Chapter 6
Contaminant Partitioning in the Aqueous Phase

One way that contaminants are retained in the subsurface is in the form of a dissolved fraction in the subsurface aqueous solution. As described in Chap. 1, the subsurface aqueous phase includes “retained water,” near the solid surface, and “free” water. If the “retained water” has an apparently static character, the subsurface “free” water is in a continuous feedback system with any incoming source of water. The amount and composition of incoming water are controlled by natural or human-induced factors. Contaminants may reach the subsurface liquid phase directly from a polluted gaseous phase, from point and nonpoint contamination sources on the land surface, from already polluted groundwater, or from the release of toxic compounds adsorbed on suspended particles. Moreover, disposal of an aqueous liquid that contains an amount of contaminant greater than its solubility in water may lead to the formation of a type of emulsion containing very small droplets. Under such conditions, one must deal with “apparent” solubility, which is greater than “handbook” contaminant solubility values.

It is understood that contaminant solubility in an aqueous solution may be affected by environmental factors, such as ambient pressure, temperature, and composition of the aqueous solution. However, reference data usually found in the literature are related to “pure” water and a conventionally accepted temperature of 25 °C. These are considered standard conditions for a standard state of the chemicals. Any deviation from standard conditions might be explained by defining the effect of each isolated factor on the amount and rate of chemical solubility.

The solubility of most inorganic and organic contaminants in water increases with temperature. Changes in the “real” concentration of a solute during changes in ambient temperature should be considered when dealing with the partitioning of pollutants among subsurface phases. Temperature has a direct effect on chemical solubility, but it also has an indirect effect on various reactions occurring in the subsurface. Moreover, the seasonal variations in temperature might affect the solubility of toxic chemicals in subsurface solutions; an observed solubility equilibrium therefore only reflects the solubility of a compound at a given time and ambient temperature.

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6.1 Solubility Equilibrium

The solubility equilibrium, subject to natural processes in the subsurface matrix, was examined in Chap. 2. The process of contaminant dissolution is affected by the molecular properties of the compound, the composition of the aqueous solution, and the ambient temperature. Here, we focus our discussion on pollutant behavior.

The subsurface system contains a dynamic and complex array of inorganic and organic constituents. The fate of pollutants in the aqueous phase therefore is governed by a variety of reactions, including acid–base equilibria, oxidation–reduction equilibria, complexation with organic and inorganic ligands, precipitation and dissolution, ion exchange, and adsorption. The rate at which these reactions occur, together with the rate of volatilization and biologically or chemically induced degradation, controls contaminant concentrations in subsurface water. Figure 6.1 shows the relationships among these reactions.

Solubility equilibrium is the final state to be reached by a chemical and the subsurface aqueous phase under specific environmental conditions. Equilibrium provides a valuable reference point for characterizing chemical reactions. Equilibrium constants can be expressed on a concentration basis (K^c), on an activity basis (K^o), or as mixed constants (K^m) in which all parameters are given in terms of concentration, except for H^+, OH^-, and e^- (electron) which are given as activities.

Next, we provide a short description of the reactions involving transfer of protons and electrons that affect the solubility equilibria.

Acid–base equilibria are described by a group of reactions covering the transfer of protons, in which the proton donor is an acid and the acceptor is a base, acid $\rightleftharpoons$ base $+$ proton, with the equilibrium constant given by

$$K_A^\circ = [\mathrm{H}^+][\mathrm{base}]/[\mathrm{acid}] \tag{6.1}$$

where K_A^o is an acidity constant, and concentrations are denoted by []. From Eq. 6.1, it follows that, for a given ratio of activities of a particular acid and its conjugate base, the proton activity has a fixed value. In a system with a complex of two bases and two acids, the relation becomes $\mathrm{acid}_1 + \mathrm{base}_2 \rightleftharpoons \mathrm{base}_1 + \mathrm{acid}_2$ and the corresponding equilibrium becomes

$$K_{1,2}^\circ = K_{A1}^\circ / K_{A2}^\circ = [\mathrm{base}_1][\mathrm{acid}_2]/[\mathrm{acid}_1][\mathrm{base}_2], \tag{6.2}$$

where K_{A1}^o and K_{A2}^o denote the acidity constants of the two acids.

Water is the ever-present proton acceptor in the subsurface. During the dissociation of an acid in subsurface water, H_3O^+ is one of the dissociation products and the acid strength is a measurable parameter. In a dilute solution, the activity of the hydrated protons equals that of H_3O^+ and the pH value characterizes the H-ion activity. Substituting for pH in Eq. 6.1, we obtain

