophoresis, the discussion concerning electrokinetics focuses on these contaminant transport mechanisms.*

**KEY WORDS:** cosolvents, electrokinetics, electroosmosis, flushing, PAHs, remediation, soils, surfactants

## I. INTRODUCTION

During the last few decades the production of synthetic organic chemicals has been growing exponentially, and numerous organic compounds have been introduced into the environment in vast quantities (Schwarzenbach et al., 1993, p. 1). The most familiar pollutants are associated with fossil fuels, and this is understandable since the global annual production of liquid petroleum products is close to 3 billion metric tons (Schwarzenbach et al., 1993, p. 34). One large group of persistent and toxic contaminants is the hydrophobic organic contaminants (HOCs), and, obviously, the main characteristic that differentiates these pollutants from other contaminants is that they are hydrophobic—they are repelled from water and have a low aqueous solubility. In addition, they are unusually stable and resistant to chemical attack (Sawyer and McCarty, 1978, p. 98; Connell, 1997, p. 211; Gillette et al., 1999). Therefore, as a result of their unique chemical properties, HOCs tend to remain concentrated in the environment, and they are not appreciably diluted or transported by precipitation, groundwater, or surface water. The hydrophobicity and persistence of HOCs has also made them notoriously challenging to clean up, and, as a result, they have become extremely widespread environmental contaminants (Luthy et al., 1994; Loehr and Webster, 1996; Connell, 1997, pp. 205–218; U.S. Environmental Protection Agency [U.S. EPA], 1997).

Although the chemical properties of HOCs make them relatively immobile compared to other more soluble contaminants, they still pose a major threat to the environment because they slowly leach into groundwater or surface water, and this contamination may continue for as long as 100 years (National Research Council, 1997, p. 122). Thus, for remediation techniques such as in situ flushing, the restoration goal is often to completely remove the HOCs that are contributing to the residual, long-term contamination problem. Extremely-low-solubility compounds may be considered to be fairly immobile, and therefore some investigators may assume that they do not pose a significant public health or environmental risk. To the contrary, since these compounds or their metabolites could be toxic and low concentrations may leach into the groundwater for long periods of time, it is beneficial to remove as much low-solubility contamination as possible.

HOCs are classified by their low aqueous solubility, and this is appropriate because solubility is a fundamental chemical characteristic and an essential indicator of environmental behavior. It is defined as the maximum concentration of the compound in pure water at equilibrium with the pure compound in its actual aggregation state (gas, liquid, solid) (Schwarzenbach et al., 1993, p. 76). Solubility is of primary importance for the enhanced in situ flushing process because the objective is to solubilize the pollutants via an extracting solution, and, ultimately, it is this extracting solution that is responsible for purging the HOCs from the soil matrix. Solubility is also very important because it is used along with other partition coefficients to model and estimate contaminant fate and transport (Mackay et al., 1996; Cole and Mackay, 2000; Valsaraj, 2000, pp. 70–74).

Organic compounds range in aqueous solubility from almost infinitely soluble, or miscible, to virtually insoluble; therefore, HOCs must have solubilities that fall beneath some maximum value. Schwarzenbach et al. (1993, p. 77) defines moderately or sparingly water-soluble compounds as those compounds with solubilities that are much less than 1 mol/L, and this category includes most of the environmentally relevant organic compounds. There are many “relevant” environmental pollutants however, and the performance of a remediation technique, such as in situ flushing, is often dependent upon contaminant properties, such as solubility, so it is advantageous to delineate the range of applicable solubilities and be specific about which contaminants are targeted.

A review of several studies that specifically mention HOCs shows that some environmental researchers consider organic chemicals such as chloroform, trichloroethylene (TCE), and perchloroethylene (PCE) as HOCs (Luthy et al., 1997; Farrell et al., 1999), and these substances have aqueous solubilities of approximately 7700, 1200, and 150 mg/L, respectively (Schwarzenbach et al., 1993, pp. 618–625). Other studies consider polycyclic aromatic hydrocarbons (PAHs) as representative HOCs (Edwards et al., 1994a, b, c; Ko et al., 1998a, b), and PAHs, such as naphthalene, phenanthrene, and pyrene, have significantly lower aqueous solubilities of about 31.5, 1.1, and 0.14 mg/L, respectively (Schwarzenbach et al., 1993, pp. 618–625). Karickhoff et al. (1979) evaluated a group of about 10 different HOCs that included aromatic and chlorinated hydrocarbons, and the aqueous solubilities of these compounds ranged over several orders of magnitude, from around 0.0005 to 1800 mg/L. Thus, the term “HOC” appears to apply to a wide range of organic compound solubilities, and researchers seem to vary in opinion over what solubility constitutes a compound to be a HOC.

Electrokinetically enhanced in situ flushing is applicable for low-solubility as well as moderately soluble organic compounds, but compounds such as PAHs, which have aqueous solubilities lower than about 30 mg/L, are frequently the most challenging for conventional remediation methods. Therefore, the term “HOC” in this review article is generally applied to

denote those organic compounds with solubilities of 30 mg/L or lower. More soluble organic compounds, such as phenol, gasoline, or TCE, have been removed from clays electrokinetically by flushing with water (Bruell et al., 1992; Acar et al., 1992), but the more hydrophobic organic compounds, such as PAHs, usually require enhancing solutions (Pamukcu, 1994; Acar et al., 1995; Ko, 1998; Hatem, 1999; Li et al., 2000).

Water is occasionally used in the in situ flushing process, and, historically, groundwater was used in conventional pump-and-treat systems (National Research Council, 1997, pp. 32–35; Roote, 1998). For in situ flushing, water may perform reasonably well for soluble or moderately soluble organic compounds, or under optimal subsurface conditions, but it has many limitations, and surfactant/cosolvent solutions can significantly enhance the process (Luthy et al., 1994; Sabatini et al., 1996; Roote, 1997, p. 10). Many environmental professionals may consider in situ flushing with water to be the same as a pump-and-treat system; however, the term “pump-and-treat” usually refers to a conventional groundwater treatment technology, whereas “in situ flushing” applies to a more modern and advanced approach that is applicable for both groundwater and soils.

Pump and treat generally involves drilling an extraction well into an aquifer and pumping out the contaminant-laden groundwater. The water is then treated and may or may not be recycled back to the subsurface via an injection well (Jafvert, 1996, p. 1). Conversely, in situ flushing with water is an enhancement of the pump-and-treat technique, and uses the flushing action of the water to purge the contaminants (Roote, 1997, p. 1). The flushing action may be improved by increasing the natural flow rate using a variety of different configurations and methods of fluid injection and extraction, such as pressurized systems, multi-injection and/or extraction wells, horizontal wells, trenches, above ground sprayers, and subsurface collection drains (Roote, 1997, p. 1, 11). Due to the diverse assortment of injection and infiltration schemes, in situ flushing is applicable for vadose zone and/or saturated subsurface regions (Roote, 1997, p. 1). Although in situ flushing with water can be used successfully in limited situations, generally this process includes the use of solubility-enhancing additives such as surfactants/cosolvents, especially for low-aqueous-solubility HOCs such as PAHs.

## II. CHARACTERISTICS OF HYDROPHOBIC ORGANIC COMPOUNDS

### A. Toxicity

Research into the toxicology of HOCs is ongoing, but presently many of these pollutants are considered to be mutagenic and/or known carcinogens (Harvey, 1991; Menzie et al., 1992; Connell, 1997, pp. 213–215; NIEHS, 1997). HOCs are found throughout a list of priority hazardous substances compiled by the U.S. EPA and the Agency for Toxic Substances and Disease

Registry (ATSDR, 1999). This list ranks substances according to their frequency, toxicity, and potential for human exposure at National Priority List (NPL) (Superfund) sites in the United States. Polychlorinated biphenyls (PCBs), benzo[a]pyrene, and PAHs as a group were numbers 6, 8, and 9, respectively, on the 1999 list of priority hazardous substances (ATSDR, 1999). In addition, in the 1997 report on carcinogens, the U.S. Department of Health and Human Services cited evidence that 15 PAHs caused various types of cancer in experimental animals (NIEHS, 1997). According to Lee et al. (1981, p. ix), PAHs are the largest class of chemical carcinogens, and both Clar (1964) and Harvey (1991) also reported in detail about the evidence of PAH carcinogenicity in animals.

## B. Basic Chemistry

Before delving into the environmental behavior of HOCs, it is important to cover some basic concepts of chemistry. Structurally, organic molecules usually form covalent bonds, or bonds in which the atoms share outer-shell electrons. The tendency of an atom to attract an electron is called its electronegativity, and it depends on the size of the atom, the charge of the nucleus, and the electron configuration (Schwarzenbach et al., 1993, pp. 14–15). Within a covalent bond, or partially ionic covalent bond, the more electronegative atom has a greater attraction for electrons. Therefore, negative charge accumulates at the end of the bond near the more electronegative atom, while positive charge accumulates at the other end of the bond (Schwarzenbach et al., 1993, p. 14).

Oxygen is a highly electronegative atom, so when it bonds with hydrogen atoms to form water, the hydrogen atoms become covalently linked to the oxygen atom (Valsaraj, 2000, p. 109). As a result, water molecules are very polarized and have dipoles, and water is a highly dielectric liquid. In addition, the polarized structure of the water molecules causes strong intermolecular interactions, and they network with each other via the formation of hydrogen bonds (Yalkowsky and Banerjee, 1992, p. 12; Valsaraj, 2000, p. 109). Conversely, organic molecules are often composed of atoms with similar electronegativities, and, as a consequence, the electrons are more evenly distributed and the molecules are often much less polarized (Schwarzenbach et al., 1993, p. 82). Though molecules may be nonpolar, instantaneous electron displacements may cause the development of different electron-deficient and electron-rich regions, and when these molecules interact, attractive van der Waals forces exist (Schwarzenbach et al., 1993, p. 63).

When dielectric materials like water are placed within an electric field, such as between two condenser plates, they have an insulating capacitance due to the molecular dipole interactions with the electric field (Callister, 1997, p. 625). For a parallel-plate capacitor with a vacuum between the plates, the capacitance is equal to the area of the plates divided by the distance

between them, multiplied by a universal constant called the permittivity of the vacuum ( $\epsilon_0$ ) (Callister, 1997, p. 625). When a dielectric material replaces the vacuum in the region between the plates, the permittivity ( $\epsilon$ ) increases, and the permittivity of the material divided by the permittivity of the vacuum is a ratio called the relative permittivity or the dielectric constant ( $D = \epsilon/\epsilon_0$ ) (Mitchell, 1993, p. 112).

The dielectric constant is a measure of the ability of a substance to disperse electrical forces and insulate, or stabilize, charge-separated systems, and it is a method of expressing the relative polarity of the material or liquid (Carey, 1987, p. 314). It can also be thought of as the tendency of the molecules to orient themselves within an electric field, and liquids such as water that have polarized molecules, which tend to become more ordered, have high dielectric constants (Mitchell, 1993, p. 112). Water has a dielectric constant of 78.54 at 25°C, while generally many organic liquids are not as polarized and have lower dielectric constants, such as ethanol with a dielectric constant of 24.3 at 25°C (Weast et al., 1984, p. E-50).

### C. PAHs

This article assumes PAHs as representative HOCs mainly because these persistent compounds are generally hazardous, ubiquitous in the environment, and prevalent at many contaminated sites, such as former manufactured gas plant (MGP) sites and wood treatment facilities (Harvey, 1991, pp. 11–23, Luthy et al., 1994; Connell, 1997, p. 205; National Research Council, 1997, p. 121; U.S. EPA, 2000, pp. 1–1, 3–43). PAHs are hydrocarbons, and, for remediation projects, the sources are usually related to fossil fuel utilization and conversion processes as well as to the treatment of wood (National Research Council, 1997, p. 120).

Generally, PAHs are composed of neutral, nonpolar molecules that comprise two or more benzene rings, which are fused together through two or more carbon atoms (National Research Council, 1997, p. 120; Connell, 1997, p. 205). A benzene ring has six carbon atoms and a conjugated system of  $\pi$  electrons (Carey, 1987, p. 392). There is a resonance energy that exists due to the delocalization of electrons in the cyclic  $(4n + 2)$   $\pi$ -bond system, and this energy causes cyclic compounds to be particularly stable compared to nonaromatic compounds (Schwarzenbach et al., 1993, pp. 27–29). PAH nomenclature and chemistry are somewhat complex because the ring structures fuse together in a variety of orientations and configurations, and there are many books on the chemistry of these unique compounds (Clar, 1964; Lee et al., 1981; Harvey, 1991).

From a remediation perspective, it is important to examine the environmental properties of these compounds. Naphthalene has the lowest melting point, at 80.6°C (Schwarzenbach et al., 1993, p. 621), so the PAHs

generally exist as solids in the environment, and some PAHs may exist as needles, plates, crystals, or prisms and range from colorless to golden yellow (NIEHS, 1997). In addition, PAHs are clearly hydrophobic. The lowest molecular weight and most soluble PAH in water is naphthalene at 31.5 mg/L (Schwarzenbach et al., 1993, p. 621), and the highest molecular weight PAH of environmental interest is coronene, and it has the lowest solubility, which is about  $1.4 \times 10^{-4}$  mg/L (Connell, 1997, p. 206). Within the PAH family, many of the properties, such as solubility, melting and boiling point, vapor pressure, and octanol–water partition coefficient ( $K_{ow}$ ), correspond to the molecular weight and structure of the compound. The linear free energy relationship (LFER) approach is commonly used to estimate a partition coefficient from the chemical structure or chemical properties, and this approach is used to relate the aqueous solubility to  $K_{ow}$  (Schwarzenbach et al., 1993, pp. 134–138; Valsaraj, 2000, p. 99).

$K_{ow}$  is the molar concentration of the compound in the octanol phase divided by its molar concentration in the aqueous phase at equilibrium (Schwarzenbach et al., 1993, pp. 125–130), and octanol is a water-immiscible organic solvent that serves as a representative substance for organisms or natural organic matter. Therefore,  $K_{ow}$  is an important measure of partitioning behavior, and it is an indication of the tendency of a compound, such as a PAH, to transition from an aqueous to an organic phase (Schwarzenbach et al., 1993, p. 124; Connell, 1997, p. 207; Cole and Mackay, 2000). Moreover, since  $K_{ow}$  is a measure of the partitioning of the compound between the aqueous and organic phases, or its affinity for the nonpolar phase, it is strongly related to aqueous solubility and vice versa (Schwarzenbach et al., 1993, pp. 132–134). Generally, PAHs have  $K_{ow}$  values that show a tendency for partitioning to organic phases in soils and bioaccumulating in organisms (Connell, 1997, p. 207).

Many microorganisms including bacteria, algae, and fungi have the ability to biodegrade the 2-ring through 6-ring PAHs, but this is generally under aerobic and optimal conditions (Luthy et al., 1994). For in situ bioremediation, the soils are largely under anaerobic conditions, and the low bioavailability of oxygen and the substrate, the PAHs, substantially limits biodegradation (Luthy et al., 1994; Pinto and Moore, 2000). It was only recently shown that the lowest molecular weight PAH, naphthalene, could be biodegraded under strictly anaerobic conditions (Rockne et al., 2000).

#### D. Interfacial or Surface Tension

When two bulk phases meet together, there may be large differences in molecular density and interaction. Consequently, at this boundary, or interface, there is often an abrupt change in the physical properties of the two phases. Essentially, all these boundaries may be considered as interfacial

regions, but if one of the bulk phases is air or gas and the other phase is a liquid or a solid, the interface is called a surface. Imagine a water molecule in a bulk liquid phase where it experiences average net attractive molecular forces due to the other water molecules in all directions. When the water molecule is at the surface, there is an absence of attractive forces in the direction of the air phase because of the much lower density of molecules and different types of molecules in the air phase. Due to the different molecular forces, the surface water molecule is unbalanced, and this condition gives it a greater energy than the bulk-phase water molecules, so it adjusts itself to minimize its surface area by exerting stronger attractive forces with other water molecules at the sides and below (Sawyer and McCarty, 1978, pp. 54–55; Valsaraj, 2000, pp. 40–41). This same tensile force is located at an interface, such as between an HOC and water, because water molecules have a much stronger attraction for themselves than to HOC molecules and vice versa. In addition, the interfacial tension of the water molecules causes the interfacial surface area between the two phases to be minimized, and this is why water droplets assume a spherical shape (Sawyer and McCarty, 1978, pp. 54–55). Furthermore, since the water molecules located at interfacial regions have greater energy, it takes work to transport them there, and the interfacial tension is defined as the minimum amount of work needed to expand the interfacial area (Rosen, 1989, pp. 1–3).

## E. Basic Thermodynamics

It is difficult to explain the behavior of HOC molecules in the environment without an understanding of a few basic concepts from thermodynamics, which describes the energy changes that accompany physical and chemical processes (Sawyer and McCarty, 1978, p. 43). The following thermodynamic background information is primarily based on the explanation given by Schwarzenbach et al. (1993).

Molecules possess a combination of internal and external energies. Internal energies are associated with the structure of the molecule, such as its chemical bonds or bond vibrations, whereas external energies are associated with the immediate environment of the molecule, such as the orientation or interaction of the molecule with other molecules (Schwarzenbach et al., 1993, p. 42). At the molecular scale, the change in enthalpy ( $\Delta H$ ) is a measure of the forces associated with the internal and external energies, and the change in entropy ( $\Delta S$ ) is a measure of the molecular volume or “freedom” in which a molecule has to move and change its position (Schwarzenbach et al., 1993, p. 49). The change in enthalpy and entropy are significant when molecular interactions occur between different or dissimilar molecules, and under these circumstances the mixture exhibits nonideal behavior (Schwarzenbach et al., 1993, p. 82).

At a larger scale, chemical reactions that require energy, or are endothermic, have a positive change in enthalpy ( $+\Delta H$ ), while reactions that return energy, or are exothermic, have a negative change in enthalpy ( $-\Delta H$ ) (Sawyer and McCarty, 1978, pp. 44–52). Moreover, reactions that result in a more random structure have a positive change in entropy ( $+\Delta S$ ), while reactions that cause the structure to become more ordered result in a negative change in entropy ( $-\Delta S$ ). The free energy ( $\Delta G$ ) concept was developed to determine if a reaction would occur on its own accord, and the change in free energy incorporates both the changes in enthalpy and entropy. The change in free energy is negative for reactions that will occur spontaneously, and it is positive for reactions that will require energy and/or will result in a more ordered molecular arrangement. In addition, if the free energy is positive, the reaction generally will occur spontaneously in the opposite direction. At constant temperature and pressure, the free energy is described by the following equation (Sawyer and McCarty, 1978, pp. 49–50):

$$\Delta G = \Delta H - T \Delta S \quad (1)$$

where  $T$  is positive because it describes the temperature (K). From this equation, it can be seen that reactions that return energy, or are exothermic ( $-\Delta H$ ), and reactions that lead to a more random structure ( $+\Delta S$ ) will produce a negative free energy, and they are favored to occur spontaneously. Furthermore, when a reaction reaches equilibrium, the free energy is zero.

Before discussing chemical mixtures in the liquid state, it may be easier to start with gases, because under environmental pressures near 1 atmosphere (atm) there are few molecular interactions and gases are ideal mixtures. In a mixture of gases such as air, the total pressure ( $P$ ) is related to the partial pressure ( $P_i$ ) of a particular component by the mole fraction ( $x_i$ ) in the following equation:  $P_i = x_i P$ . The mole fraction is

$$x_i = \frac{n_i}{\sum_j n_j}$$

where  $n_i$  is the number of moles of the component, and the denominator ( $\sum_j n_j$ ) is the total number of moles of all the constituents present (Schwarzenbach et al., 1993, p. 46). Therefore, for pure substances,  $x_i = 1$ .

The total energy of a mixture of chemicals is the sum of the contributions of each chemical component. For example, imagine a simple closed system as a sealed beaker containing air at a pressure of 1 atm at a constant temperature. This is an ideal mixture since the air molecules are similar in size and shape and their molecular interactions are not significant (Yalkowsky and Banerjee, 1992, p. 18). Moreover, for ideal mixtures, the changes in enthalpy and entropy do not greatly affect the energy of the system. If an additional gas component such as oxygen is injected into the beaker, the pressure and

the energy of the system increase in proportion to the number of oxygen molecules added. There are now more gas molecules colliding each other and the walls of the beaker. The rise in energy that occurs divided by the number of molecules of the component ( $i$ ) added is called the chemical potential ( $\mu$ ) (Schwarzenbach et al., 1993, p. 42).

Thermodynamic functions such as enthalpy, entropy, and chemical potential are difficult quantities to measure, so comparisons are made based upon reference states, such as the pure liquid state at standard conditions of 25°C and 1 atm (Sparks, 1986, p. 154; Schwarzenbach et al., 1993, pp. 46–47). Since most environmental situations near the earth's surface have temperatures and pressures that are close to standard conditions of 25°C and 1 atm, these conditions are assumed to prevail unless otherwise stated. For an ideal gas, at some pressure ( $P_i$ ) and chemical potential ( $\mu_i$ ), relative to a standard condition pressure ( $P_0$ ) and standard condition chemical potential ( $\mu_0$ ), the following relationship is obtained between the pressure and the chemical potential (Schwarzenbach et al., 1993, p. 46):

$$\mu_i = \mu_0 + RT \ln \left[ \frac{P_i}{P_0} \right] \quad (2)$$

For nonideal behavior, a term related to the pressure called the fugacity ( $f$ ) is used, and fugacity is typically described as the escaping or “fleeing” tendency (Yalkowsky and Banerjee, 1992, p. 18; Schwarzenbach et al., 1993, p. 46; Valsaraj, 2000, p. 61).

$$\mu_i = \mu_0 + RT \ln \left[ \frac{f_i}{f_0} \right] \quad (3)$$

where  $f_i = \gamma_i x_i P$  and  $\gamma_i$  is the activity coefficient. Thus, if the activity coefficient ( $\gamma_i$ ) = 1, the fugacity ( $f_i$ ) equals the partial pressure ( $P_i$ ), and the mixture behaves ideally. The activity coefficient ( $\gamma_i$ ) is used to account for nonideal behavior, or the changes in enthalpy and entropy.

The fugacity concept can be extended to the other phases by the vapor pressure ( $P_i$ ) of the liquid (L) or solid (S). The vapor pressure ( $P_i$ ) is the pressure caused by the vaporized molecules of the compound when it is at equilibrium with its pure condensed phase, and, for pure ideal substances, the fugacity of a liquid or solid may be computed based on the vapor pressure since the activity coefficient ( $\gamma$ ) is 1 (Schwarzenbach et al., 1993, pp. 48, 56; Valsaraj, 2000, pp. 61–62, 81).

$$f_{i \text{ pure liquid}} = \gamma_{i \text{ pure liquid}} P_{i \text{ pure liquid}}(\text{L}) \cong P_{i \text{ pure liquid}}(\text{L}) \quad (4)$$

$$f_{i \text{ pure solid}} = \gamma_{i \text{ pure solid}} P_{i \text{ pure solid}}(\text{S}) \cong P_{i \text{ pure solid}}(\text{S}) \quad (5)$$

Furthermore, for a component in a mixture, such as an HOC in an aqueous solution, the fugacity of the component in the mixture can be compared

to the fugacity of the component in its pure reference state. For example, assume the pure reference (ref) state is the pure liquid state.

$$f_i = \gamma_i x_i f_{i \text{ ref}} \quad (6)$$

$$f_{i \text{ mixture}} = \gamma_i x_i f_{i \text{ pure liquid}} \quad (7)$$

$$f_{i \text{ mixture}} = \gamma_i x_i P_{i \text{ pure liquid}}(L) \quad (8)$$

where  $x_i$  is the mole fraction of component ( $i$ ) in the mixture. The chemical potential of a liquid or solid in a mixture can then be expressed with the following equation:

$$\mu_{i \text{ mixture}} = \mu_{i \text{ ref}} + RT \ln \left[ \frac{f_i}{f_{i \text{ ref}}} \right] = \mu_{i \text{ ref}} + RT \ln[\gamma_i x_i] \quad (9)$$

where  $\frac{f_i}{f_{i \text{ ref}}} = \gamma_i x_i = a_i$ , which is the activity of the compound in the mixture compared to a reference state (Schwarzenbach et al., 1993, p. 49; Valsaraj, 2000, p. 63).

It is important to mention that another pathway for the environmental fate and transport of a HOC concerns the partitioning of the compound between the aqueous and air phases, and the key indicators of this process are the vapor pressure and the air–water partition coefficient (Cole and Mackay, 2000). The air–water partition coefficient, or Henry's law constant ( $K_H$ ), is basically the partial pressure of the chemical in the gas phase divided by its concentration in the aqueous phase at equilibrium (Schwarzenbach et al., 1993, pp. 109–112). Generally, compared to more hydrophilic organic compounds, HOCs have a low volatility, or low vapor pressure, and, therefore, they should not be significantly partitioning to the gas phase. However, HOCs also have a high activity, or escaping tendency when they are in water, consequently, air–water partition coefficients may be relatively high (Schwarzenbach et al., 1993, pp. 111–112).

## F. Aqueous Solubility

The following example may help explain what occurs when an organic compound, such as an HOC in a liquid phase, is placed within a second phase, such as an aqueous solution. Initially, before the pure liquid HOC contacts the water, it has a chemical potential in its own pure phase (phase 1).

$$\mu_1 = \mu_{\text{HOC}} + RT \ln[\gamma_{\text{HOC}} x_{\text{HOC}}] \quad (10)$$

Then, after the compound contacts the water, it has a chemical potential in the water (w) phase (phase 2).

$$\mu_2 = \mu_{\text{HOC}} + RT \ln[\gamma_w x_w] \quad (11)$$

Over time, the HOC molecules and water molecules interact, and the change in potential energy, or the change in molar free energy ( $\Delta G$ ), of the solution describes the molecular behavior. It may be computed by subtracting the initial (phase 1) potential energy of the HOC in its pure liquid state from the final (phase 2) potential energy of the compound in water.

$$\Delta G_s = \mu_2 - \mu_1 = RT \ln[\gamma_w x_w] - RT \ln[\gamma_{\text{HOC}} x_{\text{HOC}}] \quad (12)$$

Initially, the free energy is negative because the mole fraction of the HOC in water ( $x_w$ ) is very low. As time passes, the molecules in the organic phase at the higher chemical potential migrate into the aqueous phase at the lower chemical potential until equilibrium is reached, where the free energy is zero and the chemical potentials are equal (Schwarzenbach et al., 1993, pp. 50, 78–79). At equilibrium, the free energy equation can be rearranged into the following relationship:

$$RT \ln \left[ \frac{x_{\text{HOC}}}{x_w} \right] = -(RT \ln[\gamma_{\text{HOC}}] - RT \ln[\gamma_w]) \quad (13)$$

The left-hand side of this equation shows the relative amount of the HOC in the two phases at equilibrium and represents the partitioning of the compound, and the right-hand side of this equation exhibits the nonideal behavior (Schwarzenbach et al., 1993, pp. 50–51).

It is reasonable to assume that for HOCs, the mole fraction of water in the organic phase is very small, so the mole fraction of the HOC in its own phase is approximately 1 ( $x_{\text{HOC}} \cong 1$ ), and the HOC molecules behave ideally in their own liquid phase ( $\gamma_{\text{HOC}} \cong 1$ ). Therefore, the molar free energy for a HOC dissolving in water can be approximated by the following equation (Schwarzenbach et al., 1993, p. 79):

$$\Delta G_s = RT \ln[x_w] + RT \ln[\gamma_w] \quad (14)$$

Many HOCs behave nonideally in aqueous solutions, and the change in enthalpy and/or entropy may be substantial. Thus, for HOCs, the activity coefficient in the aqueous phase ( $\gamma_w$ ) is usually much greater than 1 (Schwarzenbach et al., 1993, p. 80; Valsaraj, 2000, p. 107). At equilibrium,  $\Delta G$  goes to zero, so using the preceding equation, the mole fraction of the HOC in water ( $x_w$ ) =  $1/\gamma_w$ . For HOCs, the solubility (mol/L) can be easily computed from the mole fraction by simply dividing the mole fraction ( $x_w$ ) by the molar volume of water ( $V_w = 0.018$  L/mol at 25°C) (Schwarzenbach et al., 1993, p. 81).

It should be remembered that organic compounds may exist as solids or gases at standard conditions, but when they are dissolved in a solvent such as water, the compounds will exist in a liquid state (Schwarzenbach et al., 1993, p. 80). Therefore, when compounds are in a solid or gaseous state at

standard conditions, a conversion must be used to bring the compound to the liquid state and account for the phase, or energy, changes. For solids, the conversion factor is the ratio of the fugacity of the pure solid to the fugacity of the subcooled liquid, and for gases it is the ratio of the fugacity of the pure gas to the fugacity of the condensed liquid (Schwarzenbach et al., 1993, p. 81).

For solid organics:

$$\Delta G = RT \ln \gamma_w + RT \ln x_w + RT \ln \left[ \frac{f_s}{f_L} \right] \quad (15)$$

$$x_w = \frac{1}{\gamma_w} \left[ \frac{f_s}{f_L} \right] \cong \frac{1}{\gamma_w} \left[ \frac{P_0(S)}{P_0(L)} \right] \quad (16)$$

where, for many rigid compounds the following approximation can be used in terms of  $T_m$ , the melting temperature of the compound (K) (Schwarzenbach et al., 1993, p. 75):

$$\ln \left[ \frac{P_0(S)}{P_0(L)} \right] \cong -0.023(T_m - 298) \quad \text{at } 25^\circ\text{C} \quad (17)$$

For gaseous organics (Schwarzenbach et al., 1993, p. 81):

$$\Delta G = RT \ln \gamma_w + RT \ln x_w + RT \ln \left[ \frac{f_g}{f_L} \right] \quad (18)$$

$$x_w = \frac{1}{\gamma_w} \left[ \frac{f_g}{f_L} \right] \cong \frac{1}{\gamma_w} \left[ \frac{1 \text{ atm}}{P_0(L)} \right] \quad (19)$$

Although it is evident from thermodynamics that enthalpy and/or entropy changes have a great influence on the solubility of an HOC, it still may be difficult to comprehend the dissolution process at the molecular level. Schwarzenbach et al. (1993, pp. 82–90) give a fairly detailed explanation. Energy is needed ( $+\Delta H$ ) to break a HOC molecule away from its pure phase, and energy is needed ( $+\Delta H$ ) to separate the water molecules so there is a vacant space or “cavity” for the incoming HOC molecule. Energy is returned ( $-\Delta H$ ) when the HOC molecule transfers into the vacant space due to the intermolecular attractions that occur as the water molecules surround and interact with the HOC molecule (Yalkowsky and Banerjee, 1992, p. 12; Schwarzenbach et al., 1993, pp. 82–84). The energy needed to create the cavity and insert the HOC molecule is often considered to be the determining factor for solubility, and this energy depends on the molecular surface area of the HOC molecule and on the interfacial tension forces between the HOC and the water (Rao et al., 1985).

Yalkowsky and Banerjee (1992, p. 13) describe the entropy of mixing as “the single most important factor” for promoting solubility, but at the

molecular scale it is more difficult to interpret than enthalpy (Schwarzenbach et al., 1993, p. 84). Theoretically, there is a negative effect on entropy ( $-\Delta S$ ) with large HOCs because nonpolar molecules are incapable of forming hydrogen bonds with the water molecules, which causes the water molecules to reestablish some hydrogen bonds by changing their orientation, and this results in a more ordered structure (Valsaraj, 2000, pp. 111–112). Conceptually, the theory is that the water molecules form a cage or shell surrounding the HOC molecule, and this phenomenon, called hydrophobic hydration, increases with the size of the HOC molecule (Valsaraj, 2000, pp. 111–112). Schwarzenbach et al. (1993, p. 89) reach the conclusion that the solubility is mainly affected by the size of the non-polar portion of the organic molecule.

Thus, it is evident that solubility is a function of the changes in enthalpy and entropy, and these factors are closely associated to the size, shape, and molecular structure of the HOC. In addition to these structural properties, HOC aqueous solubility can be affected by external variables. Temperature has a minor effect, and it may increase or decrease the solubility depending on the type of organic compound (Schwarzenbach et al., 1993, pp. 90–93), but, for most environmental conditions, pressure effects are negligible (Yalkowsky and Banerjee, 1992, p. 40). For neutral, non-polar organic compounds, the presence of dissolved salts, or inorganic ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$ , generally reduces the solubility primarily because water molecules hydrate the ions so there are less water molecules available to dissolve the organic molecules (Schwarzenbach et al., 1993, pp. 93–96; Valsaraj, 2000, pp. 67–68).

### G. Estimating Aqueous Solubility

The aqueous solubility of a HOC is an important parameter, yet it is difficult to determine experimentally. Thus, many methods have been developed to estimate solubility, and Yalkowski and Banerjee (1992, pp. 41–42) classify these methods into four categories. The first category concerns methods based on structural molecular groups. For instance, studies found that solubility decreases as the number of methyl ( $\text{CH}_3$ ) groups increase when they are linked to an aliphatic (straight or branched) carbon chain. The second category mentioned by Yalkowski and Banerjee (1992, pp. 41–42) includes methods that use experimental physicochemical properties such as the melting or boiling point or  $K_{ow}$  to estimate aqueous solubility. Since these properties are associated with the chemical structure, they often correlate well to the solubility. The third category deals with properties, such as molecular surface area or molecular connectivity, that are not experimentally determined but are computations based on molecular structure, and these are also correlated to solubility. Finally, the fourth category is comprised of methods that use a combination of two or more parameters that can be

experimentally determined or generated empirically, and these methods may be quite complex. One such method is derived from the UNIQUAC (universal quasi chemical) equation, and it is called the UNIFAC (functional-group activity coefficient) method. Li et al. (1994) found that the UNIFAC approach was convenient for estimating highly hydrophobic compounds such as polychlorinated biphenyls (PCBs).

### III. SURFACTANTS/COSOLVENTS AND HOCs

#### A. Cosolvents

Previously, when covering external variables that affect aqueous solubility, the presence of other codissolved organic molecules was purposely omitted. This is because this subject is a complicated topic of paramount importance to this article and it merits its own separate discussion. When a large amount of codissolved organic molecules, or a cosolvent, is present, hydrophobic interactions are generally reduced since the total mixture has a more organic character (Valsaraj, 2000, p. 126). Since the understanding of multicomponent mixtures can be complex, to avoid confusion it is easiest to start with the consideration of only two organic compounds in water. The first is a cosolvent, such as ethanol, that mixes well or is miscible with water due to its polar molecular structure, and the second is the solute, which in most cases consists of a HOC, such as a PAH, with a much lower solubility than the cosolvent.

According to Banerji and Yalkowsky (1988), if the concentration of the cosolvent exceeds 10% (v/v), the molar solubility of a HOC in the mixture ( $S_m$ ) can be approximated by the following equation:

$$\ln(S_m) = f_c \ln(S_c) + (1 - f_c) \ln(S_w) \quad (20)$$

where  $f_c$  is the nominal cosolvent volume fraction and  $S_c$  and  $S_w$  are the molar solubilities of the HOC in pure cosolvent and pure water, respectively. This equation is based on the linear free energy relationship (LFER) that exists between the free energy of the solution and the surface area of the HOC molecule (Banerji and Yalkowsky, 1988).

According to Schwarzenbach et al. (1993, pp. 98–104), at high cosolvent concentrations, such as greater than 10% (v/v), there are not enough water molecules to hydrate all the cosolvent molecules. Consequently, many of the hydration shells for both the cosolvent and HOC molecules are incomplete or overlap, and the nonpolar portion of the cosolvent molecule is mutually attracted to the HOC molecule. Another way to view this interaction is that the cosolvent and HOC molecules are both repelled by the cohesive forces between the polar water molecules. The cosolvent molecules partially enclose the HOC molecules nearly in proportion to their concentration, and it

is as if the HOC is partially dissolved in water and partially dissolved in the cosolvent (Banerji and Yalkowsky, 1988).

Since the cage or shell created by the water molecules and the cosolvent around the HOC molecule is a function of its molecular surface area as well as the interfacial tension forces between the HOC molecule and the water and the HOC molecule and the cosolvent, a solubility equation has been developed that incorporates these interfacial tension forces (Schwarzenbach et al., 1993, pp. 98–104). However, interfacial tension forces between liquids are difficult to evaluate and an approximation is often used. Schwarzenbach et al. (1993, p. 99) shows that the solubility of hydrophobic compounds dissolved in a 40% methanol and 60% water mixture increased exponentially in proportion to the hydrophobic surface area of the HOC molecule. Valsaraj (2000, p. 127) used a simplified approach that employs constants to represent the HOC–water, HOC–cosolvent, and water–cosolvent interactions. He found that a graph of the enhanced solubility of a HOC versus the cosolvent concentration was exponential in nature, and the effect is more pronounced for HOCs that are more hydrophobic and solvents that have a higher molecular weight (Valsaraj, 2000, pp. 127–128).

Fu and Luthy (1986a) tested eight different organic compound–cosolvent–water systems and compared the results predicted by several solubility estimation methods to the results observed in their experiments. The solubility estimation methods included the UNIFAC, excess free energy, log-linear relationship, and molecular surface area approaches. The cosolvents included methanol and acetone, and the organic compounds consisted of naphthalene, naphthol, and 3,5-dichloroaniline. In addition to their own experiments, they compared results from the estimation methods to the results from 10 other previously published experiments. Fu and Luthy (1986a) showed reasonable agreement between predicted and experimental values for the UNIFAC approach, and, with only one exception, the predicted over observed ratios ranged within a factor of two. These researchers concluded that the log-linear relationship approach was easily applied and it suggested that there would be greater solubility enhancement for more hydrophobic compounds. Fu and Luthy (1986a) also found a general trend that the solubility of an organic compound increased semilogarithmically with an increase in the volume fraction of the cosolvent.

Ternary phase diagrams are sometimes used to show the relationship between the component volume fractions of HOC, cosolvent, and water within the mixture (Peters and Luthy, 1993; Lowe et al., 1999, pp. 63–65). Peters and Luthy (1993) did experiments with coal tar and three solvents, *n*-butylamine, 2-propanol (isopropyl alcohol), and acetone, and used ternary phase diagrams to show the equilibrium-phase composition. It appears that the phase diagrams were constructed using measurements of the volume fraction of coal tar, cosolvent, and water that were in two phases, cosolvent–water and coal tar. As the volume fraction of cosolvent increased in these phases, the

volume fraction of coal tar increased in the cosolvent–water phase and decreased in the coal tar phase, whereas the volume fraction of water decreased in the cosolvent–water phase and varied within the coal tar phase, first increasing then decreasing.

Cosolvents have molecular structures that are polarized so they mix well with water, but they are also organic so they mix better with HOCs than water. Peters and Luthy (1993) showed that *n*-butylamine solubilized much more coal tar into the cosolvent–water phase than isopropyl alcohol or acetone, and in a 30% coal tar, 40% cosolvent, and 30% water mixture, the cosolvent–water phase contained about 20%, 5%, and 1% coal tar for the *n*-butylamine, isopropyl alcohol, and acetone cosolvents, respectively. Since the molecular weights of *n*-butylamine, isopropyl alcohol, and acetone are about 73.1, 60.1, and 58.1, respectively, the higher molecular weight cosolvent facilitated more coal tar solubilization. Amines such as *n*-butylamine have less polar molecules than alcohols such as isopropyl alcohol (Carey, 1987, p. 867), and the presence of a carbonyl group in the acetone molecule causes it to be a relatively polarized molecule (Carey, 1987, p. 644). Thus, it appears that less polar and higher molecular weight cosolvents may enhance HOC solubilization.

## B. Surfactants

Until this point we have primarily been concerned with codissolved organic molecules, such as ethanol, that are more or less miscible in water and act as a cosolvent. A cosolvent basically increases the solubility of a HOC by lowering the interfacial tension of the mixture. There is another large group of organic compounds called surfactants that also lower the surface and interfacial tension, but are capable of increasing HOC solubility through a different process called micellar solubilization (Myers, 1988, pp. 154–156). In order to understand this process though, it is necessary have some basic background knowledge of surfactants and their chemical properties (Attwood and Florence, 1983).

Surfactant science and technology is an enormous field and it has been growing rapidly in the United States since World War II (Ash and Ash, 1981a, Myers, 1988, p. 17). The word “surfactant” is actually just a shortened version of a longer term “surface-active agent” (Rosen, 1989, p. 1), and this term originates from the behavior of these chemicals, which may greatly affect interfacial and surface tension. Surfactants are used in many different industries for a variety of applications, such as detergents, emulsifiers, lubricants, wetting agents, and pharmaceuticals (Myers, 1988, p. 16). Since the objective of this study is to use a surfactant for HOC remediation, or to increase the solubility of a HOC in an aqueous solution, this discussion is restricted to the situation where the bulk phase is aqueous with a dilute surfactant concentration. Moreover, to reduce surfactant adsorption to the soil and optimize

contaminant transport during electrokinetic remediation, only nonionic surfactants are considered. Nonionic surfactants are often good for solubilization and they are relatively nontoxic (Lowe et al., 1999, p. 43). Generally, surfactants are of very low toxicity to mammals, but aquatic organisms may be more sensitive, and toxicity usually increases with the increasing hydrophobic nature of the surfactant molecule (Connell, 1997, pp. 233–237).

Basically, surfactant molecules, or monomers, have a distinct structure that is composed of two separate groups. The head group is polar and hydrophilic, or attracted to the water phase, while the tail group is nonpolar and hydrophobic (Myers, 1988, pp. 11–13). The ionic charge of the polar head is commonly used to classify surfactants, and the four major types of charge are negative, positive, negative and positive, and no apparent charge, which corresponds to anionic, cationic, zwitterionic, and nonionic surfactants, respectively (Rosen, 1989, p. 4). For nonionic surfactants, the polar head is often composed of a polyoxyethylene (POE) group, and the tail section may be much more varied but usually consists of a long hydrocarbon chain (Myers, 1988, pp. 13–14). Surfactants are classified according to the balance between the hydrophilic and hydrophobic, or lipophilic, portions of the molecule. A lipophilic substance is one with a high affinity for fatty or organic solvents and it is essentially a hydrophobic substance (Myers, 1988, p. 24). Surfactants with a high hydrophile–lipophile balance (HLB) number are more soluble in water, and a low HLB indicates the surfactant is more soluble in an organic solvent (Sabatini et al., 1995).

When the characteristically divergent surfactant monomer is placed in water, the hydrophobic group disrupts the cohesive interaction of the water molecules and increases the free energy of the system (Myers, 1988, p. 11, 94). Since the water molecules repel the hydrophobic groups, the monomers have a greater energy and they are more easily transported to interfacial regions than water molecules. Thus the monomers congregate at the interfacial regions and they are oriented with their hydrophobic tails directed away from or out of the bulk water phase. This congregation and orientation of the monomers increases the order of the system, thereby reducing entropy and minimizing the free energy (Myers, 1988, p. 94). In addition, because less work is required to expand the interfacial area, the interfacial tension is reduced (Myers, 1988, p. 11, 94; Rosen, 1989, pp. 1–3). Moreover, the reduction in interfacial tension at a grease–water interface may be dramatic, by a factor of 100,000 or more, and the effect is such that large surface-area structures such as foams and emulsions may be formed (Connell, 1997, pp. 222–223).

When surfactants are added at very low concentrations, the monomers may be initially dissolved in the aqueous solution, but due to their divergent structure, they begin adsorbing at interfacial regions. If the surfactant concentration is increased, adsorption increases, and the adsorbed monomers at the interfaces start interacting laterally due to the mutual attraction between

their hydrophobic tails. Thus, surfaces and interfaces may become covered with a thin monolayer of surfactant (Hunter, 1993, p. 12). At this stage, when all available interfacial regions are saturated and more surfactant is added, the monomers may continue to reduce the energy of the system through a variety of different mechanisms or formations, and one of these mechanisms is to aggregate into colloidal-size structures called micelles (Myers, 1988, pp. 82–94; Rosen, 1989, p. 111).

The formation of micelles begins at a specific surfactant concentration termed the critical micelle concentration (CMC), where the physical properties of the solution, such as interfacial tension, electrical conductivity, and light scattering behavior, often change significantly due to the existence of micelles (Rosen, 1989, p. 110). The surface tension of a surfactant solution decreases until it reaches the CMC and then it stays fairly constant. This is because increasing the number of surfactant monomers above the CMC leads to the formation of more micelles, while the number of monomers at the interfacial regions remains at the saturated, CMC condition. Therefore, the effectiveness of a surfactant to reduce interfacial tension can usually be measured at the CMC, and factors that affect the CMC include the structure of the surfactant, the presence of electrolytes or other organic compounds, and the temperature (Rosen, 1989, pp. 120–142). In addition, for nonionic micelles, methanol and ethanol were found to cause a CMC increase that is attributed to the weakening of hydrogen bonding (Attwood and Florence, 1983, p. 95).

For micelles in aqueous surfactant solutions above the CMC, the hydrophilic head groups are directed toward the aqueous phase and the hydrophobic tails are directed toward the interior region. The interior of the micelle thus becomes a hydrophobic region suitable for a HOC, and, when both micelles and a HOC are present, the HOC molecules partition, or solubilize, into the micelles. Micelles are commonly spherical, ellipsoidal, disk-shaped, or rod-like structures with the radius of the interior region roughly equal to the length of the tail, or hydrophobic chain, of the monomer, and, for common surfactants, micelle diameters are approximately three nanometers (Vold and Vold, 1983, p. 593; Myers, 1988, p. 95; Rosen, 1989, pp. 112, 120). There are many theories of micellization, and an explanation detailing the thermodynamics, molecular structures, forces, and kinetics would be complicated and beyond the scope of this study, but, conceptually, it is important to understand that the means by which surfactants reduce interfacial tension and enhance HOC solubility is through micellar solubilization (Vold and Vold, 1983, pp. 623–628; Attwood and Florence, 1983, pp. 98–111; Myers, 1988, pp. 90–104).

After HOC solubilization has occurred, the total solubility consists of the HOC solubility in the aqueous phase plus its solubilization in the micelles, where it exists as micellar pseudophase (Edwards et al., 1991; Jafvert, 1996, p. 5). A graph of the amount of HOC solubilized versus the surfactant concentration commonly shows a slight rise in HOC solubility below the CMC, and

this amount of HOC solubilization remains nearly constant until the surfactant concentration reaches the CMC. Once the CMC is reached, HOC solubilization increases greatly, and the rise in solubilization is approximately linear with the rise in surfactant concentration (Rosen, 1989, p. 171). The molar solubilization ratio (MSR) is the slope of the line above the CMC, and it is equal to the moles of HOC solubilized divided by moles of surfactant added above the CMC.

Edwards et al. (1991) performed batch testing on three PAHs, naphthalene, phenanthrene, and pyrene, using four different nonionic POE surfactants, and the MSRs averaged to about 0.05 for pyrene, 0.1 for phenanthrene, and 0.3 for naphthalene. From this data, it is evident that adding 10 moles of surfactant would only solubilize about half a mole of pyrene, 1.0 mole of phenanthrene and 3.0 moles of naphthalene. Therefore, sites that are heavily contaminated with low-solubility compounds such as pyrene may need much larger quantities of surfactant than the quantity of contaminant present to achieve adequate solubilization. At first this may appear to be discouraging, but it should be remembered that surfactants can substantially enhance the HOC solubility above its aqueous solubility, and surfactants may also be recycled (Lowe et al., 1999, pp. 77–88). For example, using the MSR for phenanthrene calculated by Edwards et al. (1991) and its aqueous solubility of about  $6.3 \times 10^{-6}$  mol/L (Schwarzenbach et al., 1993, p. 621), the addition of a 30 g/L Igepal CA-720 (molecular weight [MW] = 735) surfactant solution should increase phenanthrene solubility by about 600 times its aqueous solubility!

Micelles form spontaneously without mixing, and they may aggregate and disconnect rapidly when there are changes in surfactant concentration (Jafvert, 1996, p. 5). Increasing the length of the hydrophobic chain generally increases the amount of solubilization (Myers, 1988, p. 160), and the incorporation of the HOC molecules into the micelle may greatly alter the micellar structure (Rosen, 1989, p. 190). Jafvert (1996, p. 5) admits the differentiation is vague, but uses the terms “micelle,” “swollen micelle,” and “single phase microemulsion (SPME)” to describe low, moderate, and large amounts of organic molecule solubilization, respectively. The type of surfactant, contaminant, and solution chemistry may greatly affect micelle size and behavior, but SPMEs, which contain the greatest amount of organic molecules, may contain micelles that range from 10 to 100 nm in diameter (Jafvert, 1996, p. 4).

The addition of surfactant to an oil-water system can result in a continuum of different phase behaviors, and the following example is based on the one given by Rosen (1989, pp. 228–235). First, it may be beneficial to define a phase as a “separate fluid having a characteristic density, viscosity, and chemical composition” (Lowe et al., 1999, pp. 53–54). Imagine a beaker containing oil and water in two separate phases. If a nonionic POE surfactant with a high HLB is added to the beaker, the surfactant is soluble in water

and it reduces the interfacial tension between the two phases as described previously. At a concentration above the CMC a Winsor Type I system exists, where the surfactant forms micelles and instantaneously solubilizes some oil into the aqueous phase. This Type I system is commonly used for HOC remediation and it is strongly associated with this present discussion.

As the temperature is increased, nonionic POE surfactants tend to become increasingly hydrophobic and they solubilize more oil into the aqueous phase (Rosen, 1989, pp. 228–235). Moreover, the additional solubilization is accompanied by a further decrease in interfacial tension between the oil and water phases. At a higher temperature, the conditions may reach the Winsor Type III system where surfactant micelles and solubilized oil begin to separate from the aqueous phase to form a completely separate third or middle phase containing large surfactant micelles with solubilized oil and water. If the temperature is increased further, the aqueous phase decreases and the middle phase grows in size as more micelles separate carrying solubilized oil and water with them. If the temperature rises even further, the system reaches a point where the interfacial tension between the middle and the aqueous phases becomes nearly zero, and at this point, the middle phase has grown further, the aqueous phase has reduced further, and the aqueous phase contains only a small amount of surfactant monomers without micelles (Rosen, 1989, pp. 228–235). The volume of the middle phase depends on the amount of surfactant in the system, so, if there is a large amount of surfactant, the oil phase may be completely solubilized. Under these conditions, when the oil phase is completely solubilized into micelles and two distinct phases exist, it is called a Winsor Type IV system, and the separate phase containing the micelles with solubilized oil and water is called a microemulsion (Rosen, 1989, pp. 228–235).

A further increase in temperature leads to the surfactant becoming more and more hydrophobic and the middle phase begins to dissolve into the oil phase. The surfactant carries solubilized water in inverted or reverse micelles that have hydrophobic exteriors and hydrophilic interiors because the hydrophilic heads create a region suitable for water to be solubilized into the oil phase. Eventually, at higher temperatures, the middle phase completely dissolves into the oil phase leaving the two phases, oil with reverse micelles and water, in a Winsor Type II system. A further increase in temperature causes the surfactant to become more hydrophobic, the water separates out of the reverse micelles, and the interfacial tension between the oil and water phases increases. Although it was assumed that an increase in temperature led to these different phase systems, similar results may be produced by using surfactants that have different HLB balance numbers or by adding cosurfactants/cosolvents that will change the hydrophobic character of the system (Rosen, 1989, pp. 228–235).

It is difficult to distinguish microemulsions from solubilization because they are similar and their definitions somewhat overlap (Myers, 1988, p. 173).