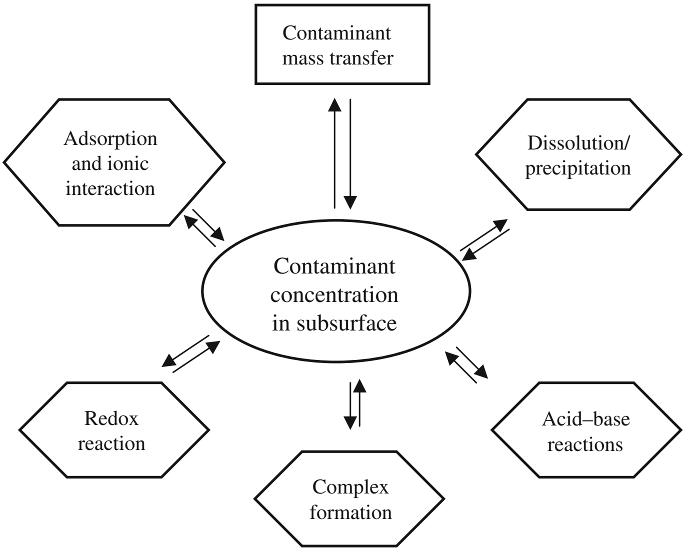


Fig. 6.1 Major processes controlling the fate of contaminants in subsurface water

$$\mathrm{pH} - \mathrm{p}K_A = \log([\mathrm{base}]/[\mathrm{acid}]). \tag{6.3}$$

Oxidation–reduction equilibria exhibit a conceptual analogy to acid–base equilibria. Similar to the approach of acids and bases acting as proton donors and proton acceptors, reducing and oxidization agents are electron donors and electron acceptors, respectively (recall Sect. 2.2.2). The redox reaction between m moles of an oxidant A_{ox} and n moles of a reductant B_{red} can be written as

$$mA_{\mathrm{ox}} + nB_{\mathrm{red}} \rightleftharpoons nA_{\mathrm{red}} + mB_{\mathrm{ox}}, \tag{6.4}$$

which is equivalent to the proton exchange equation.

Every redox reaction includes a reduction half-reaction and an oxidation half-reaction. A reduction half-reaction involving water, in which a chemical species accepts electrons, may be written in the form

$$aA_{\mathrm{ox}} + b\mathrm{H}^+ + \mathrm{e}^- \rightleftharpoons zA_{\mathrm{red}} + g\mathrm{H_2O}, \tag{6.5}$$

where A represents a chemical species in any phase and the subscripts ox and red denote its oxidized states. The parameters a, b, z, and g are stoichiometric coefficients, while H^+ and e^- denote the proton and the electron in the water.

The potential for redox reactions to take place in subsurface aqueous solutions always exists, but these reactions do not necessarily occur, even though the redox reaction may be favored thermodynamically. When the reaction is slow, in some cases, thermodynamic equilibrium can be achieved only in the presence of a catalysis process. In the subsurface, mainly in the near surface (soil layer) region, conditions may favor microbial populations that act as a catalyst in redox reactions.

6.2 Aqueous Solubility of Organic Contaminants

Aqueous solubility of organic contaminants from a gaseous, liquid, or solid source is of major interest in contaminant geochemistry. To define the solubilities and activity coefficients of organic gases, the partial pressure of a compound in the gas phase at equilibrium above a liquid solution is considered identical to the fugacity (see Sect. 7.3) of the compound in the solution. Figure 6.2 conceptualizes the fugacity of a compound in a nonideal liquid mixture (e.g., water solution) where the gas and liquid phases are in equilibrium. Fugacity is a measure of chemical potential that indicates the tendency of a substance to move from one phase to another or from one site to another.

It is known that water is an associated liquid, in which molecules are hydrogen-bonded forming packets of a number of H_2O molecules. In this situation, the organic solutes are not in direct contact with individual water molecules. During the transfer of organic contaminant from its pure liquid phase into a pure aqueous phase, a number of water molecules surround each organic molecule. The water molecules adjacent to the organic solute are different than the bulk water molecules, because of the presence of hydrogen bonds (Schwarzenbach et al. 2003). Meng and Kollman (1996) suggest that water surrounding a nonpolar (organic) molecule maintains but does not enhance its H-bonding network. At ambient temperature, water molecules adjacent to a nonpolar organic molecule lose only a very small proportion of their total hydrogen bonds and, consequently, are able to host a nonpolar solute of limited size (Blokzijl and Engberts 1993).

Organic compounds exhibit, as a function of their molecular properties, a spectrum of solubility values starting from almost zero (for compounds completely immiscible with water, mainly nonpolar organic compounds) and reaching a large value for polar organic compounds. Because of their very low solubility in water, nonpolar organic compounds often are referred to as *nonaqueous phase liquids* (NAPLs). When an NAPL comes into contact with a water source, some organic molecules leave the organic phase and dissolve into the water, while some water molecules enter the organic liquid. When the flux of molecules into and out of the organic phase reaches an equilibrium, the amount of organic matter in the water is constant.

The dissolution of composite nonaqueous phase liquids (CNAPLs) in water is of major importance when considering the fate of organic contaminants in the subsurface. In spite of their limited aqueous solubility, these organic contaminants generally are toxic even in relatively minute amounts. Based on a laboratory experiment examining the dissolution in water of a mixture of seven structurally similar polycyclic aromatic hydrocarbons in toluene, Weber et al. (1998) concluded that variations from predictions using Raoult's law by up to a factor of 2

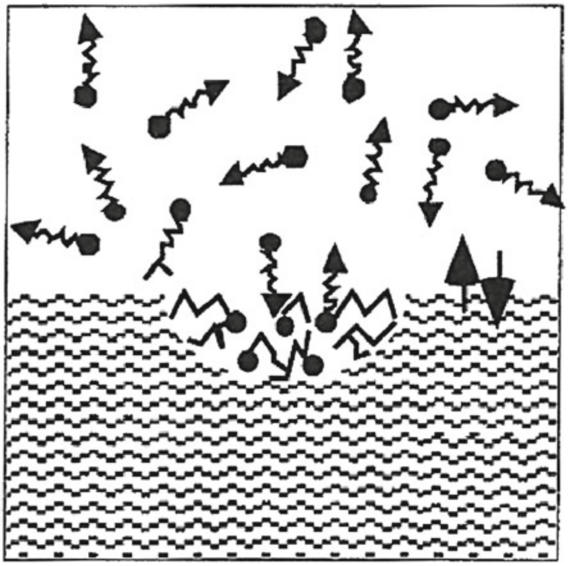


Fig. 6.2 Conceptualization of the fugacity of a compound in a nonideal liquid mixture when gas and liquid phases are in equilibrium (Schwarzenbach et al. 2003)

may be expected in activity coefficients for components deviating significantly from an average mixture. Moreover, the single-impedance mass transfer coefficient determined for one component can be representative of others with similar free liquid diffusivity but is limited when a CNAPL is incompletely characterized, with uncertainties in bulk property values and mole fraction composition.

6.3 Ligand Effects

A molecule or an ion present in a solution in various forms is called a *chemical species* or, more concisely, a *species*. Any combination of cations with molecules or anions that contain free pairs of electrons is called a *complex formation* and might be electrostatic, covalent, or a mixture of both. Ligands are the molecules coordinated around a central cation atom. If a molecule contains more than one ligand, the atoms form a multidentate complex; such complexes are called *chelates*. In a broad classification of chemical reactions, formation of these complexes involves a coordination reaction, similar to acid–base and precipitation–dissolution reactions. Coordination reactions of cations in the subsurface aqueous solution are exchange reactions, wherein the coordinated water molecules are exchanged for some preferred ligands. On the basis of Bjerrum's ion association model, Stumm and Morgan (1996) distinguished two types of complex species: ion pairs formed by two ions that approach a critical distance and are no longer electrostatically effective, and complexes resulting from the formation of largely covalent bonds between a metal ion and an electron donating ligand.

Table 6.1 Hard and soft Lewis acids and bases in solution (Sposito 1981)

Lewis acids
Hard acids
H^+, Li^+, Na^+, K^+ (Rb^+, Cs^+), Mg^{2+}, Ca^{2+}, Sr^{2+} (Ba^{2+}), Ti^{4+}, Zr^{4+}, Cr^{3+}, Cr^{6+}, MoO^{3+}, Mn^{2+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Al^{3+}, Si^{4+}, CO_2
Borderline acids
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (Pb^{2+})
Borderline acids
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} (Pb^{2+})
Soft acids
Cu^+, Ag^+, Au^+, Cd^{2+}, Hg^+, Hg^{2+}, CH_3Hg^+; pi-acceptors such as quinones; bulk metals
Lewis bases
Hard bases
NH_3, RNH_2, H_2O, OH^-, O^{2-}, ROH, CH_3COO^-, ${CO_3}^{2-}$, ${NO_3}^-$, ${PO_4}^{3-}$, ${SO_4}^{2-}$, F^-
Borderline bases
$C_6H_5NH_2$, C_2H_5N, N_2, ${NO_2}^-$, ${SO_3}^{2-}$, Br^- (Cl^-)
Soft bases
C_2H_4, C_6H_6, R_3P $(RO)_3P$, R_3As, R_2S, RSH, ${S_2O_3}^-$, S^{2-}, I^-

R = organic molecular unit. ( ) indicates a tendency to softness

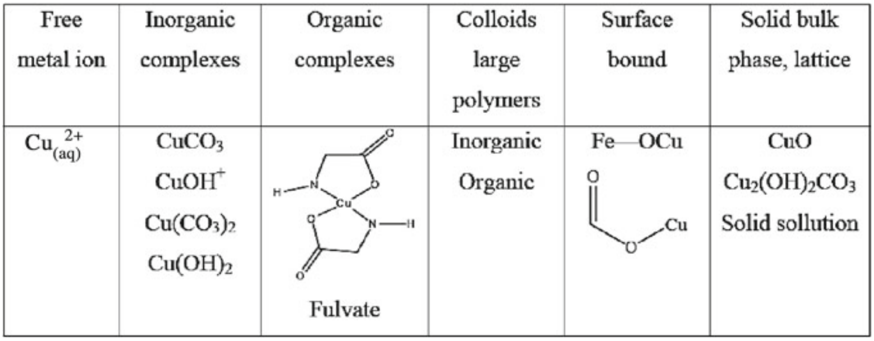
The principle of hard and soft Lewis acids and bases, proposed by Pearson (1963), is useful to describe these reactions. A Lewis acid is any chemical species that employs an empty electronic orbital available for reaction, while a Lewis base is any chemical species that employs a doubly occupied electronic orbital in a reaction. Lewis acids and bases can be neutral molecules, simple or complex ions, or neutral or charged macromolecules. The proton and all metal cations of interest in subsurface aqueous solutions are Lewis acids. Lewis bases include H_2, O_2, oxyanions, and organic N, S, and P electron donors. A list of selected hard and soft Lewis acids and bases found in soil solutions is presented in Table 6.1.