Both microemulsions and solubilization are considered to be thermodynamically stable and isotropic. Rosen (1989, p. 322) describes a microemulsion as a transparent dispersion containing two immiscible liquids with particles 10–100 nm in diameter that is generally obtained upon mixing the ingredients gently. In solubilization, the HOC, water, and surfactant are essentially considered to be in the same phase (Rosen, 1989, p. 171; Myers, 1988, p. 155). In addition, the micelles and aggregates of micelles during solubilization generally have particle diameters that are roughly a few tens of nanometers to a nanometer in size (Myers, 1988, pp. 173–174).

Emulsification is different than solubilization because it refers to the dispersion of one liquid in another liquid with the two liquids remaining in separate phases (Rosen, 1989, p. 171). Although microemulsions are considered to be stable, other emulsion types are basically unstable and eventually they will separate. However, they may remain stable for long periods of time, and they are considered stable relative to their intended use (Rosen, 1989, p. 304). Researchers classify emulsions based on particle size (Rosen, 1989, pp. 304–307). Macro and mini emulsions are quite different from solubilization because they have much larger particle diameters, which are greater than 400 nm and between 100 and 400 nm, respectively, and these emulsions require intense agitation to form (Rosen, 1989, pp. 304–325). Largely due to the oil industry, numerous research studies and thousands of papers have been written on emulsions and studies of surfactant phase behavior, because these principals are used to mobilize residual oil deposits and enhance oil recovery by reducing interfacial tension and capillary forces (Pope and Wade, 1995).

For highly nonpolar hydrophobic contaminants such as PAHs, the surfactant generally has a low solubility in the PAH phase. Thus, the adsorption of the surfactant monomers at the interfacial region between the PAH and the aqueous solution is similar to that at the interface between the aqueous solution and the air phases. Under these conditions, the surface tension behavior is similar to the condition when the surfactant is alone in the solution, and the greatest reduction in interfacial tension corresponds to the points of lowest interfacial and surface tension, which exists at or near the CMC (Rosen, 1989, p. 228).

Surfactants can be essentially used in two ways for HOC remediation applications. They can be used to reduce interfacial tension and mobilize the contaminants, or they can be used to substantially increase HOC solubility through micellar solubilization (Ganeshalingam et al., 1994). Ganeshalingam et al. (1994) found that for various PAHs in sand, the dominant removal mechanism was micellar solubilization as opposed to experiments performed to reduce interfacial tension. They could not detect a large difference between washing with water and washing with low-surface-tension solutions containing surfactants near or below the CMC (Ganeshalingam et al., 1994). Moreover, the mobilization of pollutants has the potential to produce downward

or horizontal contaminant movement and migration into uncontaminated or finer grained soils (Luthy et al., 1994; Pennell et al., 1993; Mulligan et al., 2001).

#### IV. HOCs IN SOIL

Before attempting to explain the behavior of HOCs in soil, it is important to recognize that soils are extremely variable and complex environmental media, both structurally and compositionally (Mitchell, 1993, pp. 4–17; Evangelou, 1998, pp. 100–164). Soil heterogeneity has been observed from the micro to the macro scale, and the differences in the structural and chemical properties of the soil constituents generally lead to different interactions with HOCs (Johnston, 1996; Luthy et al., 1997; Gillette et al., 1999). The term “sorption” describes the association of the contaminant to solid phase by both adsorption to the two-dimensional surface of the particle and by absorption into the three-dimensional matrix (Schwarzenbach et al., 1993, p. 255; Stumm and Morgan, 1996, p. 520).

There are various mechanisms for HOC sorption, and Luthy et al. (1997) lists the primary macroscopic observations as absorption into soft and hard organic matter, adsorption onto wet organic or mineral surfaces, and absorption into microvoids or microporous minerals. Absorption into soft organic matter and adsorption onto wet organic or mineral surfaces may happen rather quickly, in less than a minute, while it may take days or longer for absorption into hard organic matter or absorption into micropores (Luthy et al., 1997). Desorption has also been linked to fast and slow behavior, and the dissolution and precipitation of minerals has been shown to block micropores thereby trapping HOCs, which may help explain why aged contaminants are often resistant to desorption (Karickhoff and Morris, 1985; Loehr and Webster, 1996; Farrell et al., 1999). Since different mechanisms are responsible, sorption and desorption characteristics depend on the chemical and structural properties of both the contaminant and the soil.

Sorption behavior is typically shown by a relationship called the sorption isotherm, which shows the concentration of the contaminant in the soil ( $C_s$ ) as a function of its concentration in solution ( $C_w$ ) at a constant temperature and at equilibrium. Isotherms commonly show different shapes that depend on the mechanisms responsible for the sorption behavior (Schwarzenbach et al., 1993, p. 258; Sawyer and McCarty, 1978, pp. 85–90). There are many different equations that have been used to describe sorption and desorption phenomena, but the following equation, called the Freundlich isotherm, is commonly applied for HOCs in soil (Schwarzenbach et al., 1993, p. 258; Li et al., 2000):

$$C_s = K(C_w)^n \quad (21)$$

In this equation,  $K$  is the Freundlich constant and  $n$  is a constant that represents the degree of nonlinearity. When  $n < 1$  the sorption sites are becoming filled as the contaminant concentration in solution increases, so at higher concentrations, more contaminant remains in solution. Conversely, when  $n > 1$  the sorbed contaminant molecules are changing the surface to facilitate even greater adsorption to the solid phase as the contaminant concentration in solution increases. Lastly, when  $n = 1$ , contaminant sorption, or attraction to the solid phase, is the same regardless of the contaminant concentration in solution (Schwarzenbach et al., 1993, pp. 258–259).

### A. HOCs and Organic Matter

Stumm and Morgan (1996, p. 521) make the important point that at the molecular scale the attraction of nonpolar groups to each other is primarily due to the strong attractive forces between the water molecules, and not due to a particular affinity of these groups for each other. Thus, hydrophobic groups are more or less repelled by water molecules toward similar substances, and this may be thought of as the driving force of hydrophobic sorption. Indeed, many researchers attribute the strong binding characteristics of soil and HOCs to the percentage of organic matter in the soil, because organic matter contains substances that have hydrophobic sites and characteristics similar to HOCs (Karickhoff et al., 1979; Means et al., 1980; Liu and Amy, 1993; Chiou et al., 1998; Gillette et al., 1999).

Schwarzenbach et al. (1993, pp. 266–267) classifies organic matter into two types of substances, which are either humin or humic. Humin or kerogen substances are not water-soluble under either acidic or basic conditions, but humic substances are water-soluble. Humic substances are subdivided into fulvic acids, which are soluble under acidic conditions, and humic acids, which are not soluble under acid conditions but are soluble under basic conditions. Other researchers consider all organic matter, humin, fulvic acids, and humic acids, to be humic substances, and Evangelou (1998, p. 135) describes them as decomposed plant and animal residues that are produced by microbial action. They are comprised of condensed polymers of aromatic and aliphatic compounds.

Humic substances contain a variety of functional organic groups such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O), and humic molecules are commonly negatively charged due to proton dissociation from these functional groups. Humic substances may also be adaptable and the molecular structure may change in response to pH and electrolyte concentration changes (Evangelou, 1998, p. 135). The structure of organic substances contains about 40–50% carbon by weight but also contains a significant amount of oxygen and some nitrogen (Schwarzenbach et al., 1993, pp. 266–268).

Therefore, the structure of these substances causes them to have a polarity that is not as strong as water but is considerably stronger than hydrocarbons (Schwarzenbach et al., 1993, pp. 266–268).

The molecular structure of organic matter is complicated, and the different organic functional groups can bind with HOCs as well as with clay mineral surfaces through a variety of chemical mechanisms. At the mineral surface, protonation may occur at low pH, where surface bound protons may associate with a functional group. In addition, hydrogen bonding, cation and anion exchange, and van der Waals interactions may occur, as well as the trapping of organic matter in crystal pores and adsorption in interlayer spaces (Sposito, 1989, pp. 59–61; Evangelou, 1998, p. 138). Liu and Amy (1993) found that PAH sorption was dependent on the type of organic matter that was present and the mineralogy of the soil, and these investigators determined that dissolved, or aqueous phase, organic matter facilitated PAH transport while sorbed, solid phase, organic matter retarded, or prevented, PAH transport. However, the bond between organic matter and PAHs is usually through weak intermolecular attractions, and the reversibility of these reactions has been demonstrated (Karickhoff et al., 1979; Schwarzenbach et al., 1993, p. 276).

Ghosh et al. (2000) used mass spectrometric and spectroscopic techniques to observe PAH-contaminated sediments and found that in some samples the coal particles constituted only 5% of the sediment by weight but contained 62% of the total PAHs. The remaining 38% of the PAHs were located in a clay/silt fraction, and the PAHs in this clay/silt fraction could be desorbed rather quickly compared to the portion associated with the coal particles (Ghosh et al., 2000). The portion of the PAHs associated with the coal particles was strongly bound, and only about 8% was released after 3 months of desorption. After sectioning different coal particles, Ghosh et al. (2000) determined that the PAH concentration diminished significantly from the exterior to the interior regions, and they concluded that a pore diffusion model would be inappropriate because sorption was primarily due to mechanisms near the particle surface. The PAHs on the surfaces of silica particles were associated with attached organic matter deposits, and PAHs were not detected in the interior of the silica particles.

Therefore, it appears that HOC sorption is largely related to the organic content and the percentage of clay/silt sized particles in the soil. Johnston (1996) explains that clay minerals are important sorbents because they have large surface areas, which often have electrical charges associated with them due to isomorphic substitution, mineral defects, and broken edges, and the clay mineral surfaces are frequently coated with amorphous oxides and organic matter. Moreover, Johnston (1996) lists several molecular scale sites on clay minerals where organic cations or anions can bind to the mineral surface.

## B. HOCs and Clay Minerals

It has been established that HOC sorption occurs predominately in soils with a large percentage of organic matter and clay/silt-sized particles (Schwarzenbach et al., 1993, pp. 265–285). Furthermore, higher HOC sorption occurs in the clay/silt-size fraction of the soil because smaller particles have large surface areas, and, as stated earlier, clay minerals have electrical charges associated with them (Johnston, 1996). Therefore, clay soils were selected as the primary topic of this article, and this discussion is devoted to briefly describing their chemical nature. Greater emphasis is placed on the kaolinite clay mineral since it is a common clay mineral used in the electrokinetic laboratory analyses. It should be remembered that this discussion only presents some basic concepts, and for a more complete description of the vast subjects of clay mineralogy, soil chemistry, and soil and surface behavior, books such as the ones by Grim (1968), Greenland and Hayes (1978), Sposito (1984, 1989), Mitchell (1993), and Stumm and Morgan (1996) should be consulted.

Initially, it should be known that in most soil investigations the term “clay-sized particles” means particle sizes finer than  $2\ \mu\text{m}$  (Grim, 1968, p. 2), whereas “clay minerals” usually refers to a small group of aluminum silicate minerals that are largely formed through physical and chemical weathering processes of parent rock material (Greenland and Hayes, 1978, pp. 12, 31; Grim, 1968, pp. 2, 21). One or a mixture of the clay minerals often predominates in the clay-sized particle fraction of a soil, or in clay soils, which are soils primarily composed of particles less than  $2\ \mu\text{m}$  (Sposito, 1989, p. 31). Clay soils may also contain a variety of other substances that are present in smaller amounts and are not clay minerals, and these substances include organic matter, iron oxides, quartz and feldspars, oxides and hydroxides of aluminum and manganese, oxides of titanium, and carbonates, principally calcite (Greenland and Hayes, 1978, p. 31).

Clay minerals have layered structures, and this characteristic causes them to be members of a much larger group of silicate minerals, which are called phyllosilicates (Mitchell, 1993, p. 19). In clay minerals, there are two types of basic atomic structural units, either tetrahedral or octahedral, that comprise a sheet, and a layer may be composed of two, three, or four sheets (Mitchell, 1993, p. 20). The tetrahedral, or silica, sheet is made of silica tetrahedrons, which consist of a silicon atom centered within four oxygen atoms, or hydroxyls if needed to electrically balance the structure. The tetrahedral tips point in one direction, and the bases of the tetrahedral groups are arranged hexagonally in the same plane (Grim, 1968, p. 52). The tetrahedral sheet structure basically consists of a perforated plane of oxygen atoms that forms the base of the tetrahedrons, a plane of silicon atoms that are located in the cavity formed by the three basal oxygen atoms, and a plane of hydroxyl atoms at the tip of the tetrahedrons (Grim, 1968, p. 52). In addition,

the basal plane of oxygen atoms that form the tetrahedral sheet is referred to as a siloxane surface (Sposito, 1984, p. 13). The octahedral sheet is made of octahedrons, which consist of an aluminum, iron, or magnesium atom that is centered within six oxygen atoms, or hydroxyls (Grim, 1968, pp. 51–52).

The type of clay mineral that is formed largely depends on the factors that lead to its creation, such as the environment, parent rock, and physical and chemical weathering processes. These factors produce a wide variety of different clay minerals because atoms may substitute with one another in the tetrahedral and octahedral structural units, and the sheets may bond in different layering patterns. For example, an aluminum atom may substitute for the silicon atom in the tetrahedral unit, and an iron or magnesium atom may substitute for an aluminum atom in the octahedral unit. In all the clay minerals, except possibly kaolinite, isomorphic substitution results in the clay particles having a net negative charge (Mitchell, 1993, p. 26). The origin of the kaolinite surface charge is discussed in the next section.

The tetrahedral and octahedral sheets may also bond together in variety of configurations to form different unit layers. For example, a 1:1 unit layer consists of one tetrahedral sheet bonded to one octahedral sheet, while a 2:1 unit layer consists of two tetrahedral sheets with one octahedral sheet sandwiched between them. The bond between the sheets is strong compared to the bonds that exist between the stacked unit layers, and layers of water, or water and cations, may become sandwiched between the unit layers creating different hydrated clay minerals (Mitchell, 1993, pp. 24–25). The kaolinite group has the structure of the 1:1 type of mineral, and its general chemical formula is  $[\text{Si}_4]\text{Al}_4\text{O}_{10}(\text{OH})_8 \cdot n\text{H}_2\text{O}$ , where Si is the cation in tetrahedral coordination and  $n$  is the number of moles of hydration water (Sposito, 1989, p. 32).

### C. Surface Charge and the Diffuse Double Layer

As seen with clay minerals, particle surfaces commonly have electrical charges associated with them, and this is important since many organic molecules, such as organic matter and polar surfactants, have electrical properties and may be attracted and adsorb to the charged particle surfaces. According to Schwarzenbach et al. (1993, pp. 285–291), most mineral surfaces are covered with both electron-deficient atoms and electron-rich atoms or compounds. The electron-deficient atoms may include the cations from oxides such as silicon, aluminum, and iron, and electron-rich atoms include oxygen, or electron-rich compounds called ligands, such as carbonate, that may bind with metals. Surface functional groups, such as hydroxyls, may bind with the electron-deficient atoms and protrude from the particle surface, and the hydroxyl and electron-rich atoms or ligands prefer to form hydrogen bonds with molecules near the mineral surface, such as with water

molecules (Schwarzenbach et al., 1993, pp. 285, 298; Stumm and Morgan, 1996, pp. 533–534).

The electrical charge of the mineral surface plays a significant role in sorption behavior even when the organic molecules are neutral, or uncharged, because the surface exhibits attractive dispersion, or London–van der Waals, forces (Schwarzenbach et al., 1993, p. 285; Stumm and Morgan, 1996, p. 518). Moreover, as functional groups possessing dipoles or hydrogen bond capabilities are added, stronger bonding was observed on mineral surfaces such as silica (Schwarzenbach et al., 1993, p. 285). Furthermore, since charged mineral surfaces may interact strongly and form hydrogen bonds with water molecules, it is difficult for neutral organic molecules to penetrate the adsorbed water layer, so they may preferentially partition to locations with adsorbed organic substances (Schwarzenbach et al., 1993, pp. 265–266). Several investigators found that there was little or no attraction between non-polar organic molecules and clay mineral surfaces in aqueous solutions, and, if present, the dominant place for PAH sorption was with organic matter (Karickhoff and Morris, 1985; Johnston, 1996; Weber et al., 1998; Valsaraj, 2000, pp. 264–267). Nevertheless, under some environmental conditions the amount of organic matter is very low, and sorption of neutral organic chemicals to mineral surfaces may occur (Schwarzenbach et al., 1993, pp. 284–291).

It is difficult for neutral HOCs to displace water molecules near mineral surfaces because these “adsorbed” water molecules become strongly oriented, and this “vicinal” water has properties that are quite different from the bulk water molecules (Hunter, 1981, pp. 40–42; Sposito, 1989, p. 143; Valsaraj, 2000, p. 250). Experiments have shown that the dielectric constant of the vicinal water adjacent to the surface is between 2 and 50 compared to 80 in the bulk water (Sposito, 1989, p. 143). Schwarzenbach et al. (1993, pp. 297–298) classifies the solution very near the particle surface into three distinct regions. Region I consists of the charged surface layer, which contains atoms or molecules such as hydroxyls that are directly bound to the electron-deficient atoms at the surface. Region II is called the diffuse double layer, and it includes the vicinal water and a high concentration of ions, called counterions, which carry an electrical charge that is equal and opposite in sign to the net charge on the particle surface. Region III contains the bulk water and the ions in this region have equal and opposite charges (Schwarzenbach et al., 1993, pp. 297–298).

In order to understand the formation of the diffuse double layer, first consider a dry mineral particle. The negative charge on the particle surface may be balanced by adsorbed cations and associated anions that are present as salt precipitates, and, when the particle surface is covered with water, the precipitated salts go into solution (Mitchell, 1993, p. 111). Once they are in the solution, the concentration of ions may be initially high near the particle surface, so the ions diffuse away in the direction of decreasing concentration gradient. However, the negative electrical field originating from the particle

surface counteracts the diffusion process, and the cations and anions distribute themselves in a diffuse double layer configuration (Mitchell, 1993, pp. 111–112).

The diffuse double layer theory is a complicated subject that has received wide coverage in literature and is still a hot topic of research, so this discussion is to simply illustrate some basic concepts. A more thorough explanation of the double layer theory may be found in such books as the ones by Dukhin and Derjaguin (1974), Hunter (1981), Sposito (1984), Sparks (1986), Mitchell (1993), Stumm and Morgan (1996), and Evangelou (1998). Since soil minerals have not been sufficiently characterized at the microscopic scale, the electric double layer theory is difficult to quantify, but it can be useful from a qualitative perspective to explain the behavior of soil particles in solution (Evangelou, 1998, p. 142).

Gouy and Chapman developed the classical theory for the diffuse double layer independently, and their objective was to find a theoretical model to describe the spatial distribution of counterions near a charged surface (Dukhin and Derjaguin, 1974, p. 15). The Gouy–Chapman model is unique because their approach considers the important role of the thermal motion energy of the counterions that causes them to diffuse away from the charged surface, and they successfully used statistical physics (Dukhin and Derjaguin, 1974, p. 15). The model assumes the charge is spread evenly over a large flat surface that is submerged beneath an electrolyte solution. Moreover, the model assumes the ions in the diffuse layer are point charges without volume and the dielectric constant, or permittivity, is independent of the position in the electric field. These last two assumptions were later recognized by Stern to be unsatisfactory, so modifications have been made to the Gouy–Chapman model (Hunter, 1981, p. 33) and many other models have been developed (Stumm and Morgan, 1996, p. 557), but the main purpose of this discussion is to outline the basic concepts of double layer theory.

The fundamental equation for the Gouy–Chapman model is Poisson's equation, which basically states mathematically that the flux of an electric field into an element of volume is determined by the amount of charge in that volume (Hunter, 1981, pp. 22, 350). Basically, it relates the electric potential  $\psi(x)$  as a function of the distance ( $x$ ) from the surface to the volume charge density at that location  $\rho(x)$ . For a flat surface, it can be written as follows (Hunter, 1993, p. 205):

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\rho(x)}{D\epsilon_0} \quad (22)$$

where the electric potential  $\psi(x)$  is the work to bring a positive unit charge from a reference state, such as the bulk solution, to the specified point in the electric field (Mitchell, 1993, p. 113). In addition,  $D$  is the dielectric constant of water, which is 78.54 at 25°C, and  $\epsilon_0$  is the permittivity of a vacuum =

$8.8542 \times 10^{-12}$  Coulomb<sup>2</sup>·sec<sup>2</sup>/kg·m<sup>3</sup> (Weast et al., 1984, p. E-50; Mitchell, 1993, p. 112).

At the mineral surface there is an electric potential ( $\psi_0$ ), and the ions in the solution are regarded as point charges immersed within a dielectric medium (electrolyte solution). At equilibrium, an ion ( $i$ ) is balanced within the double layer by counteracting electrical and diffusional forces and the following relationship holds:

$$\text{grad } \mu_i = \pm z_i e \text{ grad } \psi \quad (23)$$

For this equation,  $\text{grad } \mu_i$  is the gradient of the chemical potential of the ion ( $i$ ),  $z$  is the valence of the ion ( $i$ ), where the sign of  $z_i$  is positive for cations and negative for anions,  $e$  is the unit of elementary charge ( $1.602 \times 10^{-19}$  coulomb), and  $\psi$  is the electric potential.

If the double layer is flat, the electric potential and the chemical potential are constant in planes parallel to the mineral surface, and Eq. (23) can be rewritten as the following (Hunter, 1981, p. 23):

$$\frac{d\mu_i}{dx} = \pm z_i e \frac{d\psi}{dx} \quad (24)$$

The definition of the chemical potential for one ion can then be used in the following form  $\mu_i = \mu_i^0 + kT \ln n_i$ , where  $n_i$  is the number of ions of type  $i$  per unit volume,  $k$  is the Boltzmann constant ( $1.38 \times 10^{-23}$  J/K), and  $T$  is the temperature (Kelvin). Note that by the chain rule,

$$\frac{dy}{dx} = \frac{dy}{du} \frac{du}{dx},$$

and if  $y = \ln u$ , where  $u = n_i$ , then

$$\frac{du}{dx} = \frac{dn_i}{dx} \quad \text{and} \quad \frac{dy}{du} = \frac{1}{u} = \frac{1}{n_i}$$

Therefore, Eq. (24) becomes the following equation (Hunter 1981, p. 23):

$$\frac{d \ln n_i}{dx} = \frac{1}{n_i} \frac{dn_i}{dx} = \pm \frac{z_i e}{kT} \frac{d\psi}{dx} \quad (25)$$

Equation (25) can then be integrated from a point far from the charged surface ( $x \approx \infty$ ) in the bulk solution where the electric potential  $\psi$  is zero and the number of ions of type ( $i$ ) per unit volume is equal to the number in the bulk solution ( $n_i(x) = n_i(\infty)$ ). The result is Eq. (26), which is called the Boltzmann equation (Hunter, 1981, p. 23; Morel, 1983, p. 404):

$$n_i(x) = n_i(\infty) \exp\left(\frac{-z_i e \psi(x)}{kT}\right) \quad \text{or} \quad n_i(x) = n_i(\infty) \exp\left(\frac{-z_i F \psi(x)}{RT}\right) \quad (26)$$

where  $F$  is Faraday's constant = 96,485.31 Coulombs/mol, and  $R$  is the gas constant, 8.314 J/mol·K. The Boltzmann equation gives the concentration of each type of ion in the double-layer region as a function of the electric potential. For example, if the surface is negatively charged, then cations would be attracted to the surface and the number of cations at the surface would be greater than the number in the bulk solution ( $n_i > n_i^0$ ). The volume surface charge density in the vicinity of the ion ( $x$ ) is given by the following expression, where the summation is over all the ionic species that are present (Hunter, 1993, p. 206):

$$\rho(x) = \sum_i n_i(x) z_i F = \sum_i n_i(\infty) z_i F \exp\left(\frac{-z_i F \psi(x)}{RT}\right) \quad (27)$$

Substitution of Eq. (27) into Eq. (22) gives a second-order nonlinear differential equation called the Poisson–Boltzmann equation that can be solved exactly (Sposito, 1984, p. 154; Hunter, 1993, p. 206):

$$\begin{aligned} \frac{d^2\psi(x)}{dx^2} &= -\frac{1}{D\epsilon_0} \sum_i n_i(x) z_i F \\ &= -\frac{1}{D\epsilon_0} \sum_i n_i(\infty) z_i F \exp\left(\frac{-z_i F \psi(x)}{RT}\right) \end{aligned} \quad (28)$$

Sposito (1984, p. 158) presents a number of analytical solutions to the Poisson–Boltzmann equation for single electrolytes, but for conceptual purposes, consider a simple case where the electrical surface potential is small ( $\psi_0 < 25$  mV). In this case, the exponential term in the Boltzmann equation can be linearized using the Taylor expansion ( $e^{\pm x} = 1 \pm x + \frac{x^2}{2!} \dots$ ), and by neglecting all but the first two terms in the expansion, the Boltzmann equation is approximated by the following expression (Morel, 1983, p. 404):

$$n_i(x) \cong n_i(\infty) \left(1 - \frac{-z_i F \psi(x)}{RT}\right) \quad (29)$$

Substituting Eq. (29) into Eq. (28) yields the following approximation (Morel, 1983, p. 405):

$$\frac{d^2\psi(x)}{dx^2} = -\frac{F}{D\epsilon_0} \left[ \sum_i z_i n_i(\infty) - \sum_i \frac{z_i^2 F n_i(\infty) \psi(x)}{RT} \right] \quad (30)$$

The first summation term has to be zero to preserve electrical neutrality in the bulk solution, so the equation reduces an ordinary second-order differential equation (Morel, 1983, p. 405; Hunter, 1993, pp. 206–207):

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi \quad (31)$$

where  $\kappa = \left(\frac{F^2 \sum z_i^2 n_i(\infty)}{D\epsilon_0 RT}\right)^{1/2}$  and the solution to Eq. (31) is of the form  $\psi = \psi_0 e^{-\kappa x}$  (Morel, 1983, p. 405; Mitchell, 1993, p. 114).