An *inner-sphere* complex is formed between Lewis acids and bases, while an *outer-sphere* complex involves a water molecule interposed between the acid and the base. A hard Lewis acid is a molecular unit of small size, high oxidation state, high electronegativity, and low polarizability; whereas a soft Lewis acid is a molecular unit of relatively large size, characterized by low oxidation state, low electronegativity, and high polarizability. Based on this characterization, hard bases prefer to complex hard acids, and soft bases prefer to complex soft acids, under similar conditions of acid–base strength.

The presence of outside ligands in the subsurface aqueous solution leads to an increase in the solubility of coordinating ions. A complex with any ligand, L_n, or its protonated form, H_kL_n, has a total solubility expressed by

$$A \rightleftharpoons [A]_{\text{free}} + \sum\nolimits_i [A_mH_kL_n(\text{OH})]_i, \tag{6.6}$$

where A represents the ion to be coordinated with different ligand types L_n and all values of m, n, or $k \geq 0$ must be considered in the summation.



Free metal ion	Inorganic complexes	Organic complexes	Colloids large polymers	Surface bound	Solid bulk phase, lattice
$Cu^{2+}_{(aq)}$	$CuCO_3$ $CuOH^+$ $Cu(CO_3)_2$ $Cu(OH)_2$	Fulvate	Inorganic Organic	Fe—OCu	CuO $Cu_2(OH)_2CO_3$ Solid sollution

Fig. 6.3 Forms of occurrence of metal species in natural waters (Stumm and Morgan 1996)

Humic and fulvic acids are the main natural ligands acting in the subsurface aqueous solution. An example of a metal species that may occur in natural waters as a result of potential inorganic and organic ligands is presented in Fig. 6.3. It is difficult, however, to differentiate experimentally between dissolved and colloid substances in subsurface aqueous solutions, and this should be considered when considering the solubility of toxic trace elements in the subsurface system.

6.4 Cosolvents and Surfactant Effects

Many contaminants, such as pesticides and pharmaceuticals, reach the subsurface formulated as mixtures with dispersing agents (surfactants). Such formulations increase the aqueous solubility of the active compounds, and these surfactants form nearly ideal solutions with the aqueous phase.

Addition of a cosolvent is an alternative mechanism to increase contaminant solubility in an aqueous solution. When a contaminant with low solubility enters an aqueous solution containing a cosolvent (e.g., acetone), the logarithm of its solubility is nearly a linear function of the mole fraction composition of the cosolvent (Hartley and Graham-Bryce 1980). The amount of contaminant that can dissolve in a mixture of two equal amounts of different solvents, within an aqueous phase, is much smaller than the amount that can dissolve solely by the more powerful solvent. In the case of a powerful organic solvent miscible with water, a more nearly linear slope for the log solubility versus solvent composition relationship is obtained if the composition is plotted as volume fraction rather than mole fraction.

Yalkowsky and Roseman (1981) and Rubino and Yalkowsky (1987) suggest the following equations for relating solubility of a nonpolar solute (S_m) in a binary mixture of an organic solvent and water to that in pure water (S_w):

$$\log S_m = \log S_w + \sigma_s f_s$$

with

$$\sigma_s = (A\ \log K_{\mathrm{ow}} + B), \tag{6.7}$$

where f_s is the volume fraction of cosolvent in binary mixed solvent, A and B are empirical constants dependent on cosolvent properties, and K_{ow} is the octanol–water partition coefficient of the solute. The solute mixture of interest could comprise, for example, two hydrophobic organic chemicals or one hydrophobic and one ionizable organic chemical.

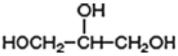
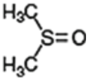
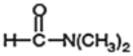
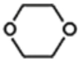
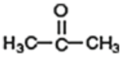
Crystalline salts of many organic acids and bases often have a maximum solubility in a mixture of water and water-miscible solvents. The ionic part of such a molecule requires a strongly polar solvent, such as water, to initiate dissociation. A mixture of water-miscible solvents hydrates and dissociates the ionic fraction of pollutants at a higher concentration than would either solvent alone. Therefore, from a practical point of view, the deliberate use of a water-soluble solvent as a cosolvent in the formulation of toxic organic chemicals can lead to an increased solubility of hydrophobic organic contaminants in the aqueous phase and, consequently, to a potential increase in their transport from land surface to groundwater.