The solution to Eq. (31) shows that the electric potential ( $\psi$ ) decreases exponentially with distance ( $x$ ), and the reciprocal ( $1/\kappa$ ) is often referred to as the thickness of the double layer (Hunter 1993, p. 207). It is interesting to observe that the thickness of the double layer is directly proportional to the square root of the dielectric constant, so in solutions with large dielectric constants, such as water, the double layer will generally extend much further into the solution phase than in a hydrocarbon solvent such as ethanol. Since most of the terms in the expression are constants, the thickness of the double layer mainly depends on the dielectric constant, temperature, the valence of the ion, and the ion concentration in the bulk fluid. If the ionic strength of the bulk concentration  $I = \frac{1}{2} \sum_i n_i(\infty) z_i^2$  is substituted into the equation for  $\kappa$ , the following expression is obtained (Hunter, 1981, p. 27):

$$\kappa = \left(\frac{2000 F^2 I}{D\epsilon_0 RT}\right)^{1/2}$$

where  $I$  is in mol/L or  $M$  and  $\kappa$  is in the unit ( $1/m$ ). For water at  $25^\circ\text{C}$ , this expression becomes approximately equal to  $3.288 \times \sqrt{I}$  ( $\text{nm}^{-1}$ ) (Hunter, 1981, p. 27). Therefore, the thickness of the double layer ( $\lambda$ ) in nanometers can be estimated by knowing the ion concentration using the following relationship:  $\lambda = 0.304/\sqrt{I}$  (nm) (Eykholt, 1992, p. 10). From this expression it can be seen that increasing the ionic strength decreases the thickness of the double layer, and for typical ionic compositions of natural waters ( $10^{-3}$  to  $0.5 M$ ), the double layer compresses from about 9.6 nm thickness at a low ( $10^{-3} M$ ) ionic concentration down to around a 0.4 nm thickness at a high ( $0.5 M$ ) concentration. Furthermore, Schwarzenbach et al. (1993, p. 298) calculates that nearly all the counterions are located within 1–30 nm of the mineral surface.

It should now be understood that in the presence of natural waters, clay mineral surfaces may become covered with hydroxyls and electron-rich atoms or ligands, and, after reaching equilibrium, a diffuse double layer of counterions forms within about 1–30 nm of the surface. Moreover, the surface hydroxyls may undergo proton-exchange reactions with the aqueous solution, and these reactions are dependent on the solution composition, and particularly the pH. Although this discussion is mostly concerned with  $\text{H}^+$  and  $\text{OH}^-$ , it should be noted that other species could also bind with the surface and affect the surface charge, and as a group they are called potential-determining species (Stumm and Morgan, 1996, p. 539). Consider an oxide molecule at the surface where the metal (M) atom is bound to the surface

and the hydroxyls exhibit the following reactions with  $H^+$  (Schwarzenbach et al., 1993, p. 298):



As the pH increases, both of these reactions move toward the right and the surface potential relative to the bulk phase generally decreases as it becomes more difficult to move  $H^+$  away from the oxide surfaces (Schwarzenbach et al., 1993, p. 299).

When only  $H^+$  and  $OH^-$  potential determining species are considered, the abundance of protonated ( $MOH_2^+$ ) and deprotonated ( $MO^-$ ) surface sites largely determines the surface charge. When these species are in equal concentrations the surface may attain a zero net charge, and the pH at which the surface potential ( $\psi$ ) exhibits a zero net charge is called the zero point of charge or  $pH_{zpc}$  (Schwarzenbach et al., 1993, p. 299). Thus, at low pH, the  $MOH_2^+$  species has the greater concentration and determines the surface charge, so the surface potential is positive, whereas at high pH, the  $MO^-$  species has the greater concentration and determines the surface charge, so the surface potential is negative.

Since some clay minerals undergo isomorphic substitution with cations of lower total positive charge, they acquire a fixed net negative charge, and, when they are exposed to solutions containing cations, some of the cations in solution become adsorbed to the clay surface, partially neutralizing the negative surface charge (Schwarzenbach et al., 1993, pp. 303–305). The amount of cations that a clay mineral may adsorb onto its surface from a solution is called its cation exchange capacity (CEC). Compared to other clay minerals such as montmorillonite, which expand as they hydrate, kaolinite has a lower CEC. However, it was determined that if, through isomorphic substitution, an aluminum atom replaced only one silicon atom out of 400, it would account for the measured CEC of kaolinite (Grim, 1968, p. 194). In addition, the smaller surface area of kaolinite compared to other clay minerals that hydrate and expand may account for its lower CEC (Schwarzenbach et al., 1993, p. 305).

Besides isomorphic substitution, broken bonds around the edges of composite silica-alumina units can lead to negative charges on the clay mineral surface. A hypothesis is that hydroxyls attach to the silicon ions and then the hydroxyls become ionized similarly to silicic acid,  $Si-OH + H_2O = SiO^- + H_3O^+$  (Grim, 1968, pp. 193–194). Thus, the negative charge on a tetrahedron can be partially satisfied by the adsorption of cations, such as  $H^+$ , and broken bonds have been speculated to be the primary cause of CEC in kaolinite (Grim, 1968, pp. 193–194). Conversely, positive charges may originate from broken bonds of octahedral groups, and the edges of

kaolinite minerals have exhibited behavior similar to pure aluminum oxides, which react as bases and accept protons such as the  $\text{MOH}_2^+$  species, thus acquiring a positive charge (Grim, 1968, pp. 193–194; Schwarzenbach et al., 1993, pp. 303–305). Since the surface obtains a positive charge, it attracts anions, and therefore has an anion exchange capacity (AEC), and many aluminum silicate particles exhibit both a CEC and an AEC at the same time (Schwarzenbach et al., 1993, pp. 303–305).

The charges on clay mineral surfaces are basically divided into two main groups, permanent or variable charge, and clay soil systems are typically comprised of mixtures of these two groups of clay minerals (Evangelou, 1998, pp. 141–149). The following brief description of the surface charge on clay minerals is based on the one given by Sposito (1989, pp. 134–137). The permanent charge ( $\sigma_0$ ) of a clay mineral surface is the negative charge due to isomorphous substitution, while the variable charge ( $\sigma_H$ ) of a clay mineral surface is due to the protonation of the surface, as mentioned previously concerning the presence of metal oxides, broken bonds, and organic matter. The variable charge ( $\sigma_H$ ) is a function of the pH and is equal to the number of moles of protons ( $\text{H}^+$ ) minus the number of moles of hydroxide ions ( $\text{OH}^-$ ) that form complexes with surface functional groups. Sposito (1984, pp. 12–13) states that a surface functional group is a chemically reactive molecular unit bound to the structure of a solid so that a fluid can bathe the reactive components of the unit. The most abundant and reactive surface functional group, the hydroxyl group, was mentioned earlier, but Sposito (1984, pp. 12–18) elaborates about that group and explains that other functional groups such as siloxane ditrigonal cavities, which are formed in the base of the tetrahedral sheet in clay minerals, and organic surface groups are also important.

In addition to the permanent and variable surface charges densities, potential-determining species besides  $\text{H}^+$  and  $\text{OH}^-$  may bind to the mineral surface, and Sposito (1989, p. 136) describes these species as inner ( $\sigma_{is}$ ) or outer-sphere ( $\sigma_{os}$ ) charges, depending on where they bind to the surface. The inner and outer sphere charges are due to the constituents that are in the solution and are adsorbed by the particle surfaces (Sposito, 1989, p. 136). Lastly, the net total particle charge ( $\sigma_p$ ) is the summation of the four surface charge densities.

$$\sigma_p = \sigma_0 + \sigma_H + \sigma_{is} + \sigma_{os} \quad (32)$$

where  $\sigma_0$  is always negative but the other charges depend on the composition of the solution and may be positive, negative, or zero (Sposito, 1989, p. 136). If the net total surface charge ( $\sigma_p$ ) is not zero, then the charge is balanced by the ions in the diffuse double layer, or, as Sposito (1989, pp. 136–137) describes it, a “diffuse-ion swarm.” The pH at which  $\sigma_p = 0$  is the  $\text{pH}_{\text{pzc}}$  since the ionic species in solution do not contribute to the charge of the mineral surface (Sposito, 1989, p. 137).

In summary, surface charges on minerals can be acquired through different chemical reactions at the surface, isomorphic replacements within the crystal lattice, and as a result of the adsorption of hydrophobic species, such as charged cationic surfactants or ionizable or neutral organic species that bond due to mechanisms such as van der Waals forces (Stumm and Morgan, 1996, pp. 549–554). The charged surface has the ability to exchange ions and may exhibit a CEC and/or an AEC, and, at a specific point called the  $\text{pH}_{\text{pzc}}$ , the surface potential has a zero net charge. Furthermore, the charged surface induces a diffuse double layer of counterions that forms in the adjacent water layer, and for ionic strengths of natural waters, the double layer is generally between 1 and 30 nm from the mineral surface.

## V. HOCs AND SURFACTANTS/COSOLVENTS IN SOIL

The effect of surfactants/cosolvents on the sorption/desorption behavior of HOC contaminants in soil has been the topic of numerous research papers. However, since many of the concepts of HOC interaction between the soil and solution were discussed previously, this section deals mainly with the effect of the solution to increase HOC desorption from soils. Since there is such a vast quantity of research concerning this subject, this section is far from comprehensive, but it is devoted to applicable investigations that are presented to illustrate some significant contributions and the primary directions of this important field of study.

### A. Cosolvents

Over a limited contaminant concentration range and for HOCs, which typically exhibit low concentrations in the aqueous phase ( $C_w$ ), the Freundlich isotherm equation,  $C_s = K(C_w)^n$ , is often linear, which means that  $n = 1$  (Li et al., 2000). Under these conditions, the Freundlich constant is  $K_d$ , and it describes the distribution ratio of the HOC, or the concentration of contaminant in the sorbed phase divided by its concentration in the aqueous phase (Schwarzenbach et al., 1993, p. 258).

$$K_d = \frac{C_s}{C_w} \quad (33)$$

$K_d$  is a complex parameter that depends on a number of factors that are related to the soil properties and the chemical species in the soil and solution, and Schwarzenbach et al. (1993, pp. 262–264) present a detailed summary of these factors. The effect on  $K_d$  that is caused by using cosolvents can

be estimated by dividing the apparent distribution ratio in a water-cosolvent mixture ( $K'_d$ ) by the distribution ratio in pure water ( $K_d$ ) (Li et al., 2000).

$$\log \left( \frac{K'_d}{K_d} \right) = -\alpha\beta\sigma f_c \quad (34)$$

where  $\alpha$ ,  $\beta$ , and  $\sigma$  are parameters that represent the molecular interactions between the soil-cosolvent, water-cosolvent, and contaminant-cosolvent, respectively, and  $f_c$  is the volume fraction of the cosolvent in the solution (Li et al., 2000). Generally, the molecular interaction parameters are a function of  $f_c$ , and at a specific  $f_c$ , the higher the product of  $\alpha\beta\sigma$ , the greater the effect of the cosolvent (Li et al., 2000). Li et al. (2000) found that molecular interaction parameters greatly favor the use of cosolvents. For a PAH, phenanthrene, and three cosolvents, *n*-butylamine, acetone, and tetrahydrofuran, the  $\sigma$  values indicated that cosolvents could increase contaminant solubility by more than five orders of magnitude (Li et al., 2000). Moreover, the  $\beta$  value for *n*-butylamine was particularly indicative of positive water-cosolvent interactions that would favor phenanthrene solubility (Li et al., 2000).

Rao et al. (1985) present a theoretical analysis of sorption and transport of HOCs in aqueous and mixed solvent systems, but they limit their theory to HOC sorption to the organic carbon fraction in the soils and assume that adsorption/desorption isotherms are identical. These investigators determined that HOC sorption from a single solvent increased logarithmically with the hydrocarbonaceous surface area of the soil particles. Their theory predicts that increasing the fraction of cosolvent produces an exponential increase in HOC solubility and causes an exponential decrease in  $K_d$ . An analysis using previous experimental studies shows that the results of their theory were reasonable (Rao et al., 1985).

Fu and Luthy (1986b) tested the sorption behavior of four aromatic contaminants (naphthalene, naphthol, quinoline, and 3,5-dichloroaniline) using different volume fractions of methanol-water or acetone-water systems and different soils. These researchers found that the magnitude of the soil-cosolvent molecular interaction parameter ( $\alpha$ ) was much smaller than expected, and, as a result, the increase of contaminant solubility with volume fraction of cosolvent was about half of the semilogarithmic behavior they had predicted based on their tests without soil and using only a cosolvent (Fu and Luthy, 1986b). These researchers elicited one possible explanation for the discrepancy, and this was that it was a result of the cosolvent-water mixture producing a swelling effect on the organic carbon fraction of the soil, which led to greater contaminant sorption to organic matter.

Zachara et al. (1988) tested the influence of water-methanol and water-acetone cosolvents on the sorption of an ionizable organic contaminant called quinoline in four low-carbon soils, a clay isolate, and montmorillonite. These investigators found that quinoline sorption occurred in a log-linear nature and

was dominated by ion exchange reactions with the mineral surface. Acetone caused greater sorption reduction than methanol, and this was attributed to its lower dielectric constant and larger dipole moment (Zachara et al., 1988).

Staples and Geiselmann (1988) found that contaminant sorption and attenuation were predictably affected by cosolvents, but low levels of cosolvents (less than or equal to 10%) produced an increase in partitioning to the aqueous phase that was only one to three times greater than the partitioning using water. They deduced that low concentrations of a cosolvent would not produce significant changes in the transport of organic contaminants, and high levels of cosolvent would be necessary (Staples and Geiselmann, 1988). Augustijn et al. (1994) conducted solvent flushing experiments on a fine-grained sand to remove two PAHs, naphthalene and anthracene, with different volume fractions of methanol-water mixtures, and they also found evidence that higher cosolvent fractions were the most efficient for remediation. Similarly, Brusseau et al. (1995) reported higher anthracene removal with increasing methanol concentration, and they also found that there was minimal adsorption of alcohols such as methanol and ethanol, to soils.

Although miscible solvents may significantly enhance HOC desorption and solubilization, the environmental properties of the cosolvent must be considered, and, generally, the main cosolvents used for in situ flushing are water-miscible alcohols, such as methanol, ethanol, and propanol (Lowe et al., 1999, p. 41). However, even alcohols can be toxic at high concentrations and precautions need to be taken because they can be flammable and explosive, which could be particularly dangerous for electrokinetic applications. Lowe et al. (1999, p. 66) emphasize that the toxic nature of alcohols requires a careful assessment of the hydrogeologic flow pattern so that the leachate from the injected alcohol solution can be completely recovered. Brusseau et al. (1995) corroborate this warning and mention that the concentrations at which alcohol biodegradation occurs are less than 1%, and concentrations greater than 3% are generally toxic to microorganisms.

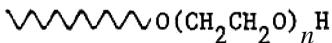
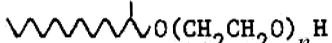
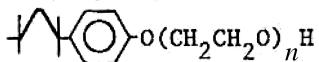
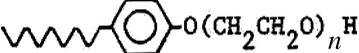
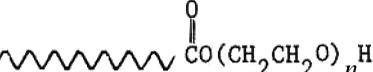
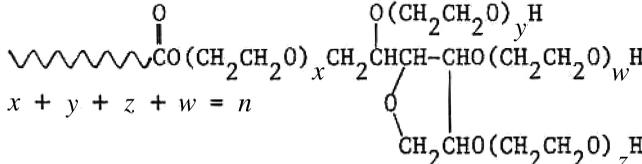
## B. Surfactants

Nonionic surfactants have been shown to enhance or inhibit PAH sorption on fine sands, and these effects were primarily dependent on the concentration of the surfactant and on the soil properties, particularly the organic content (Edwards et al., 1994b). It was found that surfactant monomers may function more effectively as a PAH sorbent than organic matter on a carbon normalized basis (Edwards et al., 1994b), and due to surfactant sorption, a much higher concentration of surfactant may be needed to produce micellization and PAH solubilization (Edwards et al., 1994c). Moreover, several studies have shown evidence that in soils with a low organic content, nonionic surfactant sorption to the soil may continue until the concentration is

well above the CMC (Pennell et al., 1993; Adeel and Luthy, 1995; Ko et al., 1998a). This result is possibly due to interactions between the monomers or bonding between the monomers and the soil surface. West and Harwell (1992) note that surfactant sorption on inorganic surfaces can be substantial because monomer aggregation may occur at the solid-liquid interface. Furthermore, Ko et al. (1998a) imply that the addition of a nonionic surfactant may lead to surfactant sorption followed by HOC partitioning to the surfactant.

Depending on the characteristics of the mineral surface, nonionic surfactants may use either their hydrophilic head or the hydrophobic tail to adsorb to the surface (Rosen, 1989, p. 5). With nonionic polyoxyethylene surfactants this can be confusing because the hydrophilic group is not a head but a polyoxyethylene chain. The structure of these types of surfactants is shown in Table 1 (Dennis et al., 1978, pp. 176–177). Generally, for nonionic ethoxylated surfactants, sorption decreases and water solubility increases as the number of oxyethylene ( $-\text{CH}_2\text{CH}_2\text{O}-$ )<sub>n</sub> groups increases (Rosen, 1989, p. 58; Pennell et al., 1993). Conversely, Brownawell et al. (1997) determined that with

**TABLE 1.** Structures of Polyoxyethylene-Containing Nonionic Surfactants (Dennis et al., 1978)

Surfactant	Examples of trade names
 <b>Polyoxyethylene alcohol</b>	Brij series Lubrol W, AL series
 <b>Polyoxyethylene isoalcohol</b>	Sterox AJ, AP series Emulphogen BC series Renex 30 series
 <b>Polyoxyethylene p-t-octyl phenol</b>	Triton X series Igepal CA series Nonidet P 40
 <b>Polyoxyethylene nonylphenol</b>	Triton N series Igepal CO series Surfonic N series
 <b>Polyoxyethylene esters of fatty acids</b>	Sterox CO series Myrj series
 <b>Polyoxyethylene sorbitan esters<sup>a</sup></b>	Tween series Emasol series

Note. *n*, Average number of oxyethylene units per molecule.

<sup>a</sup>The formula shown is just one molecular type in a complex mixture of different possible structures.

alcohol ethoxylate surfactants, the extent of sorption increased along with the number of oxyethylene groups, but there are many considerations, such as the soil type and the nature of the hydrophobic group. Most investigators agree that oxyethylene sorption behavior is due to a hydrogen bond mechanism (Rosen, 1989, p. 55; Edwards et al., 1994b; Brownawell et al., 1997; Ko et al., 1998b).

Other research concerning surfactant sorption has shown that for different soils, sorption could not be predicted based on clay or the organic matter content alone (Salloum et al., 2000). However, a correlation was found based on the atomic ratio of Si:(Al + Fe) that exists on the soil mineral surface, and based on this correlation it was predicted that nonionic surfactant sorption would be lower for soils that are highly weathered (Shen, 2000). Ko et al. (1998b) found that changes in ionic strength had a negligible effect on nonionic surfactant adsorption but adsorption increased at low pH. Several investigators have found the increased sorption of nonionic surfactants at low pH because mineral surfaces at lower pH have more protonated hydroxyl groups ( $M-OH_2^+$ ) that may bond with the oxyethylene (polar) group through hydrogen bonding (Rosen, 1989, p. 55; Edwards et al., 1994b; Ko et al., 1998b).

Bourbonais et al. (1995) conducted surfactant treatability studies with 28 different nonionic, anionic and mixed anionic/nonionic surfactants to remove petroleum hydrocarbons and other organic contaminants from a gravelly soil. These investigators found that an anionic/nonionic surfactant blend, alkylbenzene sulfonate/alcohol ethoxylate (Witcodet 100), and an anionic surfactant, thioethoxylate (Alcodet MC2000), were the most effective at contaminant mobilization, but Witcodet 100 produced a stable leachate whereas Alcodet MC2000 had an unstable leachate that separated within hours of collection. After 14 pore volumes of flushing, these surfactants were found to facilitate total petroleum hydrocarbon and PAH reduction by 80% to 90% and 49% to 99%, respectively, but concerns about the mobilization of contaminants, leachate recovery and treatability, surfactant recovery, precipitation, stability, biodegradation, and insufficient fate and toxicity data caused these researchers to oppose the use of surfactant-based flushing solutions.

Ganeshalingam et al. (1994) performed surfactant solubilization tests on silica sand. Several HOC contaminants including PAHs, phenanthrene, anthracene, and pyrene, were tested separately, and they found that nonionic alkylphenol ethoxylate surfactants were the most effective. In a comparison of water, an octylphenol ethoxylate surfactant (Igepal CA-720), a polyoxyethylene lauryl ether surfactant (Brij 35), and an anionic, nonylphenoly ethoxylate phosphate surfactant (Rexophos), Igepal CA-720 exhibited the greatest PAH solubilization (Ganeshalingam et al., 1994). The better performance of Igepal CA-720 was attributed to the presence of aromatic rings in both the octylphenol ethoxylate surfactant and the PAHs, and these

researchers also stated that nonionic surfactants generally form more micelles, which leads to greater solubilization (Ganeshalingam et al., 1994). At surfactant concentrations above the CMC, Ganeshalingam et al. (1994) observed a linear increase in PAH solubilization with increasing surfactant concentration. Due to the adsorption of the surfactant to the soil particles, they recommended using a surfactant concentration that was 2500 mg/L or greater, but the highest concentration would be limited by the handling and disposal of large quantities of surfactant in the leachate as well as by economical considerations.

Joshi and Lee (1996) selected the nonionic Igepal CA-720 surfactant due to its high water solubility, good oil dispersion and low clay dispersion, and low volatility. In their experiments, Igepal CA-720 was used to flush an industrially contaminated MGP soil that contained several PAHs at high concentrations, a high (4% or more) organic content, and good permeability. These researchers found that an Igepal CA-720 concentration of about 4–10% produced the greatest amount of solubilization and resulted in the removal of 60–70% of the PAH contamination (Joshi and Lee, 1996). Joshi and Lee (1996) also found that removal was optimized when the volume of flushing solution was four times the weight of the soil and the temperature was very high (60–80°C). Edwards et al. (1994a) developed a mathematical model for washing PAH-contaminated soils with a nonionic surfactant, and they determined that successive washings with the surfactant at a concentration greater than the CMC was more effective than a single wash using the same amount of surfactant that was present in the successive washes. These researchers also found that a continuous flow situation would achieve even greater PAH solubilization (Edwards et al., 1994a).

Patterson et al. (1999) studied the extraction of two PAH compounds, phenanthrene and anthracene, from a coal tar-contaminated soil using five different nonionic surfactants and found that the surfactants could reduce  $K_d$  by several orders of magnitude. Three of the surfactants were ethylene oxide/propylene oxide block copolymers that had a constant length propylene oxide block but the ethylene oxide block length varied. Although there are many other factors to consider, these investigators found that the most efficient nonionic surfactant was the one with the lowest ethylene oxide block size. It seems that as the ethylene oxide composition increases, the micelles become smaller, which reduces the hydrophobic core and the amount PAH solubilization (Patterson et al., 1999).

Yoem et al. (1995) evaluated three different nonionic polyoxyethylene surfactants, octylphenol (Triton X-100), lauryl ether (Brij 35), and polyoxyethylene (20) sorbitan monooleate (Tween 80), for their solubilization performance. The coal tar-contaminated MGP soil that was employed had an organic content of 75% by mass and contained a wide variety of PAHs. These investigators found that the solubilization of phenanthrene increased with increasing surfactant concentration, but there were kinetic effects due

to mass transfer limitations, and at high surfactant concentrations it took longer for the solution to reach equilibrium (Yoem et al., 1995). They also found that Tween 80 was the most efficient at solubilizing phenanthrene, but all three surfactants performed similarly, and the highest removal efficiency (mass solubilized/initial mass in soil) of about 27% occurred at the highest concentration tested (30 g/L).

### C. Biosurfactants and Cyclodextrins

Natural surfactants, or biosurfactants, are surfactants that are produced by microorganisms, plants, or animals, and, apparently, some bacteria, yeasts, and fungi may produce large amounts of surfactants as metabolic by-products or to utilize hydrophobic substances such as hydrocarbons (Connell, 1997, p. 237; Mulligan et al., 2001). A rhamnolipid was four times more effective than a nonionic surfactant, polyoxyethylene (20) sorbitan monooleate (Tween 80), and after 120 pore volumes through a sandy soil, it removed 22% of the residual hexadecane (Brusseau et al., 1995), which has a very low aqueous solubility about 0.003 mg/L (Schwarzenbach et al., 1993, p. 618). Thus, biosurfactants have a great potential for increasing the solubility of HOCs, and they also may be helpful for enhancing biodegradation (Brusseau et al., 1995).

It seems that a great deal of current research has centered on cyclodextrins, which are cyclic oligosaccharides that are formed from the degradation of starch by bacteria (Wang and Brusseau, 1993, 1995a, 1995b; Brusseau et al., 1995; McCray et al., 2000; Ko et al., 2000). Cyclodextrins may be advantageous over regular surfactants because they are stable over a wide range of pH values, they are reported to be nontoxic, biodegradable, and may increase bioremediation, and they have a low affinity for sorption to the solid phase (Ko, 1998, p. 106; McCray et al., 2000). It has been found that with the addition of cyclopentanol,  $\beta$ - and  $\gamma$ -cyclodextrin may form chemical complexes with high-molecular-weight PAHs such as pyrene (Wang and Brusseau, 1995a), and a modified cyclodextrin called hydroxypropyl- $\beta$ -cyclodextrin exhibits the ability to enhance the solubilization of a number of HOCs including PAHs such as naphthalene, anthracene, and phenanthrene (Wang and Brusseau, 1993; McCray, 2000). Moreover, research has also shown that modified cyclodextrin could simultaneously complex with low-polarity organic compounds and heavy metals (Wang and Brusseau, 1995b).

However, there are disadvantages to using cyclodextrin. One concern is that the cyclodextrin "cavity" is not as hydrophobic as the interior of a surfactant micelle, and thus cyclodextrins generally have a lower solubilization power and need the addition of a third component such as alcohol or a surfactant (Brusseau et al., 1995). Carboxymethyl- $\beta$ -cyclodextrin was found

to be costly for practical use (Jiradecha, 1998, p. 141), but hydroxypropyl- $\beta$ -cyclodextrin has the potential to be recycled (Blanford et al., 2001). Although the use of biosurfactants or modified cyclodextrins for the remediation of HOCs seems promising, surfactant biosynthesis is still an emerging technology (Connell, 1997, p. 237).

#### D. Surfactants and Biodegradation

According to Yoem and Ghosh (1998), the data surrounding the toxicity, bioremediation, and bioavailability of surfactant-solubilized PAHs and the surfactants themselves are sparse, but some aerobic and anaerobic experiments have indicated that common surfactant classes degrade rapidly within natural environments (Fountain et al., 1995). Although most surfactants will eventually biodegrade, aerobic processes are generally faster (Lowe et al., 1999, p. 60), and, for ethoxylate nonionic surfactants, decreasing the number of oxyethylene units in the hydrophilic group and increasing the linearity of the hydrophobic group generally enhances biodegradation (Swisher, 1970, p. 243). Concerning toxicity, it has been reported that the use of alkylphenol ethoxylates is restricted in the United States and some other countries because enzymes may degrade this surfactant by cutting the polyether chain thereby increasing its hydrophobicity and toxicity (Connell, 1997, pp. 234–235). Moreover, alkylphenol ethoxylates have also been reported to degrade to persistent metabolites that may show a weak potential to mimic the biological activities of the female hormone estrogen, and there are certain types of estrogen that if taken in high dosages may lead to cancer or other health problems (Lowe et al., 1999, p. 60). Thus, Lowe et al. (1999, p. 60) recommend that a low surfactant concentration should be used for in situ flushing, and, after the surfactant flush is completed, the subsurface region should be thoroughly flushed with water to remove as much of the residual surfactant and contaminant as possible.

There are a number of factors that may affect the biodegradation of PAHs in the presence of surfactant micelles, such as the type and concentration of the surfactant and the type of soil and bacteria. Although studies have established that many nonionic polyethoxylated surfactants are nontoxic to PAH-degrading bacteria at concentrations above the CMC (Yoem and Ghosh, 1998), other studies have found that these surfactants substantially inhibit the biodegradation of phenanthrene at concentrations above the CMC (Laha and Luthy, 1991). Guha and Jaffe (1996) screened number of biodegradable surfactants at concentrations above the CMC to see if they would hinder bacterial degradation of phenanthrene, and they found that inhibition was largely dependent on the type of surfactant. Moreover, these investigators determined that at concentrations above the CMC a fraction of micellar-phase phenanthrene was bioavailable, but this fraction decreased with increasing surfactant concentration (Guha and Jaffe, 1996).

Yoem and Ghosh (1998) conducted batch experiments to determine the effects of a surfactant on PAH biodegradation in soils with aged contaminants, and they concluded that biodegradation was mass-transfer limited due to the low solubility of the contaminants or their slow diffusion through the soil matrix. The surfactant, Triton X-100, improved phenanthrene biodegradation in a 10-month-old soil and significantly enhanced it in a highly weathered 20- to 30-year-old MGP soil, but little or no enhancement occurred for a 2-day-old soil (Yoem and Ghosh, 1998). Pinto and Moore (2000) also studied the solubilization and biodegradation of four field soils that had been contaminated with high-molecular-weight PAHs over different periods of time, and they found that a substantial concentration of nonionic surfactant (Tween 80), about 156 g/L ( $10^4 \times \text{CMC}$ ), was necessary to solubilize approximately 64% of the aged PAHs and 75% of the laboratory-spiked PAHs. These investigators also determined that 90% of one of the PAHs, pyrene, could be removed by adding spores of active PAH-oxidizing *Penicillium* spp. plus nutrients to the leachate from the soil washing operation, whereas the indigenous soil bacteria only oxidized 10% or less of the pyrene.

Joshi and Lee (1995) cleaned a high organic content, PAH-contaminated soil with a treatment train consisting of a soil washing operation using a single wash of a low 1–2% (v/v) concentration of nonionic surfactant, Igepal CA-720, followed by a second operation employing *Acinetobacter* sp. microorganisms for bioremediation. These investigators determined that with a 2% (v/v) concentration, the surfactant was responsible for about 40–50% of the PAH removal and the overall removal efficiency was around 80–100%. Although the surfactant may have slightly hindered the bioremediation of the PAHs in some instances, Joshi and Lee (1995) concluded that *Acinetobacter* sp. could effectively metabolize the PAHs in the presence of the surfactant.

## VI. REMEDIATION OF HOCs IN SOIL SYSTEMS

### A. Alternative Methods

HOC contamination from nonpoint sources is virtually ubiquitous, and even remote regions may have low concentrations of contaminants such as PAHs in the sediments or water (Means et al., 1980; Menzie et al., 1992; Connell, 1997, p. 205). This type of nonpoint source contamination is of great concern, but the main subject of this review article is the treatment of high contaminant concentrations at source zones such as at former MGP sites, and PAH-contaminated argillaceous soils in particular. The U.S. EPA (2000) report on MGP site characterization and current remediation methods presents a good review of some of the alternative treatments that are being employed. This report lists the applicable soil remediation technologies for MGP sites as co-burning, thermal processes, hot and cold-mix asphalt

batching, bioremediation, containment, stabilization/solidification, soil washing, and soil vapor extraction (2000, pp. 5, 1–4).

However, PAHs are very resistant to chemical or microbial attack, have low volatility and aqueous solubility, and have a strong affinity for soils, so most of the alternative remediation methods have serious limitations. Coburning PAHs with coal in utility boilers or in cement kilns and other *ex situ* thermal methods involve excavation and the possible release or spreading of contaminants through air emissions, and highly toxic by-products such as dioxins and furans may be formed (National Research Council, 1997, p. 124). Reliability and material handling problems may also occur with thermal techniques because the tarlike material deposits may clog or foul system components (National Research Council, 1997, p. 124), and highly wet and organic soils are not suitable (U.S. EPA, 2000, pp. 5, 1–4). Although *in situ* thermal processes may work for a wide range of soil types, these processes also result in the formation of toxic air emissions, so the vapors must be treated in surface facilities and these techniques often result in high utility costs (U.S. EPA, 2000, pp. 5, 1–4, 18).

Containment, stabilization, and solidification techniques are often avoided because the contamination may eventually leach from the encapsulated region and long-term monitoring is costly (National Research Council, 1997, p. 123; U.S. EPA, 2000, pp. 5, 4, 48–54). Cold and hot-mix asphalt batching techniques are basically stabilization techniques, they are not viable for fine-grained soils, and their long-term stability is questionable (U.S. EPA, 2000, pp. 5, 1–4, 24–32). Soil vapor extraction is poor for low volatility compounds such as PAHs, and this technique is generally not applicable for clayey soils (U.S. EPA, 2000, pp. 5, 4, 48–54). The bioremediation of PAHs is generally brought about through the action of aerobic microorganisms, so these techniques are often accomplished *ex situ*. Moreover, PAH biodegradation is usually not effective for higher molecular weight hydrocarbons, and the rate of biodegradation is often limited by factors such as the degree of contact between the microorganisms and the contaminants, the oxygen supply, moisture content, temperature, pH, and nutrient supply (U.S. EPA, 2000, pp. 5, 42–44).

## B. Soil Washing/Soil Flushing Using Surfactants/Cosolvents

It should now be understood that most of the alternative remediation methods for HOC contamination have drawbacks, especially under difficult conditions such as when the contaminants are located in soils that are fine-grained, highly saturated, or strongly organic. In addition to the methods previously discussed, there are two more treatment technologies, soil washing and *in situ* soil flushing, that often employ chemical enhancements to increase contaminant desorption and solubilization, and both methods are the subject of

considerable research and exhibit great promise (National Research Council, 1997, pp. 104–105, 124). Soil washing is an *ex situ* method that entails the excavation of the contaminated soil and the placement of the soil into solution filled containers. Once the contaminated soil particles are enclosed within the containers, there are two pathways for accomplishing remediation. The first pathway is to transfer the contaminants from the solid to the liquid phase by using different chemical and mechanical methods, while the second pathway is to separate and sort the particles by size thereby concentrating and reducing the amount of contaminated soil (U.S. EPA, 2000, pp. 5, 55–61). For the both soil-washing remediation pathways, the wash water, or leachate, can be cleaned using conventional wastewater treatment technologies.

The phase transfer pathway generally involves the use of surfactants/cosolvents, which generally lower interfacial tension, consequently increasing contaminant desorption and solubilization. The particle separation pathway is commonly effective because contaminants are typically more concentrated in the fine-grained soil fraction, which generally has greater contaminant adsorption due to the larger surface area of the small particles. In addition, HOC contaminants frequently partition to the organic fraction, which may often be separated due to the different density of organic particles (U.S. EPA, 2000, pp. 5, 55–61). Moreover, since the organic or fine soil particles may be difficult to clean, once they are separated, they may be sent to a landfill (U.S. EPA, 2000, pp. 5, 58). The main disadvantages of soil washing are that it is an *ex situ* process that includes potentially hazardous soil excavation, and it is not effective on low permeability soils since there is not adequate soil–solution–contaminant interaction. Soil washing or flushing is most effective when the soils are gravely or sandy, have very few fine particles, and have a very low organic content, and, under optimal conditions, chemical amendments such as surfactants/cosolvents are unnecessary (National Research Council, 1997, p. 124).

*In situ* flushing is an improved version of the conventional pump-and-treat technique, whereby the flushing action of the solution may be used to enhance contaminant removal (Augustijn et al., 1994, Annable and Sillam, 1999, Jafvert, 1995) and a wide variety of configurations and methods of solution injection, or infiltration, and extraction exist (Roote, 1997, p. 1). *In situ* flushing usually employs surfactants/cosolvents to improve contaminant removal. Although the flow systems for *in situ* flushing are usually superior to those used in pump-and-treat, the treatment zone still requires soils to have a minimum hydraulic conductivity of about  $10^{-5}$  cm/s or greater (Roote, 1997, p. 2). The hydrogeology of the subsurface is of primary importance because heterogeneities, such as soil lenses or layers of silt or clay, cause the flushing solution to travel along preferential flow paths. Consequently, the mass transfer from low permeability regions is exceedingly slow, and heterogeneous subsurface conditions typically exhibit tailing, or persistent residual

contaminant concentrations (Fountain et al., 1995; Roote, 1997, p. 3). Furthermore, mainly due to increased viscosity, surfactants have been shown to reduce the hydraulic conductivity of soils during falling-head experiments (Allred and Brown, 1995). Therefore, the main purpose of enhancing the in situ flushing technique by using electrokinetic technology is to use the phenomenon of electroosmosis to increase soil–solution–contaminant interaction in low permeability regions thereby reducing tailing, remediation time, and costs.

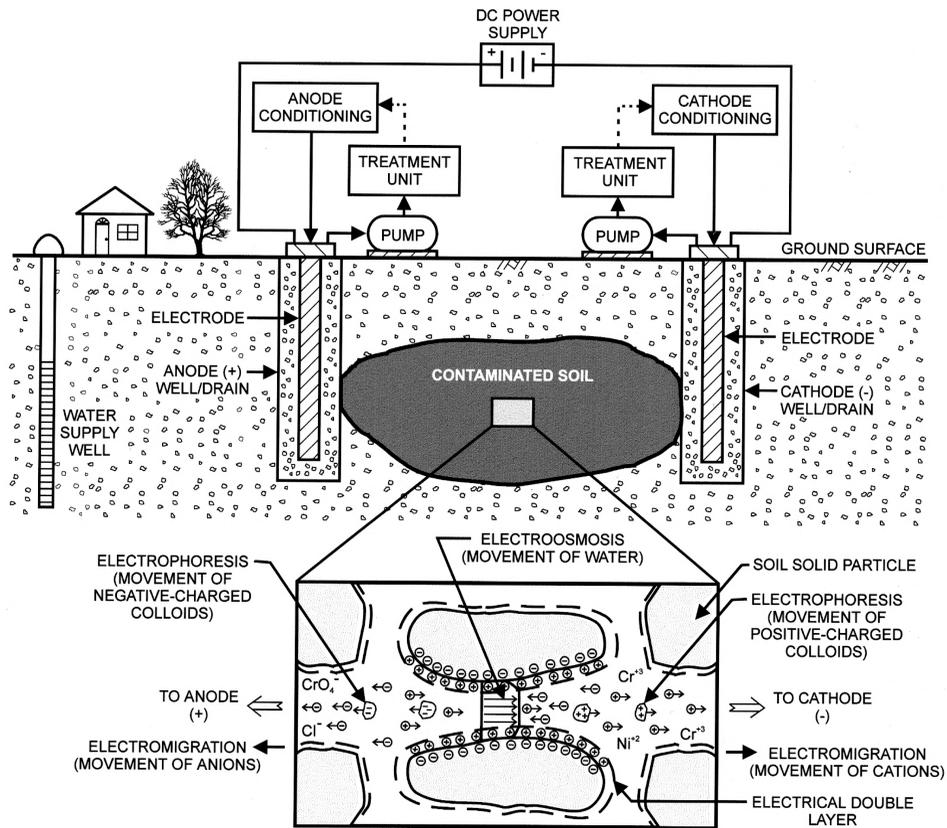
## VII. ELECTROKINETIC REMEDIATION

### A. Introduction

Compared to conventional in situ remediation technologies such as thermal treatments or stabilization or solidification processes, electrokinetics is relatively safe, effective, easy to implement, and economical. Electrokinetics is also flexible because it may be used for a variety different soil types and contaminants. Ordinarily, most of the conventional in situ methods have a difficult time treating fine-grained, high water content, and highly organic or argillaceous soils, but electrokinetics is specifically suited for these types of soil. Moreover, laboratory studies have shown that electrokinetics is appropriate for a variety of different contaminants including organic species, inorganic species, and radionuclides (Acar et al., 1995; Reddy and Parupudi, 1997).

A typical field electrokinetic system is shown in Figure 1. Initially, wells/drains are configured and drilled so they surround the contaminated region. Electrodes are then inserted into each well/drain and a low direct current (DC) electric potential is applied across them. Since the process requires a conducting pore fluid, it is generally applicable for soils with low hydraulic conductivity or subsurface regions that may be saturated due to a low-permeability horizontal layer (Acar et al., 1995).

Electrokinetic remediation is accomplished through various contaminant transport processes such as electromigration, electrophoresis, diffusion, and electroosmosis (Probstein and Hicks, 1993; Reddy et al., 1997; Azzam and Oey, 2001). Electromigration and electrophoresis refer to the migration of ionic solutes in an applied electric field. Electromigration is generally applied to ionic species, whereas electrophoresis is typically applied to the migration of colloidal or larger size particles. If the HOC is neutrally charged, electromigration should not be a dominant mode of transport, and, with non-ionic surfactants/cosolvents, electrophoresis should not control contaminant transport. Furthermore, diffusion is an important transport mechanism, but it is a very slow process, so it is estimated to only have a minor influence on HOC removal.



**FIGURE 1.** Schematic of in situ electrokinetic remediation of contaminated soils.

### B. Electroosmosis, Zeta Potential, and Electrokinetic Phenomena

The controlling mechanism for neutral HOC removal has been attributed to be electroosmosis (Probstein and Hicks, 1993; Pamukcu, 1994, pp. 1, 3). The electroosmotic flow phenomenon has been known to exist for nearly two centuries, and Reuss studied it in 1809 (Yeung, 1992, p. 312). Electroosmotic flow may provide the key for increasing soil–solution–contaminant interaction though low permeability regions because it is capable of producing a substantial flow through these regions that is far superior to the flow achieved by an ordinary hydraulic gradient. In addition, once the contaminants are desorbed from the soil and are solubilized into solution, electroosmosis facilitates advective transport of the contaminant-laden solution towards the electrode compartment for removal. Finally, after the contaminant-laden solution has been removed, it may be treated using conventional wastewater treatment technologies or bioremediation and then possibly recycled (Abdul et al., 1992; Pinto and Moore, 2000; Lee et al., 2001).

As explained earlier, many mineral surfaces, and especially the surfaces of clay mineral particles, are charged, so, when they are surrounded by an aqueous solution, counterions concentrate within a diffuse double layer region adjacent to the particle surface. Furthermore, the amount of ions that balance the charge on the mineral surface, and are distributed throughout the interfacial diffuse double layer region, are in excess or deficit to the amount of similarly charged ions in the bulk solution (Gray and Mitchell, 1967; Eykholt, 1992, p. 7; Yeung, 1994, p. 310). Under an electric potential, electroosmotic flow is produced because the locally excess ions migrate in a plane parallel to the particle surface towards the oppositely charged electrode, and, as they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces (Eykholt, 1992, p. 10).

After the application of an electric gradient, the counterions within the double layer that are located nearest to the mineral surface may be held tightly in place by electrostatic forces, but the excess counterions that are further away from the surface are mobile (Eykholt, 1992, p. 10). Therefore, within the diffuse double layer, there is a shear plane or slip surface that exists parallel to the particle surface that divides the fixed and mobile ion regions (Eykholt, 1992, p. 11). This plane is located at a specific distance from the charged particle surface, and the electric potential at this distance is called the zeta potential ( $\zeta$ ). West and Stewart (1995) define the zeta potential as “the electric potential at the junction between the fixed and mobile parts in the double layer.” The zeta potential is basically a complex function of the interfacial chemistry between the liquid and solid phases (Eykholt and Daniel, 1994), and the zeta potential has been thought to be a function of many parameters including the types of clay minerals and ionic species that are present as well as the pH, ionic strength, and temperature (Vane and Zang, 1997). If the cations and anions are evenly distributed, equal and opposite flow occurs and the net flow is zero (Gray and Mitchell, 1967). However, when the momentum transferred to the fluid in one direction exceeds the momentum of the fluid traveling in the other direction, electroosmotic flow is produced (Gray and Mitchell, 1967).

In 1879, Helmholtz introduced one of the first theories concerning electroosmosis and Smoluchowski modified it in 1914 (Mitchell, 1993, p. 269). Although it is more applicable for soils with fairly large pores and there are many debatable assumptions involved, the Helmholtz–Smoluchowski theory (H-S theory) is still widely accepted (Eykholt, 1992, pp. 11–16; Mitchell, 1993, pp. 271–272). The H-S equation is presented to gain insight into the parameters that effect electroosmotic flow, but this discussion is far from complete, and Hunter (1981, pp. 59–63), Eykholt (1992, pp. 12–14), Mitchell (1993, pp. 269–270), and Yueng (1994, pp. 312–326) all cover the H-S theory in great detail and describe the derivation of the following H-S

equation:

$$v_{eo} = -\frac{D\zeta E_z}{\eta} \quad (35)$$

Thus, the electroosmotic flow velocity ( $v_{eo}$ ) is directly proportional to the applied voltage gradient ( $E_z$ ), zeta potential ( $\zeta$ ), and dielectric constant ( $D$ ) of the fluid, and it is inversely proportional to the fluid viscosity ( $\eta$ ) (Eykholt, 1992, p. 14).

The H-S equation is considered valid when the thickness of the double layer ( $\lambda$ ) is small in comparison to the radius of the capillary ( $a$ ) so that surface of the particle may be regarded as flat. The H-S equation is restricted because it only applies when  $\kappa a > 100$ , where  $\kappa$  is  $1/\lambda$  and  $a$  is the radius of curvature of the capillary (Hunter, 1981, p. 61; Vold and Vold, 1983, p. 213; Eykholt, 1992, p. 15). Eykholt (1992, pp. 29–32) also presents extensions of the H-S theory that have been developed for smaller  $\kappa a$  and for a narrow slit instead of a capillary, and Yueng (1994, pp. 312–326) reviews several more prominent theories of electroosmosis. For negatively charged mineral surfaces, the zeta potential ( $\zeta$ ) is negative, the counterions are cations, and the electrical gradient ( $E_z$ ) is positive in the direction of the cathode, so, by the H-S equation, the velocity and the flow are directed toward the cathode (Eykholt, 1992, p. 14). Conversely, for positively charged mineral surfaces, the zeta potential ( $\zeta$ ) is positive, the counterions are anions, the electrical gradient ( $E_z$ ) remains positive in the direction of the cathode, so the H-S equation shows that the velocity and the flow are negative, or in the direction of the anode.

The H-S equation can also be expressed in terms of the volumetric flow rate ( $q_{eo}$ ) (Eykholt, 1992, p. 19):

$$q_{eo} = \frac{D\zeta E_z}{\eta} nA \quad (36)$$

For this equation,  $n$  is the porosity and  $A$  is the cross-sectional area of the specimen (Mitchell, 1993, p. 271). Furthermore, it should be noted that the use of the effective porosity ( $n_e$ ) (Eykholt, 1992, p. 19) or the porosity ( $n$ ) divided by the tortuosity squared ( $n/\tau^2$ ) (Vane and Zang, 1997) may be more accurate than using the porosity ( $n$ ). For civil engineering applications, the electroosmotic permeability coefficient ( $k_{eo}$ ) is computed as follows (Eykholt, 1992, p. 19; Mitchell, 1993, p. 271):

$$k_{eo} = \frac{D\zeta}{\eta} n \quad (37)$$

Therefore the volumetric flow rate equation becomes  $q_{eo} = k_{eo} E_z A$ . Now, the electroosmotic flow can be compared to the hydraulic flow by using the famous hydraulic equation given by Darcy's Law  $q = kiA$ , where  $q$  is

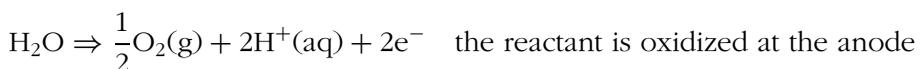
the hydraulic flow rate through the cross-sectional area  $A$ ,  $k$  is the hydraulic conductivity, and  $i$  is the hydraulic gradient, or head loss per unit length (Holtz and Kovacs, 1981, pp. 203–204). If the two volumetric flow rates, electroosmotic and hydraulic, are set equal, the electrical gradient is set to a typical value of 1 V/cm, and the electroosmotic permeability ( $k_{eo}$ ) and hydraulic conductivity ( $k$ ) are known, the hydraulic gradient ( $i$ ) required to induce the electroosmotic flow can be computed as follows (Eykholt, 1992, pp. 20–22):

$$i = \frac{k_{eo}}{k}(E_z) \quad (38)$$

Mitchell (1993, p. 270) shows that  $k_{eo} = 4.1 \times 10^{-5}$  (cm/s)/(V/cm) for fine sand and for this same soil the approximate  $k = 10^{-4}$  cm/s, which are reasonably close so electroosmosis will not greatly enhance the hydraulic flow through this soil. However, in lower permeability soils such as kaolin,  $k_{eo} = 5.7 \times 10^{-5}$  (cm/s)/(V/cm) and the approximate  $k = 10^{-7}$  cm/s, so a very high hydraulic gradient of about 600 would be needed, and Casagrande (1949) found that in a very low permeability London clay with  $E_z = 1$  V/cm,  $k$  was roughly 7000 times smaller than  $k_{eo}$ !

When the  $\text{pH} = \text{pH}_{\text{pzc}}$  and the mineral surface has a zero net charge ( $\sigma_p = 0$ ), theoretically, all the ions at the surface are in the immobile zone and the zeta potential is essentially equal to zero. Therefore, by H-S theory, when the  $\text{pH} = \text{pH}_{\text{pzc}}$ , the electroosmotic flow is zero. It is important to remember that the relationship between the surface charge of the mineral and the  $\text{pH}_{\text{pzc}}$  largely depends on the chemical structure of the mineral, and Evangelou (1998, p. 151) shows that aluminum oxide has a  $\text{pH}_{\text{pzc}}$  of 9.1 whereas for kaolinite it is 4.5. Thus, if a solution has a  $\text{pH}$  of 7, this would be below the  $\text{pH}_{\text{pzc}}$  of aluminum oxide, so a pure aluminum oxide mineral would have a positive surface charge. Alternately, a solution with a  $\text{pH}$  of 7 would be above the  $\text{pH}_{\text{pzc}}$  of kaolinite, so the kaolinite surface would be negatively charged. However, other ions, besides  $\text{H}^+$  and  $\text{OH}^-$ , may specifically adsorb or strongly influence the total net surface charge, and the  $\text{pH}_{\text{pzc}}$  may shift either higher or lower depending on the potential-determining species (Sposito, 1984, pp. 81–88; Evangelou, 1998, pp. 150–154; Stumm and Morgan, 1996, pp. 538–549).

At the electrodes of the electrokinetic cell, the decomposition of water, or electrolysis reactions, occur. The electrolysis reactions generate oxygen gas and hydrogen ions ( $\text{H}^+$ ), or protons, at the anode and hydrogen gas and hydroxyl ( $\text{OH}^-$ ) ions at the cathode (Probstein and Hicks, 1993):



Therefore, due to the electrolysis reactions, there is an increase in the pH near the cathode and a decrease in the pH near the anode. The protons ( $H^+$ ) and hydroxyl ( $OH^-$ ) ions that are generated migrate towards the oppositely charged electrode. Acar et al. (1995) determined that, generally,  $H^+$  is about twice as mobile as  $OH^-$ , so the protons dominate the system and an acid front moves across the soil until it meets the hydroxyl front in a zone near the cathode where the ions may recombine to generate water. Moreover, the variation of pH across the soil can produce many reactions such as adsorption–desorption, precipitation–dissolution, and oxidation–reduction, and this pH variation is useful because it is largely the mechanism responsible for metal desorption and/or dissolution in many electrokinetic remediation experiments performed for treating metal-contaminated soils (Reddy et al., 1997; Reddy and Parupudi, 1997; Reddy and Chinthamreddy, 1999, 2000). Acar et al. (1995) call the  $H^+$  generation and transport an “acid washing process.”