When industrial effluents or other waste materials, constituting a mixture of contaminants, are disposed of on the land surface, situations arise in which completely water-miscible organic solvents (CMOS) change the solvation properties of the aqueous phase. A similar situation may be encountered when, during remediation procedures, a mixture of water and water-miscible solvents is used to "wash" a contaminated soil (Li et al. 1996). A large number of organic solvents with various molecular properties (e.g., methanol, propanol, ethanol, acetone, dioxane, acetonitrile, dimethylformamide, glycerol) are included in the CMOS group. Each has a different effect on the activity coefficient and thus the solubility and partitioning behavior of an organic contaminant in a water/CMOS mixture.

Table 6.2 presents data showing the effect of various CMOS on the activity coefficient or mole fraction solubility of naphthalene, for two different solvent/water ratios. To examine the cosolvent effect, Schwarzenbach et al. (2003) compare the Hildebrand solubility parameter (defined as the square root of the ratio of the enthalpy of vaporization and the molar volume of the liquid), which is a measure of the cohesive forces of the molecule in pure solvent.

Schwarzenbach et al. (2003) note that, qualitatively, the more "waterlike" solvents (e.g., glycerol, ethylene glycol, methanol) have a much smaller impact on the activity coefficient of an organic solute than organic solvents for which hydrogen bonding is important but not the overall dominating factor. The CMOS are relatively small molecules with strong H-acceptor or H-donor properties. In an aqueous mixture, CMOS are able to break the hydrogen bonds between the water molecules and thus form a new H-bond solvent. In this case, the properties of the water–cosolvent solution change as a function of the nature and the relative

Table 6.2 The effect of various CMOS on the activity coefficient, γ or mole fraction solubility of naphthalene, for two different solvent–water ratios, $f_{v,\mathrm{solv}}$ (Schwarzenbach et al. 2003)

Cosolvent	Structure	Solubility parameter $(\mathrm{MPa})^{1/2}$	Naphthalene $\gamma_{iw}^{\mathrm{sat}}/\gamma_{il}^{\mathrm{sat}} = x_{il}^{\mathrm{sat}}/x_{iw}^{\mathrm{sat}}$	
			$f_{v,\mathrm{solv}} = 0.2$ (σ_i^c)	$f_{v,\mathrm{solv}} = 0.4$
Glycerol	 $HOCH_2{-}\overset{OH}{CH}{-}CH_2OH$	36.2	2.5 (2.0)	5.5
Ethylene glycol	$HOCH_2{-}CH_2OH$	34.9	3 (2.4)	9
Methanol	CH_3OH	29.7	3.5 (2.7)	14
Dimethylsulfoxide (DMSO)		26.7	5.5 (3.7)	3.6
Ethanol	H_3CCH_2OH	26.1	7 (4.2)	48
Propanol	$H_3CCH_2CH_2OH$	24.9	17 (6.2)	180
Acetonitrile	$H_3C{-}C{=}N$	24.8	14 (5.7)	140
Dimethylformamide	 $H{-}\overset{O}{\overset{\|}{C}}{-}N(CH_3)_2$	24.8	15 (5.9)	130
1,4-Dioxane		20.7	14 (5.7)	180
Acetone	 $H_3C{-}\overset{O}{\overset{\|}{C}}{-}CH_3$	19.7	20 (6.5)	270

amount of the cosolvent. In general, cosolvents can completely change the solvation properties of subsurface water; the solubility of hydrophobic organic contaminants increases exponentially as the cosolvent fraction increases. The extent of solubility enhancement is controlled by the types of cosolvent and solute.

An increase in solubilization of nonpolar organic chemicals in water is obtained when surfactants are present in the water solution, the solvating strength of surfactants being much greater than that of simple cosolvents. This situation may occur, for example, during effluent disposal on land surface, sewage water irrigation, or point disposal of municipal wastes. The structure of a surfactant solution, above a rather well-defined critical micelle concentration (denoted CMC), is that of an ultrafine emulsion. The surfactant molecules are aggregated forming a cluster of 20–200 units or more. The hydrophobic tails are oriented to the interior of the cluster, and the hydrophilic heads are oriented to the exterior in contact with the water phase. The total solvent strength is determined by the number of micelles, their size, and their structure, but it is not proportional to surfactant concentration.

This type of dissolving action has been called *solubilization,* despite the fact that it does not correspond to the mechanism involved. Hartley and Graham-Bryce (1980) showed that the solubility of a crystalline solute of low water solubility cannot increase continuously with the expansion of the micelle. The limitation comes from the fact that the micelle cannot increase indefinitely in size without modification of its structure and properties, due to reorientation of surfactant molecules. There is a disadvantage, energetic or entropic, in indefinite expansion, which sets a limit to the solubility.

Cosolvents and salts mix completely with water to form homogeneous solutions, but with different effects. Cosolvents decrease the polarity of water and reduce the ability of an aqueous system to "squeeze out" nonpolar solutes, resulting in an increase in the solubility of nonelectrolytes. On the other hand, salts decrease the solubility on nonelectrolytes by increasing the polarity of water, thereby increasing the ability of the aqueous system to "squeeze out" the nonpolar solutes.

6.5 Salting-Out Effect

Effects of electrolytes on the solubility of organic compounds in aqueous solutions were established empirically more than 100 years ago by Setschenow (1889). He found that the presence of dissolved inorganic salts in an aqueous solution decreases the aqueous solubility of nonpolar and weak polar organic compounds. This effect, known as the *salting-out effect,* is expressed by the empirical Setschenow formula

$$\log(\gamma/\gamma_0) = \log(S^0/S) = k_s C_s, \tag{6.8}$$

where γ and γ_0 are the activity coefficients of the organic solute in salt solution and in water, respectively; S^0 and S are solubilities of the solute in water and in salt solution, respectively; k_s (L/mol) is the salting-out constant; and C_s (mol/L) is the molar concentration of the salt solution. In general, the dissolution process requires overcoming water–water interactions that allow formation and occupation of a cavity (Turner 2003; Schwarzenbach et al. 2003). In the presence of dissolved salt, solutions become "salted out" or "squeezed out" due to higher organization and compressibility of the water molecules when bound up in hydration spheres (Millero 1996). In some cases, the presence of salts leads to increases in solubility of organic compounds; this behavior is known as the *salting-in effect,* and the value of the Setschenow constant in this case becomes negative. Several examples of "salting in" and "salting out" are given in Table 6.3.

The salting-out constant expresses the potential of a salt or a mixture of salts to change the solubility of a given nonpolar compound. On contact between organic and aqueous phases, some of the organic molecules dissolve in the water, while some water molecules enter the organic phase. The values of the activity coefficients or relative solubilities of nonelectrolytes in electrolyte solutions have been examined over the years, mainly for saline concentrations close to seawater salinity (Randall and Failey 1927; Xie et al. 1997; Millero 2000; Dror et al. 2000a, 2000b). Because it is virtually impossible to quantify (experimentally) the contribution of individual ions, salting-out constants are available only for combined

Table 6.3 Effects of salts on the solubility of selected organic compounds expressed as Setschnow constant (L/mol). Reprinted from Xie WH, Shiu WY, Mackay DA (1997) review of the effect of salts on the solubility of organic compounds in seawater. Marine Envir Res 44:429–444. Copyright 1997 with permission of Elsevier

Salt	Benzene	Toluene	o-Xylene	m-Xylene	p-Xylene	Naphthalene
Salting out						
NaCl	0.195	0.225	0.227	0.248	0.251	0.260
KCl	0.166	0.206	0.205	0.222	0.217	0.204
$NaNO_3$	0.119	0.144	0.141	0.165	0.146	0.131
$MgSO_4$	0.488	0.457	0.491	0.531	0.491	0.516
$BaCl_2$	0.344	0.376	0.393	0.412	0.407	0.401
CH_3COONa	0.165	0.209	0.206	0.237	0.208	0.21
Salting in						
$(C_2H_5)_4NBr$	−0.56	−0.323	−0.414	−0.402	−0.413	−0.11
$(CH_3)_4NBr$	−0.24	−0.163	−0.198	−0.178	−0.2	−0.5

salts. Salting-out constants for selected organic compounds and aqueous electrolyte solutions at 25 °C are presented in Table 6.3.

Dror et al. (2000a, 2000b) report an experiment dealing with the effect of type and concentration of electrolytes, in an artificial soil aqueous solution, on the solubility of kerosene, a petroleum product containing more than 100 hydrocarbons. At increasing concentrations in water of NaCl or $CaCl_2$, from 0.2 to 2.0 M, a linear decrease in kerosene solubility occurred. It was also observed that the decrease in kerosene dissolution in the artificial soil solution is controlled by the electrolyte concentration but is not influenced by the sodium adsorption ratio (SAR; defined in Eq. 2.46). As noted previous, the SAR is an important factor in the relationship between soil solutions and soils. The salting-out effect is consistent with published data (Xie et al. 1997; Schwarzenbach et al. 2003).

It is interesting to note that smaller ions (e.g., Na^+, Mg^{2+}, Ca^{2+}, Cl^-) form hydration shells larger than bigger ions, which tend to bind water molecules only very weakly. In a simple way, the salting out of nonpolar and weakly polar compounds was explained by Schwarzenbach et al. (2003) by imagining that the dissolved ions compete successfully with the organic compound for solvent molecules. The freedom of some water molecules to solvate an organic molecule depends on the type and concentration of salts.