For the removal of HOCs, it is beneficial to optimize the electroosmotic flow and the movement of excess ions, such as the ones in the mobile region of the diffuse double layer, and the electrical current is often used as a measure of the ionic movement. Based on the electrolysis reactions, it may appear that the movement of  $H^+$  and  $OH^-$  toward opposing electrodes generates the current and electroosmotic flow. Dzenitis (1997), however, points out that if inert carbon electrodes are used and the  $H^+$  and  $OH^-$  react to form water, they will not contribute to the current. Nevertheless, the pH variation probably produces reactions that result in additional charged species becoming soluble and migrating, thereby increasing the current and the electroosmotic flow. Enhancing the solution with nonreactive ions as charge carriers may also increase electroosmotic flow (Dzenitis, 1997), but this may have a countereffect because it could reduce the zeta potential, or the thickness of the diffuse double layer.

Furthermore, to maintain electroosmotic flow towards the cathode, it is necessary to sustain a high pH, negative surface charge, and  $\zeta < 0$  so the pH will remain above the  $pH_{pzc}$ . Since the electrolysis reaction at the anode could lower the pH below the  $pH_{pzc}$  in that region, a cessation of electroosmotic flow may occur. Several investigators have found with kaolinite that if there is a significant adsorption of cations besides  $H^+$ , an increase in ionic strength, a lowering of the pH, or a combination of these factors, the surface charge can become positive ( $\zeta > 0$ ), which could result in a stoppage or reversal in the direction of electroosmotic flow (Eykholt and Daniel, 1994; Acar et al., 1995; Vane and Zang, 1997). It should be remembered though, that many factors such as the pH, zeta potential, pore pressures, and electrical gradient often vary along length of the soil sample (Eykholt and Daniel, 1994; Eykholt, 1997), so a low pH and positive surface charge with  $\zeta > 0$  in one region, such as near the anode, does not necessarily mean there will be a flow stoppage or flow reversal throughout the sample.

Clearly, the electrokinetic remediation process is inextricably linked to the soil chemistry, and for electroosmotic flow, the surface charge is of particular importance. Kaolinite is usually used in laboratory electrokinetic experiments because its physical and chemical properties have been studied extensively, and an in-depth overview of the nature and physicochemical properties of kaolinite is given by Eykholt (1992, pp. 38–62). Even with a relatively pure clay soil such as kaolinite, there are complications due to the variability of soil constituents. Impurities such as titanium and iron oxides and smectite have been found to exist in kaolinite, and, although these impurities may be small and difficult to assess by x-ray diffraction, they can greatly affect properties such as the surface charge and CEC (Eykholt, 1992, pp. 40–42).

In addition, it seems the electrochemical behavior of clay minerals can be difficult to interpret. Kaolinite is commonly perceived to have a surface charge that is variable with pH (Evangelou, 1998, p. 146), but apparently there is some debate about this issue, and investigators have found that, although the CEC of kaolinite is small, it is largely due to isomorphic substitution and it is pH-independent (Eykholt, 1992, pp. 42–47). Evidently, the dissolution and adsorption of aluminum can make the surface charge of kaolinite appear to be pH-dependent (Eykholt, 1992, pp. 46–47). It should be clarified that the evaluation of pH-dependent surface charge ( $\sigma_H$ ) is often by a procedure called potentiometric titration (Eykholt, 1992, p. 45), but Sposito (1984, p. 42) found that due to other proton-consuming reactions this method can be unreliable and it should be limited to suspensions of well-characterized substances such as metal oxides, hydroxides, or purified organic material.

The dissolution of kaolinite has electrokinetic implications because the presence of dissolved species such as aluminum ions could generate additional electroosmotic flow or affect the charge on the mineral surface. Carrol-Webb and Walther (1988) found that there was a pH dependence of the dissolution rate of kaolinite at 25°C, and the rates of Si and Al dissolution were often not equal. Long-term kaolinite dissolution decreased from low pH to pH 4, was constant from pH 4 to 8, and then increased with pH when the pH was greater than 10 (Carrol-Webb and Walther, 1988). The short-term dissolution rate was higher, and Eykholt (1992, p. 49) explains that when kaolinite is placed in an acid environment, the exposed aluminum surface groups readily dissolve, and, after roughly 100 h, the rates become steady because of the reduction in aluminum group exposure.

There are many variables in electrokinetic remediation such as pH, surface charge, ionic strength, temperature, and the types of ions in solution that are basically lumped into one variable in the H-S equation, which is the zeta potential. Zeta potential measuring instruments provide a rapid determination of the zeta potential as a function of the solution properties,

and it is valuable information because it enables investigators to get around quantities, such as pH-dependent surface charge ( $\sigma_H$ ), that may be difficult to measure using methods such as potentiometric titration. Furthermore, since the zeta potential is, by the H-S equation, directly proportional to the electroosmotic flow, the solution properties, such as pH or ionic strength, may be altered to assess their effect on zeta potential, and, consequently, electroosmosis (Vane and Zang, 1997; West and Stewart, 1995). For kaolinite, zeta potential is reported to be a strong function of pH and cation concentration. Vane and Zang (1997) determined that the zeta potential of kaolinite ranged from +0.7 mV at pH 2 to -54 mV at pH 10, and, at pH 5, the zeta potential reversed charge when the solution contained 100 ppm  $Pb^{2+}$  with a background electrolyte of 0.01 M KCl, or when it contained 10 ppm  $Pb^{2+}$  with a background electrolyte of  $5 \times 10^{-4}$  M KCl.

It should be recognized that the analysis of solid-solution interfaces can be extremely complex, and the entire study of colloid science is largely devoted to this subject. Zeta potential measurements are definitely useful for understanding the electrokinetic process, but there are a number of additional considerations and complications that are beyond the scope of this discussion. A book written by Robert Hunter (1981) about the zeta potential in colloid science explores this interesting area in detail. Zeta potential measurements are usually based on the electrophoretic mobility of soil particles, where the particles are located in a dilute fluid suspension within an electric field. Thus, it may be questionable as to whether the conditions at which zeta potential measurements are made can be applied to situations with compacted soil, where there may be significant particle-particle interaction and the overlapping of double layers (Hunter, 1993, pp. 262-268; Mitchell, 1993, pp. 115-117). Vane and Zang (1997) note that the "benefit of zeta potential measurements is not whether exact electroosmosis values can be calculated, but whether the simpler dilute suspension experiments can predict trends and effects of ions on packed bed electroosmosis." These researchers used bench-scale experiments and verified that the zeta potential measurements in dilute suspensions were closely related to the electroosmotic changes in saturated, packed kaolinite samples (Vane and Zang, 1997).

The electrokinetic remediation process can be further complicated by other electrochemical changes that may occur, especially at high voltages, and some of the electrochemical effects listed by Mitchell (1993, pp. 281-283) include the dessication of the soil due to the heat generated at the electrodes, mineral decomposition, oxidation and reduction, ion diffusion or exchange, and the precipitation of salts and secondary minerals. Grundl and Michalski (1996) conclude that the modes for the transmission of electricity through a soil/water system are; (1) two-way ionic migration and redox reactions at electrode surfaces, (2) electroosmosis and redox reactions at

electrode surfaces, (3) conduction along sediment surfaces, and (4) electrolysis of water.

Grundl and Michalski (1996) state that under a constant voltage and at a hydraulic steady state, electroosmosis should continue as long as there is a supply of active redox ions and the permeability is unaltered. After completing their electrokinetic experiments with two different soils, kaolin and glacial till, these investigators concluded that the electroosmotic flow stopped in kaolinite due to ion depletion or a cessation of current flow, and it stopped in the glacial till due to an undetermined set of physicochemical changes as a result of the electrolysis reactions (Grundl and Michalski, 1996). Since the current continued in the glacial till test even after the flow stopped, they postulated that the basic mechanism of electrical conduction changed over time (Grundl and Michalski, 1996).

Employing a computer model and experimental tests, Dzenitis (1996, pp. 112–113) formulates a different conclusion as to why the flow stops in electrokinetic tests using kaolinite. This investigator found that there is a low conductivity region that develops near the cathode as a result of the reaction between  $H^+$  and  $OH^-$  ions generated by the electrolysis reactions, and the low ionic strength of this region causes the double layer to expand, which consequently attenuates the electroosmotic flow. Furthermore, due to the low conductivity of the region, this is where the largest electrical gradient develops, and, by H-S theory, this is where the electroosmotic flow should be the highest. However, the low conductivity of this region essentially neutralizes the effect of the electrical gradient so the flow is minimal, and Dzenitis (1996, p. 113) notes that the large electrical gradient may also produce low pressures that may cause additional problems.

Since surfactants/cosolvents are to be used during the electrokinetic experiments, it is essential to assess the effects due to the flushing solution. Basically, the ability of an electrolyte solution to sustain the passage of electrical current mainly depends on the mobility of its dissolved ions that are within the electric field ( $E$ ) (Hamann et al., 1998, p. 12). The ions are subjected to a frictional force ( $K_r$ ) given by Stokes formula,  $K_r = 6\pi\eta rv$ , where  $\eta$  is the viscosity of the solution,  $r$  is the radius of the ion, and  $v$  is the velocity of the ion (Hamann et al., 1998, p. 12). The frictional force  $K_r$  is also equal to the charge of the ion ( $ze_0$ ) multiplied by the strength of the electric field ( $E$ ), and the terminal velocity of the ion is then given by the following equation (Hamann et al., 1998, p. 12):

$$v_{\max} = \frac{ze_0 E}{6\pi\eta r} \quad (39)$$

Solutions that possess high conductivities are generally ones that have high concentrations of ions that are able to dissociate. If the ion concentration becomes too high however, ionic interaction may decrease conductivity.

Generally, pure solvents such as benzene, methanol, or even distilled water are poor conductors because the ions only slightly dissociate (Hamann et al., 1998, p. 19).

In summary, although the electrokinetic remediation process may be relatively safe, effective, easy to implement, and economical compared to other conventional in situ remediation technologies, there needs to be a greater understanding of the process from the molecular scale. There are many physical and electrochemical reactions and transport effects that must be taken into consideration, but with additional research and more rigorous analyses, electrokinetics should be more successful for the heterogeneous subsurface conditions found at many contaminated sites.

### C. Organic Compounds

There have been a number of laboratory studies performed to evaluate the electrokinetic remediation process and contaminant transport by electroosmosis for soils contaminated with various organic compounds, and this section briefly describes some previous research papers and presents a few of the trends, important concepts, and conclusions. In several investigations, the compounds are relatively soluble compared to PAHs and high removal efficiencies can be obtained by using ordinary purging solutions such as distilled or tap water (Acar et al., 1992; Bruell et al., 1992; Shapiro and Probstein, 1993; Schultz, 1997).

The study conducted by Bruell et al. (1992) is of particular interest because they employed several different HOCs with a range of aqueous solubilities and conducted experiments and used calculations to predict contaminant removal from kaolin by electroosmosis. These researchers determined that an organic chemical with a relatively high aqueous solubility and low Freundlich constant ( $K_d$ ), such as benzene, toluene, trichloroethylene (TCE), or *m*-xylene, could be easily removed by electroosmosis, but a chemical with a low aqueous solubility and high  $K_d$ , such as hexane or isooctane, was transported at a much slower rate (Bruell et al., 1992). For example, Bruell et al. (1992) predicted that under their specified conditions, a 90% removal of benzene (approximate solubility = 1780 mg/L and experimental  $K_d = 0.89$ ) from kaolin could be accomplished in 314 days using 2.0 pore volumes of water, while a 90% removal of isooctane (approximate solubility = 2.4 mg/L and experimental  $K_d = 24$ ) from kaolin would require 4730 days and 30 pore volumes of water.

### D. pH Control

The investigations conducted by Acar et al. (1993) and Shapiro and Probstein (1993) focused on a water-soluble groundwater pollutant, phenol, and a high

(85–95%) phenol removal from kaolin was accomplished without the use of surfactants/cosolvents. The research conducted by Shapiro and Probstein (1993) was particularly informative because they found that in some situations the electroosmotic flow could be sustained and/or increased by controlling the pH of the purging solution. These investigators explained that whether the electroosmotic flow was directed towards the anode or the cathode, the electrolysis reaction would tend to decrease the flow.

Shapiro and Probstein (1993) indicate that in most situations if the surface charge and zeta ( $\zeta$ ) potential are initially negative, the electroosmotic flow is towards the cathode, and, due to the electrolysis reaction at the anode, a low-pH solution flows into the electrokinetic cell. The inflow of  $H^+$  ions increases the surface charge and decreases the magnitude of the zeta potential, consequently decreasing the electroosmotic flow. Conversely, when the surface charge and zeta potential are initially positive, the flow is towards the anode, so a high-pH solution flows into the cell due to the electrolysis reaction at the cathode, and the inflow of  $OH^-$  ions has the effect of lowering the surface charge and the zeta potential, so once again the result is a decrease in electroosmotic flow.

Shapiro and Probstein (1993) state that the flow persists until the regions of positive and negative zeta potential balance the “spatially dependent electroosmotic driving force.” However, it should be remembered that there are many variables to consider, such as the soil particle sizes and mineralogy, contaminant and electrolyte concentrations, pore pressures, and electrical gradient, so controlling the pH at the electrode may only increase or sustain the electroosmotic flow under certain conditions. In their experiments with Albion-Kaolin clay, Shapiro and Probstein (1993) found that a 0.01 *M* NaOH purge solution nearly doubled the electroosmotic flow rate over that of a 0.01 *M* HCl purge solution (Shapiro and Probstein, 1993), and subsequent investigations have corroborated that using pH control at the anode enhances electroosmotic flow, and this generally reduces contaminant removal time or increases removal efficiency (Schultz, 1997; Ko, 1998, pp. 161–162). Soils such as glacial till that have a significant carbonate content usually buffer the acid produced by the electrolysis reaction, so the pH remains high near the anode (Reddy and Shirani, 1997) and pH control in these soils is unnecessary.

### E. Electrokinetic Remediation Using Surfactants/Cosolvents

Bruell et al. (1992) showed that high removal efficiencies of relatively water-soluble organic compounds could be accomplished using water as the purging solution. However, even relatively soluble organic pollutants may be difficult to remove and adsorb to some soils, so surfactants/cosolvents have been used to enhance contaminant removal time and efficiency. To compare phenol desorption and/or solubilization from two types of soil, kaolin and

silica, Cicek and Govind (1997) conducted electrokinetic experiments that varied in electrolyte (NaCl) concentration, and they also tested three different types of surfactants (cationic, cetyltrimethylammonium chloride [CTAC], anionic, sodium dodecyl sulfate [SDS]; and nonionic, Triton X-100). Without surfactants, these investigators found that a low electrolyte (NaCl) concentration of about 5 mM or 10 mM slightly increased the electroosmotic flow through kaolin, but an electrolyte concentration of 15 mM or higher resulted in flow reduction, and this was attributed to changes in the surface charge of the soil and a compression of the thickness of the double layer (Cicek and Govind, 1997).

In the tests employing surfactants, Cicek and Govind (1997) found that for each soil, kaolin and silica, the cationic surfactant (CTAC) produced the highest flow and phenol removal (about 92% from kaolin and 99% from silica) because the electrophoretic transport of the micelles was congruent with the electroosmotic flow towards the cathode. The test employing the anionic surfactant (SDS) had the lowest flow and phenol removal (about 50% from kaolin and 85% from silica) since the electrophoretic flow of the micelles towards the anode opposed the electroosmotic flow towards the cathode. The test using the nonionic surfactant (Triton X-100) had an electroosmotic flow and phenol removal (about 90%) from silica that was comparable to tap water, but it was evident that the nonionic surfactant enhanced phenol removal (about 85% for Triton X-100 compared to around 70% for tap water) from the kaolin soil even though the flows were similar.

From the investigation conducted by Cicek and Govind (1997), it can be concluded that the charge on the micelles affects the electroosmotic flow. Since anionic surfactants migrate toward the anode, they could be detrimental to the electrokinetic remediation process, because they would tend to counteract the electroosmotic flow, which is usually toward the cathode. Cationic surfactants are unfavorable because they are commonly more toxic than anionic or nonionic surfactants (Lowe et al., 1999, p. 43), and their positively charged micelles are attracted to the negatively charged soil particles, so there is usually greater surfactant and contaminant adsorption with cationic surfactants. Bourbonais et al. (1995) avoided cationic and zwitterionic surfactants because of their expected strong complexation with soil minerals. Although the cationic surfactant slightly enhanced phenol removal in the investigation conducted by Cicek and Govind (1997), other studies, such as the ones by and Taha (1996, p. 95), Taha et al. (1994), and Qian (1998, p. 137), have shown that cationic surfactants often result stronger adsorption and lower contaminant removal. Thus, it is apparent that cationic and anionic surfactants have major drawbacks, and nonionic surfactants are often the best purging solution additives for optimizing the electrokinetically enhanced in situ flushing process.

Although the electrophoretic flow of anionic micelles commonly opposes the electroosmotic flow, anionic surfactants may be advantageous,

because compared to cationic surfactants, they are good solubilizers, relatively nontoxic (Lowe et al., 1999, p. 43), and the negatively charged micelles tend to be repelled from negatively charged soil particles, so there is often less surfactant adsorption. Several investigators, such as Taha et al. (1994), Taha (1996), Thomas (1996), and Bhattacharya (1996) all chose an anionic surfactant, sodium dodecyl sulfate (SDS) for enhancing electrokinetic remediation. Taha et al. (1994) injected SDS from the anode side of the electrokinetic cell using different concentrations (8 mM and 20 mM) to remove an HOC, 1,3-hexachlorobutadiene (HCB) (approximate solubility = 3.2 mg/L), at a concentration of 1000  $\mu\text{g/g}$  in kaolinite. At the low SDS concentration (8 mM), these investigators found that little transport took place, but at 20 mM, about 75% of the contaminant was removed from the anode region and it migrated toward the cathode. These investigators postulated that an increased HCB concentration near the center of the electrokinetic cell was caused by the SDS micelles clogging and precipitating as they increased in concentration, or by the transport of the anionic micelles toward the anode, which may have started to dominate over the electroosmotic flow toward the cathode (Taha et al., 1994).

Taha et al. (1997) performed experiments on a field soil that was contaminated with trinitrotoluene (TNT) (approximate solubility = 130 mg/L). In one experiment, Taha (1996, p. 106) used SDS in the anode compartment and hypothesized that TNT would be transported to the cathode by electroosmosis; in another experiment, SDS was placed in the cathode compartment and it was hypothesized the micelles would solubilize TNT and migrate toward the anode by electrophoresis (Taha, 1996, p. 127). Although SDS enhanced TNT solubilization in desorption tests, the results of the SDS electrokinetic experiments were not significantly improved over the test performed with deionized water (Taha, 1996, pp. 106, 128), so it was difficult to reach conclusions.

Thomas (1996) conducted SDS enhanced electrokinetic experiments on a silica sand and a clayey field soil that were spiked in the laboratory with hydrocarbons such as toluene, ethylbenzene, and xylenes. One of the conclusions that Thomas (1996, pp. 213–215) made was that the electrophoretic mobility of the SDS micelles was a dominant factor, and since SDS was placed in the anode, the surfactant did not migrate into the soil and contaminant removal was not enhanced.

Using SDS enhanced electrokinetics, Bhattacharya (1996) removed 99.9% of the gasoline from a contaminated kaolin soil, but only 40% of the gasoline was removed from a field soil. The low removal in the field soil was attributed to the higher organic content and the presence of metal cations, which caused adsorption of the SDS micelles. Bhattacharya (1996, p. 147) found that at high concentrations, above 8 mM, SDS micelles adsorbed to the electrode at the anode and slowed or stopped the electrokinetic process, which contradicts the findings of Taha et al. (1994) that were mentioned

earlier. Taha et al. (1994) concluded that better removal occurred when using a 20 mM SDS concentration. Although Bhattacharya (1996) obtained high gasoline removal efficiencies from kaolin, the procedure that was followed appeared somewhat unusual. It seems that after the gasoline was injected, water was initially flushed through the sample under pressure until the contaminant in the effluent reached a steady state (Bhattacharya et al., 1996). The flushing was then stopped, and the gasoline that remained in the apparatus was defined as the residual mass. The electrokinetic treatment was then employed without surfactant enhancement, and the voltage was applied and gradually raised from 0.5 V/cm to about 7 V/cm. It was decided that the voltage would be gradually raised when the gasoline in the effluent became negligible over a period of time (Bhattacharya et al., 1996). The surfactant enhancement process was applied near the end of testing whereby the polarity of the apparatus was switched, SDS was introduced at the cathode, and the voltage was lowered to 0.5 V/cm and then gradually raised again to about 3 V/cm using the same criteria established earlier (Bhattacharya et al., 1996).

Obviously, the results of Bhattacharya et al. (1996) show a high removal of gasoline from kaolin using SDS; however, it should be remembered that Bruell et al. (1992) exhibited a high removal of similar gasoline-type compounds, such as benzene, from kaolin using plain water, and Bruell et al. (1992) used a relatively low and constant 0.4 V/cm voltage gradient. Moreover, gasoline hydrocarbons are volatile and Bhattacharya et al. (1996) used fairly large voltage gradients. Highly hydrophobic compounds such as PAHs may be much more difficult to remove from argillaceous soils, and to obtain significant and efficient removal of these contaminants using electrokinetics, surfactants/cosolvents are generally a requirement.

Pamukcu (1994, p. xii) conducted a major project on two types of coal tar-contaminated field soils that entailed six different electrokinetic treatment schemes and the analysis of 16 PAH compounds. In some of the treatment schemes, Pamukcu (1994, pp. 3–7, 10, 4–10) used an anionic surfactant called Calsoft F-90, which is sodium dodecylbenzene sulfonate (SDBS), and in some cases it seems the surfactant solution was combined with simulated groundwater or with the groundwater and organic cosolvents. It was hypothesized that the cosolvents would aid in PAH solubilization, but Pamukcu (1994, pp. 4–10) found that the use of cosolvents did not result in improved contaminant removal. The best PAH removal (90% in the cathode region) occurred when the SDBS was injected from the cathode side of the electrokinetic cell, and it was suggested that the PAHs were swept toward the anode side due to micellar solubilization and electrophoretic flow (Pamukcu, 1994, pp. 4–9, 13, 5–2).

Clearly, the investigation by Pamukcu (1994) identifies some important findings, such as that SDBS enhanced PAH desorption and/or solubilization and caused electrophoretic contaminant migration toward the anode

during electrokinetics. Nevertheless, there are inherent problems associated with conducting experiments on field soils because the soils are typically heterogeneous, comprised of many different sized particles and minerals, and the contamination is often unevenly distributed. Thus, the analyses from field investigations are commonly ambiguous because processes, such as the electrokinetic transport mechanisms, are difficult to assess, the initial contaminant concentrations may be poor estimations, and accurate mass balances and contaminant removal efficiencies are usually hard to determine with precision.

In spite of the difficulties involved in performing experiments on field soils, Pamukcu (1994) made many noteworthy observations. One important insight was that in the clay soil some of the PAH compounds were transported while other compounds were retained. This selectivity was attributed to properties of the particular PAH compound in addition to the properties of the soil, because selectivity was not apparent in the granular specimens (Pamukcu, 1994, pp. iii, 5–2). Probably due to its somewhat higher aqueous solubility, naphthalene was the most consistently transported PAH (Pamukcu, 1994, p. iii), and chrysene had the lowest removal rate, which could be attributed to its very low solubility. Some PAH transport was achieved in all the soil specimens, and clayey samples treated by electrokinetics alone, without the anionic surfactant, showed PAH transport towards the cathode suggesting migration due to electroosmosis (Pamukcu, 1994, pp. 4–8, 5–2). This indicates that although PAHs have low solubilities, the flushing action of electroosmosis may cause some contaminant transport, especially in granular soils where PAH adsorption is weak due to poor bonding mechanisms (Pamukcu 1994, pp. 1–4).

In a project conducted by Hatem (1999, pp. 97–102, 153), an elaborate polyethylene electrokinetic apparatus was developed with a top-open structure, specially designed stainless-steel electrodes, multiple probe electrodes, a conditioning liquid/surfactant supply system, and a pump-powered washing system. Hatem (1999, pp. 168, 174, 218) tested the performance of surfactants, including a cationic and a zwitterionic, alkyl dimethylbetaine, surfactant, and the soil was uniquely prepared so it was composed of clay-sized particles (Hatem, 1999, pp. 94–95). Many experiments were performed to establish the effectiveness of the systems and to analyze the pH and electric potential gradients, and the pilot scale test used a soil contaminated with a representative HOC, phenanthrene (Hatem, 1999, pp. 196–198). It was difficult to assess many of the details, including those regarding the different systems, surfactants, mass balances, or the determination of removal efficiencies, but Hatem (1999) indicates that the process would remove 80% of the phenanthrene from the soil.

In the preliminary portion of the investigation, Hatem (1999, pp. 197–198) indicated that almost no contaminant adsorbed to the soil when it was mixed with stock solutions of phenanthrene in methanol and shaken for

42 h, but the calculations concerning this determination were vague. The reasons given for the low desorption were that the time was too short and the phenanthrene had a greater affinity for the methanol; however, in subsequent desorption tests lasting 67 h, it seems that only about 28% of the phenanthrene was measured in the methanol phase. Thus, it appears that there may be some inconsistencies in the phenanthrene measuring techniques used by Hatem (1999). In addition, the phenanthrene concentrations were analyzed using an ultraviolet/visible (UV/Vis) spectrophotometer, and the explanations of the experimental methods used by Hatem (1999, pp. 200–202) were relatively unclear compared to other studies employing spectrophotometric analysis of PAHs (Ko, 1998, pp. 33–36; Jiradecha, 1998, pp. 62–65).

It should be realized that the measurement of PAH concentration is often a difficult task due to the low aqueous solubility of these compounds, and the presence of additional additives, such as surfactants that may solubilize organic matter or produce emulsions, complicates PAH analysis. Typically, after the PAHs have been extracted and separated from the aqueous phase or soil, they are concentrated to an adequate detection level, if necessary, and then analyzed using gas chromatography/mass spectrometry (GC/MS) or high-performance liquid chromatography (HPLC). Lee et al. (1981) explain a variety of the PAH analysis instruments and techniques, and the U.S. EPA has developed stringent standardized methods.

The main advantage of using chromatography is that the contaminant of interest is eluted, or separated from the other chemical species by passing the sample through a specially designed column. Instrumental analysis using spectrophotometers is difficult since extreme care must be used to avoid the interference of other chemical species, and the standards and calibration curves must be prepared in the same manner as the regular tests are to be run (Sawyer and McCarty, 1978, p. 301; Traina and Chattopadhyay, 1996, p. 177). Desorption testing and the electrokinetic remediation of soil often leads to the increased solubilization of additional chemical species other than the contaminant, especially when surfactants are used and organic matter is present, so even after filtration, the ability of spectrophotometry by itself to produce accurate measurements is questionable.

Jiradecha (1998, pp. xi, 51, 78) used two field soils, loam and sandy loam and employed the biosurfactant carboxymethyl- $\beta$ -cyclodextrin (CMCD) to remediate the laboratory spiked organic contaminants, naphthalene and 2, 4-dinitrotoluene that have aqueous solubilities of about 35.5 and 322 mg/L, respectively. Emphasis is placed on naphthalene since it was the contaminant that had the lower solubility and was more difficult to solubilize. Desorption batch tests were performed at different pH values, and the Freundlich constants ( $K_d$ ) that were plotted showed that pH did not affect the sorption capacity of the soil. Therefore, Jiradecha (1998, p. 88) concluded that the dominant force for sorption was hydrophobic interaction.

Jiradecha (1998, p. 110) performed column tests without electrokinetics, and the soils were flushed with 0.01 *N* NaNO<sub>3</sub> and 2000 mg/L CMCD solutions. These flushing experiments yielded naphthalene removal efficiencies of 32% and 70% with the NaNO<sub>3</sub> and CMCD solutions, respectively. For the electrokinetic experiments, it was difficult to determine what actual voltage was applied because the study mentions that 30 and 40 V were applied across a 4.0 cm column, which translates to 7.5 and 10 V/cm, but Jiradecha (1998, p. 118) translates the distributed voltages as 0.13 and 0.1 V/cm, respectively. At the higher voltage, the CMCD enhanced electrokinetic process increased naphthalene removal to 83%. Generally, electrokinetics improves the removal for low-permeability soils, and, since these soils used by Jiradecha (1998, pp. 77–78) had only 17 and 7% clay for the loam and sandy loam, respectively, the application of electrokinetics probably enhanced the removal of the contaminants adsorbed to the clay-sized particles. Therefore, since the finer sized particles are treated more efficiently during the electrokinetic process, the remediation rate is reduced compared to flushing (Jiradecha, 1998, p. 141), and the electrokinetic process will generally perform better on soils that have a large amount of small-sized or organic particles and a significant fraction of clay minerals.

Ko (1998, p. 170) also used a cyclodextrin called hydroxypropyl- $\beta$ -cyclodextrin (HPCD) to remediate a kaolin soil contaminated with phenanthrene, and this investigator indicates that with 6.85 mM HPCD prepared in a 0.0033 *M* Na<sub>2</sub>CO<sub>3</sub> buffering solution, about 75% of the contaminant was removed in a short, 6.2-day, time period. Ko et al. (2000) found that increasing the HPCD concentration increased removal efficiency. The original study by Ko (1998) and a subsequent paper by Ko et al. (2000) generally give detailed information, but some calculations and procedures are ambiguous or vague. For example, Ko (1998, p. 146) indicates that the permeability of the sample without HPCD is  $1.36 \times 10^{-10}$  cm<sup>2</sup>, but, generally, with primarily aqueous solutions, most studies express permeability in terms of the hydraulic conductivity, or coefficient of permeability ( $k$ ) from Darcy's law in units such as cm/s (Holtz and Kovacs, 1981, pp. 206–212). It appears that the permeability given by Ko (1998, p. 146) is actually the *specific* or *absolute* permeability ( $K$ ) in units of cm<sup>2</sup> given by the following equation (Lambe and Whitman, 1969, p. 287):

$$K = \frac{k\mu}{\gamma} \quad (40)$$

In this equation,  $k$  (cm/s) is the hydraulic conductivity, also known as the coefficient of permeability, or the simply the permeability, from Darcy's law, and  $\mu$  (N s/cm<sup>2</sup>) and  $\gamma$  (N/cm<sup>3</sup>) are the viscosity and specific weight of the permeant. Although  $K$  is a much more precise definition, Ko (1998, p. 146) could have been more clear and presented the viscosity and specific

weight that was used for the calculation. If the solution used by Ko (1998, pp. 143, 146) in the falling-head permeability measurement was water at 20°C,  $k$  would be approximately  $1.3 \times 10^{-5}$  cm/s, which appears to be in the upper range for kaolinite (Lambe and Whitman, 1969, p. 291; Eykholt, 1992, p. 40), and this may be due to low compaction and the high water content, which was 45% to 50% (Ko et al., 2000). This upper range permeability along with the high water content of the kaolin could help explain the substantial electroosmotic flow obtained over a short time period with relatively low voltage.

In addition, Ko et al. (2000) calculate the initial concentration of phenanthrene based on measured solid-to-water ratios and a previously determined distribution coefficient. These researchers explain that calculations show that over 80% of the phenanthrene initially present in the column was adsorbed to the kaolinite, but these calculations were not apparent. The procedure that Ko et al. (2000) used to contaminate the kaolinite with phenanthrene seems unusually complicated. The air-dried kaolinite was spiked with an aqueous 0.01 M NaCl solution that contained phenanthrene at just below its solubility limit, where the solid-to-solution mass ratio was 300 g/L (Ko et al., 2000). After mixing for 2 days, the soil solution was centrifuged at 5000 rpm for 5 min, the supernatant was decanted, and then the soil was suspended again in the phenanthrene and 0.01 M NaCl solution for 5 days. In addition, this whole process was then repeated and the soil-solution mixture was run in the centrifuge at 9000 rpm for 30 min (Ko et al., 2000). The solubility of phenanthrene is about 1.1 mg/L but the presence of the salt would tend to lower it (as mentioned in the section on solubility), and Ko et al. (1998a) gives the distribution coefficient between phenanthrene and the kaolinite to be about 0.002 L/g. Since the details regarding the water content of the kaolin after centrifuging and the amount of solution decanted are not given, it seems as if assumptions were made, such as based on the distribution coefficient the phenanthrene in the solution was completely adsorbed to the soil, but these details were vague.

Although there are many laboratory methods for spiking soil with an HOC, it should be mentioned that a typical procedure usually begins with dissolving the compound in a more volatile organic solvent where the HOC has a much higher solubility. Then the solvent-HOC solution is mixed with the soil, and the combined mixture is placed under an evaporation hood or someplace where the more volatile solvent can safely evaporate and the HOC is left to adsorb to the drying soil (Ganeshalingam et al., 1994; Edwards et al., 1994a; Guha and Jaffe, 1996; Li et al., 2000). With surfactant testing, it is important that the soil is completely dried because small amounts of organic additives could greatly affect the CMC of the surfactant (Rosen, 1989, pp. 138–142). The amount of HOC that was adsorbed can be estimated by calculations and verified by performing an extraction technique such as Soxhlet extraction, since some HOC may adhere to the glass container or evaporate along with the solvent.

In the study by Ko et al. (2000), they calculated the initial concentration of phenanthrene to be 1.9 mg/kg of kaolinite. According to the U.S. EPA (2000, pp. 3–44), typical background concentrations of PAHs, such as benzo[a]pyrene, range in soils around the world from about 0.1 to 1.0 mg/kg, and an average concentration for New England urban soils was estimated as 3.0 mg/kg (toxic equivalents) for benzo[a]pyrene. Source zones such as former MGP sites have much higher PAH concentrations, and, for example, the U.S. EPA (2000, pp. 5, 48, 14, 51) lists concentrations of 9000, 3000, and 2400 mg/kg at the Jackson, MI, Mason City, IA, and Columbus, GA, locations, respectively. Therefore, it seems that the relatively low concentration of phenanthrene used by Ko et al. (2000) was a level similar to a background concentration in an urban area, so, evidently, the experiments were not targeted for the heavy source concentrations that are present at many PAH-contaminated sites.

Since Ko et al. (2000) used a low concentration of phenanthrene in the electrokinetic experiments, it remains to be seen if HPCD or other cyclodextrin products will perform as well with high PAH concentrations or different HOC compounds. In addition, Jiradecha (1998, p. 110), who also used a cyclodextrin with electrokinetics, was unclear about the initial contaminant concentration and only expressed removal in terms of percentage. In spite of the ambiguities, the high removal efficiency of the cyclodextrins and the increased electroosmotic flow due to a continuously fed 0.0033 *M* Na<sub>2</sub>CO<sub>3</sub> buffer in the experiments by Ko et al. (2000) are encouraging results. As mentioned earlier, modified cyclodextrins are unique because they accomplish the solubilization of HOCs through a complexation mechanism and a hydrophobic cavity, whereas surfactants solubilize HOCs through micellization, and it appears that both cyclodextrins and surfactants have their advantages and disadvantages.

Li et al. (2000) has shown moderate success with use of cosolvents as purging solutions in electrokinetics. These investigators conducted experiments using acetone, tetrahydrofuran, and *n*-butylamine to remove phenanthrene from a glacial till soil. The most effective cosolvent, *n*-butylamine at a 20% concentration, removed 43% of the initial phenanthrene concentration, which was 26 mg/kg. Batch test results demonstrated that at a 20% concentration, acetone, tetrahydrofuran, and *n*-butylamine were superior to ethanol, methanol, and isopropanol at solubilizing phenanthrene from glacial till. Nevertheless, although these other cosolvents are more effective at HOC solubilization, as mentioned previously, the toxicity of acetone, tetrahydrofuran, and *n*-butylamine may be a concern, and water-miscible alcohols are the major cosolvents used in environmental applications (Lowe et al., 1999, p. 43).

In a recent study by Saichek (2002), several parameters were evaluated for optimizing the electrokinetically enhanced in situ flushing technique. These parameters included the ability of different surfactants/cosolvents to

increase HOC desorption and solubilization in soils with low permeability and different mineralogical composition and organic content, the effects of soil type on electrokinetically enhanced remediation, the effects of different operational electrokinetic variables, such as pH buffering, voltage gradient and periodic voltage application, on electrokinetically enhanced remediation, and the effects of heterogeneous soil conditions, such as soil lenses and layers, on electrokinetically enhanced remediation. The testing program consisted of performing 96 batch tests to screen various surfactant/cosolvent solutions for the treatment of two different types of low permeability soils, and then 17 bench-scale one-dimensional (1-D) and 5 bench-scale two-dimensional (2-D) electrokinetic tests were conducted to assess the effects of different electrokinetic variables and to optimize the electrokinetically enhanced in situ flushing process.

In the study by Saichek (2002), the batch tests and 1-D electrokinetic tests provided valuable information about the effects of the flushing solution, the soil type, and the optimal electrokinetic variables. Based on the batch tests, the most promising flushing solution was determined to be a nonionic surfactant with the trade name Igepal CA-720. Although the batch tests were helpful, the 1-D electrokinetic experiments revealed that the mass transport and contaminant removal mechanisms that function during batch tests and those that function during electrokinetic remediation are quite different. As a result, the remedial efficiency for the majority of the 1-D electrokinetic tests was low compared to the batch tests. The use of different low permeability soil types during the batch tests and 1-D electrokinetic tests showed that the contaminant sorbed more strongly to the soil with the greater organic content due to the affinity of HOCs for organic matter. Moreover, the 1-D electrokinetic tests showed that the soil with the greater carbonate content had higher electroosmotic flow because the carbonate minerals were able to neutralize the acid solution generated by the electrolysis reaction at the anode. For the soil with the low carbonate content, a pH buffer was combined with the flushing solution and this significantly improved the electroosmotic flow compared to plain water. However, combining the buffering solution with a surfactant/cosolvent solution only marginally improved the electroosmotic flow.

As mentioned previously, Saichek (2002) performed many 1-D electrokinetic tests to assess and optimize different test variables, such as the surfactant or buffering concentration, voltage gradient, or mode of voltage application, and though the remedial efficiency was low for the majority of the 1-D tests, contaminant migration was usually evident based on the chemical analysis of the soil samples extruded at the conclusion of testing. A systematic analysis and assessment of the electrokinetic variables revealed that the critical factors responsible for producing a high amount of contaminant removal were the use of a high, 2.0 VDC/cm, voltage gradient and a periodic mode of voltage application. Where the periodic voltage was applied according to a

cycle consisting of 5 days of continuous voltage application followed by two days when the voltage was not applied. Apparently, the pulsing or kinetic mass transfer mechanisms that occur between the soil–solution–contaminant are crucial to the remedial process and control contaminant removal. The critical high voltage gradient and periodic application were used along with a flushing solution containing a 5% Igepal CA-720 surfactant concentration and 0.01 *M* NaOH buffering concentration to result a high, 91%, removal efficiency.

Saichek (2002) then applied the critical operating conditions determined from the 1-D tests to larger 2-D tests that employed different heterogeneous soil profiles containing layers, lenses or mixtures of two soils, sand and clay, that possessed extremely different hydraulic conductivities. In these experiments, it was evident that the HOC was weakly sorbed to the sand particles, because the contaminant was rapidly removed from the higher hydraulic conductivity sand by flushing alone, without the use of electrokinetics. The HOC was more difficult to remove from the clay soil, and electrokinetic enhancement was necessary to generate adequate flow through electroosmosis. Spatial voltage measurements were conducted on the 2-D electrokinetic tests, and these measurements showed that without the addition of a pH buffer, the voltage gradient through the most of the soil was substantially less than the applied voltage gradient across the electrodes. In addition, a steep voltage drop occurred near the cathode region, which was attributed to a low conductivity zone that formed as a result of the electrolysis reactions. The addition of the NaOH solution to control the pH near the anode increased the conductivity near the cathode, because, when the NaOH was added, the voltage gradient through the soil approached the voltage gradient applied across the electrodes.

Overall, the 2-D tests conducted by Saichek (2002) indicated that electrokinetically enhancing in situ flushing greatly contributes to increasing contaminant removal from low permeability soils or heterogeneous (lens, layer, or mixture) soil profiles containing soils with high and low hydraulic conductivities. This research showed that the electrokinetically enhanced in situ flushing process has potential, but it is essential to have a fundamental knowledge of the transport mechanisms and physical, chemical, and electrochemical processes that are involved.

## F. Pore Blockage

When presenting their permeability measurements, Ko et al. (2000) convey a crucial message, which is that the purging solution molecules must be capable of traveling through the pore spaces of the soil. They verified that there was flow passage and no blockage by comparing the permeability of the fluid through the soil with and without the presence of HPCD when the

voltage gradient was not applied. This may be applicable for soil flushing experiments, but during electrokinetics, significant changes in the soil typically take place, such as those due to the electrolysis reactions, physicochemical processes, and a variable electrical gradient. Furthermore, pore pressures can develop and consolidation can occur by electroosmosis-induced suction (Eykholt, 1997), and the soil particles may move toward each other, flocculate, or move away from each other, disperse, depending on system variables. Lambe and Whitman (1969, p. 57) indicate that clay particles tend to flocculate with an increase in electrolyte concentration, ion valence, and/or temperature, and they also flocculate with a decrease in dielectric constant, size of hydrated ion, pH, and/or anion adsorption.

The saturated permeability of compacted kaolinite is near  $1 \times 10^{-7}$  cm/s when it is compacted wet of the optimum water content using standard compaction procedures, and the mean pore size diameter ranges from about 30 to 400 nm (Eykholt, 1992, p. 40). As discussed earlier under the topic of surfactants, during solubilization, micelles have particle diameters less than a few tens of nanometers, but at higher surfactant concentrations, SPMEs may form, which have diameters that range from about 10 to 100 nm. Thus, during solubilization, clogging should not be a concern for kaolinite, but systems should be optimized to increase pore size, and low surfactant concentrations should be used to avoid SPMEs. When the spacing between clay particles decreases to small distances, the charges at the faces and edges become very important. Although instinctually it may seem as if the pore spaces would become smaller when clay particles flocculate, Lambe and Whitman (1969, p. 58) show that in some clays, when attractive forces exist, there is an “edge-to-face linkage” that results in larger pore spacing. Conversely, dispersive forces, where the clay particles are repelled from each other may cause small pore spacing, because the particles stack in an efficient arrangement similar to a deck of playing cards (Lambe and Whitman, 1969, p. 58). Therefore, to increase pore size with kaolinite, it may be advantageous to optimize the system variables that will tend towards clay particle flocculation.

Filter papers and porous stones are typically used in laboratory electrokinetic experiments to inhibit the flow of clay particles into the electrode compartments, but the pore sizes of these items are magnitudes larger than the diameters of micelles or the pore spaces in kaolinite, so they are of little concern. A larger concern may be clogging as a result of organic matter or biological activity. Although it is advantageous to use a biodegradable surfactant, under field conditions, the rate of biodegradation may be important, because if it is not controlled, it could lead to the biofouling and clogging of the soil and/or injection wells (Fountain et al., 1995). Rapidly degrading surfactants or cyclodextrins may require system modifications such as a reduced retention time (Fountain et al., 1995). In summary, it is apparent that with low-permeability soils there is a significant potential for the clogging of soil pores, and adequate preliminary and feasibility testing with electrokinetics

should be performed at the bench and pilot scales to ensure flow paths remain open.

### G. Field Experiments

Electrokinetic remediation has been used at actual field locations but most of these projects were applied for the removal of nonorganic or toxic heavy metal contaminants (Lageman, 1993). Recently though, a large-scale electrokinetic test was performed for the remediation of TCE-contaminated soil using the Lasagna process (Ho et al., 1999b). The Lasagna process is basically an electrokinetic remediation method where the electrodes and treatment zones are distributed across the site in a layered configuration, and bench and pilot scale tests as well as small and large field tests were performed to assess this technology for TCE removal. For the small field test (3.0 m × 4.6 m × 4.6 m), Ho et al. (1999a) described the soil in the treatment zone as a sandy clay loam with a low organic content of about 0.2% and hydraulic conductivity of  $1 \times 10^{-7}$  cm/s. This test had an applied voltage gradient of 0.45 to 0.35 V/cm, which induced an electroosmotic flow that averaged approximately 4 to 5 L/h. In situ treatment zones consisting of carbon “wicks” were used to remove the TCE, which had an estimated average initial concentration of about 80 mg/kg, and they computed that there was an overall average TCE removal of 98.4% (Ho et al., 1999a).

For the large field test (6.4 m × 9.2 m × 13.7 m), the treatment zones were composed of iron filings contained in wet kaolin clay, and TCE removal was accomplished through a reductive chlorination process (Ho et al., 1999b). It seems as though several problems arose during the large field test, such as the discovery of higher than estimated levels of TCE and distribution wells filling up with clay, which caused the anode electrode well to dry out. Posttest soil sampling revealed that excellent TCE removals of about 95 to 99.7% occurred in some locations, but other regions had much lower removals, and the poor results were mainly attributed to the position of the region within the treatment zones.

## VIII. SUMMARY

Although it may seem as if a significant amount of subject matter was covered in this review, a good understanding of electrokinetically enhanced in situ flushing for HOC contaminants requires a broad knowledge of a variety of different physicochemical processes. The chemical changes that occur due to the combination of soil–solution–contaminant interactions as well as those caused by the electrical gradient are complex, and there is a vast amount of information and ongoing research concerning these fields of chemistry. The

purpose of this paper was simply to introduce some concepts and impart perspective into the enormous fields of study involved in the electrokinetic remediation of HOCs, such as soil, aquatic, colloid, organic, and environmental chemistry, and electrochemistry and surfactant science. Other areas of concern, such as those concerning the specific mechanisms of mass transfer (phase transitions for different compounds, kinetics, temperature and pressure effects, quantitative chemistry, micelle formation and structures, fate and contaminant transport computer modeling, etc.) were deemed to be beyond the scope of this article. The main topics emphasized were HOCs, their solubility in surfactant and cosolvent solutions with and without the presence of soil, HOC-contaminated soil remediation techniques, and the electrokinetically enhanced in situ flushing method for HOCs.

The ideas and literature reviews presented in this review article illustrate that the electrokinetically enhanced in situ flushing process for HOC-contaminated soils has potential, yet there is a substantial need for further research. Currently, the use of solutions containing surfactants/cosolvents appears to be one of the most effective and environmentally safe means of electrokinetically enhancing the treatment of PAHs at the high concentrations typically found at source zones, such as former MGP sites.

## REFERENCES

- Abdul, A.S., Gibson, T.L., Ang, C.C., Smith, J.C., and Sobczynski, R.E. *In-situ* surfactant washing of polychlorinated biphenyls and oils from a contaminated site, *Ground Water* 30, 219–231, 1992.
- Acar, Y.B., Gale, R.J., Alshawabkeh, A.N., Marks, R.E., Puppula, S., Bricka, M., and Parker, R. Electrokinetic remediation: Basics and technology status, *J. Hazard. Mater.* 40, 117–137, 1995.
- Acar, Y.B., Li, H., and Gale, R.J. Phenol removal from kaolin by electrokinetics, *J. Geotech. Eng.* 118, 1837–1852, 1992.
- Adeel, Z., and Luthy, R.G. Concentration-dependent regimes in sorption and transport of a nonionic surfactant in sand-aqueous systems. Chapter 4 in *Surfactant enhanced subsurface remediation—Emerging technologies*, ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 39–53, 1995. ACS Symposium Series 594. Washington, DC: American Chemical Society.
- Agency for Toxic Substances and Disease Registry. *Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) List of priority hazardous substances*, U.S. Department of Health and Human Services, Washington, D.C., 1999.
- Allred, B., and Brown, G.O. Surfactant-induced reductions of saturated hydraulic conductivity and unsaturated diffusivity. Chapter 16 in *Surfactant enhanced subsurface remediation—Emerging technologies*, ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 217–229. 1995. ACS Symposium Series 594. Washington, DC: American Chemical Society.

- Annable, M., and Sillan, R. DNAPL flushing with alcohol, *Ground Water Currents* 32, 1–2. EPA 542-N-99-004, 1999.
- Ash, M., and Ash, I. *Encyclopedia of surfactants*, vol. II. New York: Chemical Publishing, 1981a.
- Ash, M., and Ash, I. *Encyclopedia of surfactants*, vol. III. New York: Chemical Publishing, 1981b.
- Attwood, D., and Florence, A.T. *Surfactant systems, Their chemistry, pharmacy and biology*. New York: Chapman and Hall, 1983.
- Augustijn, D.C.M., Jessup, R.E., Rao, S.C., and Wood, A.L. Remediation of contaminated soils by solvent flushing, *J. Environ. Eng.* 120, 42–57, 1994.
- Azzam, R., and Oey, W. The utilization of electrokinetics in geotechnical and environmental engineering, *Transport Porous Media* 42, 293–314, 2001.
- Banerji, S., and Yalkowsky, S.H. Cosolvent-induced solubilization of hydrophobic compounds into water, *Anal. Chem.* 60, 2153–2155, 1988.
- Bhattacharya, S.J. *Surfactant enhanced electrokinetic remediation of gasoline contaminated soils*. PhD dissertation, Dept. of Civil and Architectural Engineering, University of Wyoming, 1996.
- Bhattacharya, S.J., Foster, D.H., and Reddy, J.M. Surfactant enhanced electrokinetic remediation of gasoline contaminated soils. In *Nonaqueous phase liquids (NAPLs) in subsurface environment: Assessment and remediation. Proc. ASCE Specialty Conference*, Nov. 12–14, 1996, Washington, DC, 311–322, 1996.
- Blanford, W.J., Barackman, M.L., Boving, T.B., Klingel, E.J., Johnson, G.R., and Brusseau, M.L. Cyclodextrin-enhanced vertical flushing of a trichloroethene contaminated aquifer, *Ground Water Monitor. Remediat.* 21, 58–66, 2001.
- Bourbonais, K.A., Campeau, G.C., and MacClellan, L.K. Evaluating effectiveness of *in situ* flushing with surfactants. Chapter 12 in *Surfactant enhanced subsurface remediation—Emerging technologies*, ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 161–176, ACS Symposium Series 594, Washington, DC: American Chemical Society, 1995.
- Brownawell, B.J., Chen, H., Zhang, W., and Westall, J.C. Sorption of nonionic surfactants on sediment materials, *Environ. Sci. Technol.* 31, 1735–1741, 1997.
- Bruell, C.J., Segall, B.A., and Walsh, M.T. Electrokinetic removal of gasoline hydrocarbons and TCE from clay, *J. Environ. Eng.* 118, 68–83, 1992.
- Brusseau, M.L., Miller, R.M., Zhang, Y., Wang, X., and Bai, G. Biosurfactant- and cosolvent-enhanced remediation of contaminated media. Chapter 7 in *Surfactant enhanced subsurface remediation—Emerging technologies*, ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 82–94, ACS Symposium Series 594, Washington, DC: American Chemical Society, 1995.
- Callister, W.D., Jr. *Materials science and engineering*, An introduction, 4th ed. New York: John Wiley and Sons, 1997.
- Carey, F. *Organic chemistry*. New York: McGraw-Hill, 1987.
- Carrol-Webb, S.A., and Walther, J.V. A surface complex reaction model for the pH-dependence of corundum and kaolinite dissolution rates, *Geochim Cosmochim. Acta* 52, 2609–2623, 1988.
- Casagrande, I.L. Electro-osmosis in soils, *Geotechnique* 1, 159–177, 1949.
- Chiou, T.C., McGroddy, S.E., and Kile, D.E. Partitioning characteristics of polycyclic aromatic hydrocarbons on soils and sediments, *Environ. Sci. Technol.* 32, 264–269, 1998.