Under natural conditions, we usually deal with the solubility of nonelectrolytes in *mixed electrolyte* solutions. This aspect has not been thoroughly studied to date. Early studies of Randall and Failey (1927) used ionic strength fractions for modeling salting coefficients in mixed electrolyte solutions. No changes were observed in the Setschenow constant values when the electrolyte concentration was held constant, but NaCl ions were replaced with $CaCl_2$, showing that the ionic composition did not affect the dissolution in water of NAPL compounds. The solubility of naphthalene in some electrolyte mixtures was determined by Gordon and Thorne (1967a, b) using the simple mixing rule

$$\log(S^0/S) = kM_T = \sum\nolimits_i N_i k_i M_{T,} \tag{6.9}$$

where M_T is the total molar concentration of the salts and N_i is the mole fraction of salt i $(M_T = \sum_i M_i.)$; S^0 and S are solubilities of the organic compound measured in water and in salt solution, respectively; and k is the salting-out constant. This calculated solubility was validated experimentally for seawater. Millero (2000) used the Pitzer parameters for ions, which are related to the interaction of an ion with a nonelectrolyte, to estimate the activity coefficients and the solubility of nonelectrolytes in a water solution containing an electrolyte mixture.

A *salting-in* effect is promoted when there is a simultaneous presence of large organic molecules (e.g., tetramethyl-ammonium) and electrolytes in a water solution. In contrast to the salting-out process, salting in leads to an increase in organic compound solubility or a decrease in activity coefficient (Table 6.3). Almeida et al. (1983) observed a similar salting-in effect for very polar compounds, which may interact strongly with certain ions.

Despite the possibility of a salting-in route in some particular cases, the salting-out effect—and the decrease in organic compound solubility—in a saline environment is the main process controlling organic contaminant solubility in subsurface water solutions. Whitehouse (1984) studied the effect of salinity (from 0 to 36.7 %) on the aqueous solubility of polycyclic aromatic hydrocarbons (PAHs) and found that phenanthrene, anthracene, 2-methylanthracene, 2-ethylantracene, and benzo(a)pyrene experienced salting out, while only 1,2-benzanthracene exhibits a salting-in effect. Where salting out was observed, fairly large changes in salinity were required to cause significant changes in the solubility; such was not the case for the compound exhibiting a salting-in effect.

A simple correlation was determined for estimating the Setschenow constants for a variety of organic solutes in seawater, which yields an overall reduction in solubility by a factor 1.36 (Xie et al. 1997). The hydrophobicity of organic solutes increases by this factor, but the salting-out effect must be quantified when comparing the behavior of specific organic contaminants in freshwater and in subsurface aqueous solutions.

Under certain environmental conditions, when subsurface water contains potential organic ligands, trace metals also may be subject to salting out following their organic complexation. Turner et al. (2002) demonstrated that sediment–water partitioning of Hg(II) in estuaries characterized by high salinity may be controlled by a salting-out process. This partitioning applies to the aqueous solubility of nonelectrolytes and suggests that the organic complexes of mercury are removed from the aqueous phase via a coupled sorption–salting-out mechanism. Evidence of salting out of other metal complexes (Cd, Cr, Cu, Ni, Pb, Zn) also was reported (Turner et al. 2002). In highly contaminated, organic-rich estuaries, an increase in the sediment–water distribution of metal complexes was observed as salinity increased, except for Cd. Such behavior contradicts conventional speciation and partitioning processes and may be explained only by a salting-out effect. Turner et al. (2002) propose a mechanism by which trace metals are complexed and

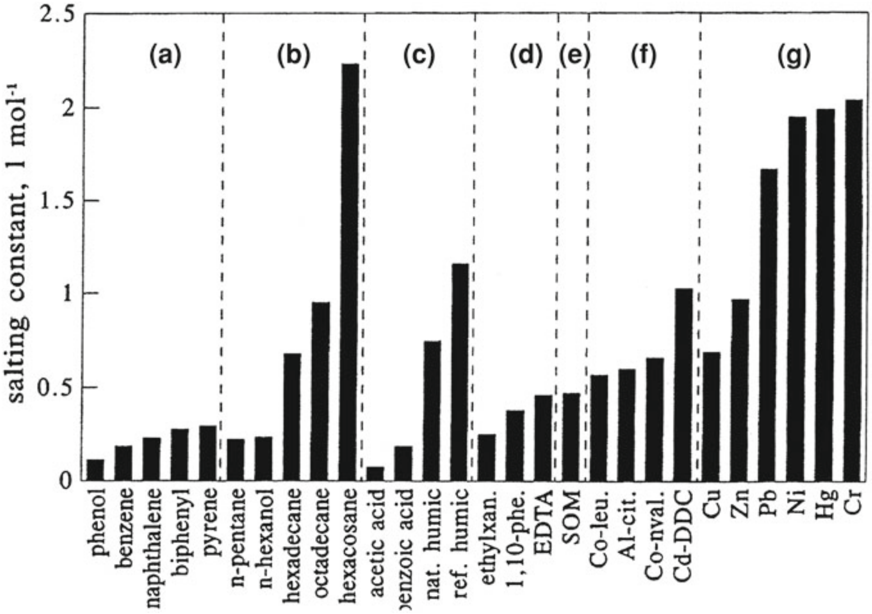


Fig. 6.4 Calculated, estimated, or apparent salting-out constants for various chemicals: **a** selected aromatic compounds, **b** selected aliphatic compounds, **c** natural or surrogate ligands, **d** anthropogenic ligands, **e** sediment organic matter (SOM), **f** transition metal complexes, **g** trace metal complexes in the Mersey Estuary. Reprinted with permission from Turner A, Martino M, Le Roux SM (2002) Trace metal distribution coefficients in the Mersey Estuary UK: Evidence for salting out of metal complexes. Environ Sci Technol 36:4578–4584. Copyright 2002 American Chemical Society