- Cicek, N., and Govind, R. Micellar enhanced electrokinetic remediation of contaminated soils, *Water Environment Federation (WEFTEC) Conference Proceedings, 70th Annual Conf. Exposition Chicago 3*, 89–100, 1997.
- Clar, E. *Polycyclic hydrocarbons*. New York: Academic Press, 1964.
- Cole, J.G., and Mackay, D. Correlating environmental partitioning properties of organic compounds: The three solubility approach, *Environ. Toxicol. Chem.* 19, 265–270, 2000.
- Connell, D.W. *Basic concepts of environmental chemistry*. New York: Lewis, 1997.
- Dennis, E.A., Ribeiro, A.A., Roberts, M.F., and Robson, R.J. Nonionic surfactant micelles and mixed micelles with phospholipids. In *Solution chemistry of surfactants*, vol. 1, ed. K.L. Mittal. New York: Plenum Press, 1978.
- Duhkin, S.S., and Derjaguin, B.V. Electrokinetic phenomena. In *Surface and Colloid Science*, vol. 7, ed. E. Matijevic. New York: John Wiley and Sons, 1974.
- Dzenitis, J.M. *Soil chemistry effects and flow prediction in remediation of soils by electric fields*. PhD dissertation, Dept. of Mechanical Engineering, Massachusetts Institute of Technology, 1996.
- Dzenitis, J.M. Steady state and limiting current in electroremediation of soil, *J. Electrochem. Society* 144, 1317–1322, 1997.
- Edwards, D.A., Liu, Z., and Luthy, R.G. Experimental data and modeling for surfactant micelles, HOCs, and soil, *J. Environ. Eng.* 120, 23–41, 1994a.
- Edwards, D.A., Adeel, Z., and Luthy, R.G. Distribution of nonionic surfactant and phenanthrene in a sediment/aqueous system, *Environ. Sci. Technol.* 28, 1550–1560, 1994b.
- Edwards, D.A., Liu, Z., and Luthy, R.G. Surfactant solubilization of organic compounds in soil/aqueous systems, *J. Environ. Eng.* 120, 5–21, 1994c.
- Edwards, D. A, Luthy, R.G., and Liu, Z. Solubilization of polycyclic aromatic hydrocarbons in micellar nonionic surfactant solutions, *Environ. Sci. Technol.* 25, 127–133, 1991.
- Evangelou, V.P. *Environmental soil and water chemistry, Principles and applications*. New York: John Wiley and Sons, 1998.
- Eykholt, G.R. *Driving and complicating features of the electrokinetic treatment of contaminated soils*. PhD dissertation, Dept. of Civil Engineering, University of Texas at Austin, 1992.
- Eykholt, G.R. Development of pore pressures by nonuniform electroosmosis in clays, *J. Hazard. Mater.* 55, 171–186, 1997.
- Eykholt, G.R., and Daniel, D.E. Impact of system chemistry on electroosmosis in contaminated soil, *J. Geotech. Eng.* 120, 797–815, 1994.
- Farrell, J., Grassian, D., and Jones, M. Investigation of mechanisms contributing to slow desorption of hydrophobic organic compounds from mineral solids, *Environ. Sci. Technol.* 33, 1237–1243, 1999.
- Fountain, J.C., Waddell-Sheets, C., Lagowski, A., Taylor, C., Frazier, D., and Byrne, M. Enhanced removal of dense non-aqueous phase liquids using surfactants; Capabilities and limitations from field trials. Chapter 13 in *Surfactant enhanced subsurface remediation—Emerging technologies*. ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 177–190, ACS Symposium Series 594. Washington, DC: American Chemical Society, 1995.

- Fu, J., and Luthy, R.G. Aromatic compound solubility in solvent/water mixtures, *J. Environ. Eng.* 112, 328–345, 1986a.
- Fu, J., and Luthy, R.G. Effect of organic solvent on sorption of aromatic solutes onto soils, *J. Environ. Eng.* 112, 346–367, 1986b.
- Ganeshalingam, S., Legge, R.L., and Anderson, W.A. Surfactant-enhanced leaching of polycyclic aromatic hydrocarbons from soil, *Trans. Inst. Chem. Eng.* 72(Part B), 247–251, 1994.
- Ghosh, U., Gillette, J.S., Luthy, R.G., and Zare, R.N. Microscale location, characterization, and association of polycyclic aromatic hydrocarbons on harbor sediment particles, *Environ. Sci. Technol.* 34, 1729–1736, 2000.
- Gillette, J.S., Luthy, R.G., Clemett, S.J., and Zare, R.N. Direct observation of polycyclic aromatic hydrocarbons on geosorbents at the subparticle scale, *Environ. Sci. Technol.* 33, 1185–1192, 1999.
- Gray, D.H., and Mitchell, J.K. Fundamentals aspects of electro-osmosis in soils, *J. Soil Mech. Foundations Div. ASCE* 93, 209–236, 1967.
- Grim, R.E. *Clay mineralogy*. New York: McGraw-Hill, 1968.
- Greenland, D.J., and Hayes, M.H.B. *The chemistry of soil constituents*. New York: John Wiley and Sons, 1978.
- Grundl, T., and Michalski, P. Electroosmotically driven water flow in sediments, *Water Res.* 30, 811–818, 1996.
- Guha, S., and Jaffe, P.R. Biodegradation kinetics of phenanthrene partitioned into the micellar phase of nonionic surfactants, *Environ. Sci. Technol.* 30, 605–611, 1996.
- Hamann, C.H., Hamnett, A., and Vielstich, W. *Electrochemistry*, New York: Wiley-VCH, 1998.
- Harvey, R.G. *Polycyclic aromatic hydrocarbons; Chemistry and carcinogenicity*, New York: Cambridge University Press, 1991.
- Hatem, G. 1999. *Design of the surfactant enhanced electrokinetic system for hydrocarbons removal from clayey soils in pilot scale conditions*. Master of science thesis, Concordia University, Montreal, Quebec, Canada.
- Ho, S.V., Athmer, C., Sheridan, P.W., Hughes, B.M., Orth, R., McKenzie, D., Brodsky, P.H., Shapiro, A., Thornton, R., Salvo, J., Schultz, D., Landis, R., Griffith, R., and Shoemaker, S. The lasagna technology for in situ soil remediation. Small field test, *Environ. Sci. Technol.* 33, 1086–1091, 1999a.
- Ho, S.V., Athmer, C., Sheridan, P.W., Hughes, B.M., Orth, R., McKenzie, D., Brodsky, P.H., Shapiro, A., Sivavec, T.M., Salvo, J., Schultz, D., Landis, R., Griffith, R., and Shoemaker, S. The lasagna technology for in situ soil remediation. Large field test, *Environ. Sci. Technol.* 33, 1092–1099, 1999b.
- Holtz, R.D., and Kovacs, W.D. *An introduction to geotechnical engineering*. Englewood Cliffs, NJ: Prentice Hall, 1981.
- Hunter, R.J. *Zeta potential in colloid science*. New York: Academic Press, 1981.
- Hunter, R.J. *Introduction to colloid science*. New York: Oxford University Press, 1993.
- Jafvert, C.T. *Surfactants and cosolvents*. Technology Evaluation Report, TE-96-02. Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, 1996.
- Jafvert, C.T., Wei, C., and Van Hoof, P.L. A quantitative structure-activity relationship for solubilization of nonpolar compounds by nonionic surfactant micelles.

- Chapter 3 in *Surfactant enhanced subsurface remediation—Emerging technologies*, ed. D.A. Sabatini, R.C. Knox, and J.H. Harwell, 24–37, ACS Symposium Series 594. Washington, DC: American Chemical Society, 1995.
- Jiradecha, C. *Enhanced electrokinetic remediation of soils contaminated by low polarity organic compounds*. PhD dissertation, Dept. of Environmental Engineering, Illinois Institute of Technology, 1998.
- Johnston, C.T. Sorption of organic compounds on clay minerals: A surface functional group approach. In *Organic pollutants in the environment, CMS Workshop Lectures*, vol. 8, ed. B. Sahwney, 2–44, Boulder, CO: Clay Mineral Society, 1996.
- Joshi, M.M., and Lee, S. A novel treatment train for remediation of PAH contaminated soils, *Fresenius Environ. Bull.* 4, 617–623, 1995.
- Joshi, M.M., and Lee, S. Optimization of surfactant-aided remediation of industrially contaminated soils, *Energy Sources* 18, 291–301, 1996.
- Karickhoff, S.W., Brown, D.S., and Scott, T.A. Sorption of hydrophobic pollutants on natural sediments, *Water Res.* 13, 241–248, 1979.
- Karickhoff, S.W., and Morris, K.R. Sorption dynamics of hydrophobic pollutants in sediment suspensions, *Environ. Toxicol. Chem.* 4, 469–479, 1985.
- Ko, S. *Electrokinetic/surfactant-enhanced remediation of hydrophobic organic pollutants in low permeability subsurface environments*. PhD dissertation, Dept. of Civil Engineering, Texas A&M University, 1998.
- Ko, S., Schlautman, M.A., and Carraway, E.R. Partitioning of hydrophobic organic compounds to sorbed surfactants. 1. Experimental studies, *Environ. Sci. Technol.* 32, 2769–2775, 1998a.
- Ko, S., Schlautman, M.A., and Carraway, E.R. Effects of solution chemistry on the partitioning of phenanthrene to sorbed surfactants, *Environ. Sci. Technol.* 32, 3542–3548, 1998b.
- Ko, S., Schlautman, M.A., and Carraway, E.R. Cyclodextrin-enhanced electrokinetic removal of phenanthrene from a model clay soil, *Environ. Sci. Technol.* 34, 1535–1541, 2000.
- Lageman, R. Electroreclamation: Applications in the Netherlands, *Environ. Sci. Technol.* 27, 2648–2650, 1993.
- Laha, S., and Luthy, R.G. Inhibition of phenanthrene mineralization by nonionic surfactants in soil-water systems, *Environ. Sci. Technol.* 25, 1920–1930, 1991.
- Lambe, W.T., and Whitman, R.V. *Soil mechanics*, New York: John Wiley and Sons, 1969.
- Lee, M.L., Novotny, M.V., and Bartle, K.D. *Analytical chemistry of polycyclic aromatic compounds*, New York: Academic Press, 1981.
- Lee, D., Cody, R.D., and Hoyle, B.L. Laboratory evaluation of the use of surfactants for ground water remediation and the potential for recycling them, *Ground Water Monitor. Remed.* 21, 49–57, 2001.
- Li, A., Doucette, W.J., and Andren, A.W. Estimation of aqueous solubility, octanol/water partition coefficient, and Henry's law constant for polychlorinated biphenyls using UNIFAC, *Chemosphere* 29, 657–669, 1994.
- Li, A., Cheung, K.A., and Reddy, K.R. Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene, *J. Environ. Eng.* 126, 527–533, 2000.

- Liu, H., and Amy, G. Modeling partitioning and transport interactions between natural organic matter and polynuclear aromatic hydrocarbons in groundwater, *Environ. Sci. Technol.* 27, 1553–1562, 1993.
- Loehr, R.C., and Webster, M.T. Behavior of fresh vs. aged chemicals in soil, *J. Soil Contam.* 5, 361–383, 1996.
- Lowe, D.F., Oubre, C.L., Ward, C.H., et al. *Surfactants and cosolvents for NAPL remediation: A technology practices manual*. Boca Raton, FL: Lewis, 1999.
- Luthy, R.G., Aiken, G.R., Brusseau, M.L., Cunningham, S.D., Gschwend, P.M., Pignatello, P.M., Reinhard, M., Traina, S.J., Weber, W.J., Jr., and Westall, J.C. Sequestration of hydrophobic organic contaminants by geosorbents, *Environ. Sci. Technol.* 31, 3341–3347, 1997.
- Luthy, R.G., Dzombak, D.A., Peters, C.A., Roy, S.B., Ramaswami, A., Nakles, D.V., and Nott, B.R. Remediating tar-contaminated soils at manufactured gas plant sites, *Environ. Sci. Technol.* 28, 266A–276A, 1994.
- Mackay, D., Di Guardo, A., Paterson, S., and Cowan, C.E. Evaluating the environmental fate of a variety of types of chemicals using the EQC model, *Environ. Toxicol. Chem.* 15, 1627–1637, 1996.
- McCray, J.E., Boving, T.B., and Brusseau, M.L. Cyclodextrin-enhanced solubilization of organic contaminants with implications for aquifer remediation, *Ground Water Monitor. Remed.* 20, 94–103, 2000.
- Means, J.C., Wood, S.G., Hassett, J.J., and Banwart, W.L. Sorption of polynuclear aromatic hydrocarbons by sediments and soils, *Environ. Sci. Technol.* 14, 1524–1531, 1980.
- Menzie, C.A., Potocki, B.B., and Santodanato, J. Exposure to carcinogenic PAH's in the environment, *Environ. Sci. Technol.* 26, 1278–1284, 1992.
- Mitchell, J.K. *Fundamentals of soil behavior*, New York: John Wiley and Sons, 1993.
- Morel, F.M. M. *Principles of aquatic chemistry*, New York: John Wiley and Sons, 1983.
- Mulligan, C.N., Yong, R.N., and Gibbs, B.F. Surfactant-enhanced remediation of contaminated soil: A review, *Eng. Geol.* 60, 371–380, 2001.
- Myers, D. *Surfactant science and technology*, New York: VCH, 1988.
- National Institute of Environmental Health Science National Toxicology Program. *Eighth Report on Carcinogens (RoC)* Department of Health and Human Services, Washington, D.C., 1997.
- National Research Council. *Innovations in ground water and soil cleanup*, Washington, DC: National Academy Press, 1997.
- Oldham, H.B., and Myland, J.C. *Fundamentals of electrochemical science*, New York: Academic Press, 1994.
- Pamukcu, S. *Electrokinetic removal of coal tar constituents from contaminated soils*. Final Report, Electric Power Research Institute, EPRI TR-103320, Project 2879–21. Palo Alto, CA: EPRI, 1994.
- Patterson, I.F., Chowdhry, B.Z., and Leharne, S.A. Polycyclic aromatic hydrocarbon extraction from a coal tar-contaminated soil using aqueous solutions of nonionic surfactants, *Chemosphere* 38, 3095–3017, 1999.
- Pennell, K.D., Abriola, L.M., and Weber, W.J., Jr. Surfactant-enhanced solubilization of residual dodecane in soil columns. 1. Experimental investigation, *Environ. Sci. Technol.* 27, 2332–2340, 1993.

- Peters, C.A., and Luthy, R.G. Coal tar dissolution in water-miscible solvents: Experimental evaluation, *Environ. Sci. Technol.* 27, 2831–2843, 1993.
- Pinto, L.J., and Moore, M.M. Release of polycyclic aromatic hydrocarbons from contaminated soils by surfactant and remediation of this effluent by *Penicillium* spp, *Exper. Toxicol. Chem.* 19, 1741–1748, 2000.
- Pope, G.A., and Wade, W.H. Lessons learned from enhanced oil recovery research for surfactant-enhanced aquifer remediation. Chapter 11 in *Surfactant enhanced subsurface remediation—emerging technologies*, ed. D.A., Sabatini, R.C., Knox, and J.H., Harwell, 177–190. ACS Symposium Series 594. Washington, DC: American Chemical Society, 1995.
- Probstein, R.F., and Hicks, R.E. Removal of contaminants from soils by electric fields, *Science* 260, 498–503, 1993.
- Qian, Y. *Effect of cationic surfactant (CTAB) in the electrokinetic remediation of diesel-contaminated soils*. Master of science thesis, Dept. of Biosystems Engineering, University of Manitoba, 1998.
- Rao, P.S.C., Hornsby, A.G., Kilcrease, D.P., and Nkedi-kizza, P. Sorption and transport of hydrophobic organic chemicals in aqueous and mixed solvent systems: Model development and preliminary evaluation, *J. Environ. Qual.* 14, 376–383, 1985.
- Reddy, K.R., and Chinthamreddy, S. Electrokinetic remediation of heavy metal contaminated soils under reducing environments, *Waste Manage.* 19, 269–282, 1999.
- Reddy, K.R., and Chinthamreddy, S. Comparison of different extractants for removing heavy metals from contaminated clayey soils, *J. Soil Sediment Contam.* 9, 449–462, 2000.
- Reddy, K.R., and Shirani, A.B. Electrokinetic remediation of metal contaminated glacial tills, *Geotech. Geol. Eng. J.* 15, 3–29, 1997.
- Reddy, K.R., and Parupudi, U.S. Removal of chromium, nickel, and cadmium from clays by in situ electrokinetic remediation, *J. Soil Contam.* 6, 391–407, 1997.
- Reddy, K.R., Parupudi, U.S., Devulapalli, S.N., and Xu, C. Y. Effects of soil composition on removal of chromium by electrokinetics, *J. Hazard. Mater.* 55, 135–158, 1997.
- Rockne, K.J., Chee-Sanford, J.C., Sanford, R.A., Hedlund, B.P., Staley, J.T., and Strand, S.E. Anaerobic naphthalene degradation by microbial pure cultures under nitrate-reducing conditions, *Appl. Environ. Microbiol.* 66, 1595–1601, 2000.
- Roote, D.S. *In situ flushing*. Technology Overview Report, TO-97-02. Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, 1997.
- Roote, D.S. *In situ flushing*. Technology Status Report, TS-98-01. Ground-Water Remediation Technologies Analysis Center, Pittsburgh, PA, 1998.
- Rosen, M.J. *Surfactants and interfacial phenomena*, 2nd ed. New York: John Wiley and Sons, 1989.
- Sabatini, D.A., Knox, R.C., and Harwell, J.H. *Surfactant-enhanced DNAPL remediation: Surfactant selection, hydraulic efficiency, and economic factors*. Environmental Research Brief, EPA/600/S-96/002, Washington, D.C., 1996.
- Sabatini, D.A., Knox, R.C., and Harwell, J.H. Emerging technologies in surfactant-enhanced subsurface remediation. Chapter 1 in *Surfactant enhanced subsurface*

- remediation—emerging technologies*, ed. D.A., Sabatini, R.C., Knox, and J.H., Harwell, 177–190. ACS Symposium Series 594. Washington, DC: American Chemical Society, 1995.
- Saichek, R.E. *Electrokinetically enhanced in-situ flushing for HOC-contaminated soils*. PhD thesis, University of Illinois at Chicago, 2002.
- Salloum, M.J., Dudas, M.J., McGill, W.B., and Murphy, S.M. Surfactant sorption to soil and geological samples with varying mineralogical and chemical properties, *Environ. Toxicol. Chem.* 19, 2436–2442, 2000.
- Sawyer, C.N., and McCarty, P.L. *Chemistry for environmental engineering*, 3rd ed. New York: McGraw-Hill, 1978.
- Schonfeldt, N. *Surface active ethylene oxide adducts*. New York: Pergamon Press, 1969.
- Schultz, D.S. Electroosmosis technology for soil remediation: Laboratory results, field trial, and economic modeling, *J. Hazard. Mater.* 55, 81–91, 1997.
- Schwarzenbach, R.P., Gschwend, P.M., and Imboden, D.M. *Environmental organic chemistry*. New York: John Wiley and Sons, 1993.
- Segall, B.A., and Bruell, C.J. 1992. Electroosmotic contaminant-removal processes, *J. Environ. Eng.* 118, 84–100.
- Shapiro, A.P., and Probststein, R.F. 1993. Removal of contaminants from saturated clay by electroosmosis, *Environ. Sci. Technol.* 27, 283–291.
- Sharma, H.D., and Lewis, S.P. 1994. *Waste containment systems, waste stabilization, and landfills: Design and evaluation*. New York: John Wiley and Sons.
- Shen, Y. 2000. Sorption of non-ionic surfactants to soil: the role of soil mineral composition, *Chemosphere* 41, 711–716.
- Sparks, D.L. *Soil physical chemistry*. Boca Raton, FL: CRC Press, 1986.
- Sposito, G. *Chemistry of soils*. New York: Oxford University Press, 1989.
- Sposito, G. *Surface chemistry of soils*. New York: Oxford University Press, 1984.
- Staples, C.A., and Geiselmann, S.J. Cosolvent influences on organic solute retardation factors, *Ground Water* 26, 192–198, 1988.
- Stumm, W., and Morgan, J.J. *Aquatic chemistry*, 3rd ed. New York: John Wiley and Sons. 1996.
- Swisher, R.D. *Surfactant biodegradation*. New York: Marcel Dekker, 1970.
- Taha, M.R. *Micellar electrokinetic remediation of TNT from soil*. PhD dissertation, Dept. of Civil and Environmental Engineering, Louisiana State University and Agricultural and Mechanical College, 1996.
- Taha, M.R., Gale, R.J., and Zappi, M.E. Surfactant enhanced electrokinetic remediation of NAPLs in soils, *Proc. First Int. Conf. Environmental Geotechnics*, Edmonton, July 10–15, 373–377. BiTech Publishers, Richmond, Canada, 1994.
- Taha, M.R., Soewarto, I.H., Acar, Y.B., Gale, R.J., and Zappi, M.E. Surfactant enhanced desorption of TNT from soil, *Water Air Soil Pollut.* 100, 33–48, 1997.
- Thomas, S.P. *Surfactant-enhanced electrokinetic remediation of hydrocarbon-contaminated soils*. Master of science thesis, Dept. of Biosystems Engineering, University of Manitoba, Winnipeg, 1996.
- Tiehm, A., Stieber, M., Werner, P., and Frimmel, F.H. Surfactant-enhanced mobilization and biodegradation of polycyclic aromatic hydrocarbons in manufactured gas plant soil, *Environ. Sci. Technol.* 31, 2570–2576, 1997.

- Traina, S.J., and Chattopadhyay, S. Spectroscopic methods for characterizing surface-sorbed organic contaminants: Applications of optical, electronic measurements. In *The CMS (Clay Minerals Society) Workshop Lectures*, vol. 8, *Organic pollutants in the environment*, ed. B.L. Sawhney, Boulder, CO, 1996.
- U.S. Environmental Pollution Agency. *Test methods for evaluating solid waste, Vol. 1A: Laboratory manual, physical/chemical methods*, SW-846, 3rd ed. Office of Solid Waste and Emergency Response, Washington, DC, 1986.
- U.S. Environmental Pollution Agency. *Cleaning up the nation's waste sites: Markets and technology trends*. EPA/542-R-96-005, Washington, D.C., 1997.
- U.S. Environmental Pollution Agency. *A resource for MGP site characterization and remediation*. EPA/542-R-00-005, Washington, D.C., 2000.
- Valsaraj, K.T. *Elements of environmental engineering; Thermodynamics and kinetics*. Boca Raton, FL: CRC Press, 2000.
- Vane, L.M., and Zang, G.M. Effect of aqueous phase properties on clay particle zeta potential and electro-osmotic permeability: Implications for electro-kinetic soil remediation processes, *J. Hazard. Mater.* 55, 1–22, 1997.
- Vold, R.D., and Vold, M.J. *Colloid and interface chemistry*. Reading, MA: Addison-Wesley, 1983.
- Wang, X., and Brusseau, M.L. Solubilization of some low-polarity organic compounds by hydroxypropyl- $\beta$ -cyclodextrin, *Environ. Sci. Technol.* 27, 2821–2825, 1993.
- Wang, X., and Brusseau, M.L. Cyclopentanol-enhanced solubilization of polycyclic aromatic hydrocarbons by cyclodextrins, *Environ. Sci. Technol.* 29, 2346–2351, 1995a.
- Wang, X., and Brusseau, M.L. Simultaneous complexation of organic compounds and heavy metals by a modified cyclodextrin, *Environ. Sci. Technol.* 29, 2632–2635, 1995b.
- Weast, R.C., Astle, M.J., and Beyer, W.H. *CRC handbook of chemistry and physics*, 65th ed. Boca Raton, FL: CRC Press, 1984.
- Weber, W.J., Huang, W., and Leboeuf, E.J. A three-domain model for sorption and desorption of organic contaminants by soils and sediments. Chapter 11 in *Mineral-water interfacial reactions—Kinetics and mechanisms*, ed. D.L., Sparks, and T.J. Grundl, 222–241. ACS Symposium Series 715. Washington, DC: American Chemical Society, 1998.
- West, C.C., and Harwell, J.H. Surfactants and subsurface remediation, *Environ. Sci. Technol.* 26, 2324–2330, 1992.
- West, J.L., and Stewart, D.I. Effect of zeta potential on soil electrokinesis, *Geoenvironment 2000 ASCE Geotech Spec. Publ.* 2, 1535–1549, 1995.
- Yalkowsky, S.H., and Banerjee, S. *Aqueous solubility: Methods of estimation for organic compounds*. New York: Marcel Dekker, 1992.
- Yeung, A.T. Electrokinetic flow processes in porous media and their applications. In *Advances in porous media*, ed. M. Y., Corapcioglu. Amsterdam: Elsevier, 1994, pp. 309–395.
- Yoem, I., and Ghosh, M.M. Mass transfer limitation in PAH-contaminated soil remediation, *Water Sci. Technol.* 37, 111–118, 1998.
- Yoem, I.T., Ghosh, M.M., and Cox, C.D. Kinetic aspects of surfactant solubilization of soil-bound polycyclic aromatic hydrocarbons, *Environ. Sci. Technol.* 30, 1589–1595, 1996.

- Yoem, I., Ghosh, M.M., Cox, C.D., and Robinson, K.G. Micellar solubilization of polynuclear aromatic hydrocarbons in coal tar-contaminated soils, *Environ. Sci. Technol.* 29, 3015–3021, 1995.
- Zachara, J.M., Ainsworth, C.C., Schmidt, R.L., and Resch, C.T. Influence of cosolvents on quinoline sorption by subsurface materials and clays, *J. Contam. Hydrol.* 2, 343–364, 1988.