subsequently neutralize organic ligands, with the resulting neutral assemblage possibly being salted out via electrostriction. This behavior has significant implications for reactivity, availability, and transport of organic contaminants in saline water bodies rich in potential organic ligands. Calculated, estimated, or apparent salting constants for various chemicals are presented in Fig. 6.4.

6.6 Apparent Solubility

Changes in the pH of subsurface aqueous solutions may lead to an apparent increase or decrease in the solubility of organic contaminants. The pH effect depends on the structure of the contaminant. If the contaminant is sensitive to acid–base reactions, then pH is the governing factor in defining the aqueous solubility. The ionized form of a contaminant has a much higher solubility than the neutral form. However, the apparent solubility comprises both the ionized and the neutral forms, even though the intrinsic solubility of the neutral form is not affected.

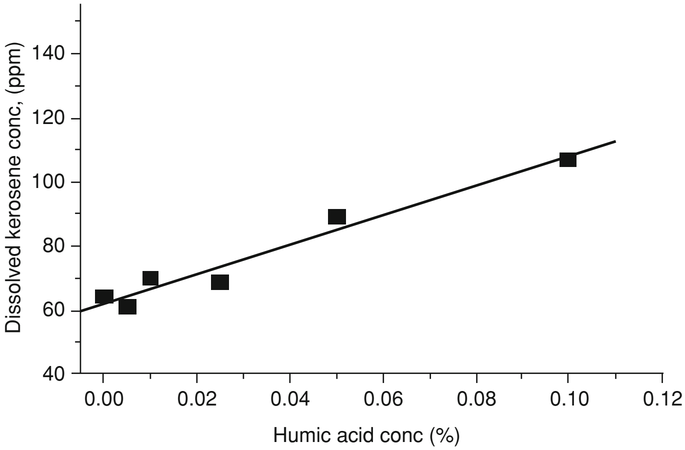


Fig. 6.5 Effect of humic substances in an aqueous solution on the dissolution of kerosene (Dror et al. 2000a)

The solubility of nonaqueous phase liquids in distilled water may be regarded as an unambiguous physical constant, whereas the apparent enhanced solubility might be due to the presence of naturally occurring organic macromolecules in subsurface solutions. Such macromolecules, including humic and fulvic substances, and negatively charged polysaccharides may increase the dissolution of organic contaminants in the subsurface aqueous solution. All the organic molecules that are constituents in subsurface organic matter and may be dissolved in the subsurface water are referred to as dissolved organic matter (DOM). Solubility in water in the presence of DOM is given by the relation

$$C_{\mathrm{sat,DOM}} = C_{\mathrm{sat}}(1 + [\mathrm{DOM}]K_{\mathrm{DOM}}), \tag{6.10}$$

where $C_{\mathrm{sat,DOM}}$ and C_{sat} are the saturated concentrations of the organic compound measured in the presence and absence of DOM, respectively; [DOM] denotes concentration of DOM in water (kg/L); and K_{DOM} is the DOM–water partition coefficient. Note that the intrinsic solubility of the compound is not affected.

As mentioned previously, the physical state of a solute is susceptible to modifications by interaction with cosolvents. In principle, a cosolvent can enhance solute solubility by changing the solvency of the medium, by direct solute interaction, by adsorption, or by partitioning (Chiou et al. 1986). In a batch experiment testing the effect of humic acid on kerosene dissolution in an aqueous solution, Dror et al. (2000a) found a linear correlation between the amount of humic acid and the amount of kerosene that dissolved (Fig. 6.5).

The enhancement of kerosene dissolution occurs even at low humic acid content in the aqueous solution. In view of the fact that humic substances are relatively high molecular weight species containing nonpolar organic moieties, Chiou et al. (1986) assumed that a partition-like interaction between a solute of very low solubility in aqueous solution and a “microscopic organic environment” of dissolved humic molecules can explain solute solubility enhancement.

When a NAPL reaches the subsurface, it may be subject to mechanical forces that lead to the formation of a mixed NAPL–water micro-/nano-emulsion characterized by the presence of micro- and nano-droplets of organic compounds. These micro- and nano-emulsions are transparent or translucent systems, kinetically (nano-) or thermodynamically (micro-) stable, and display an apparent increase in aqueous solubility as compared to the intrinsic solubility of the NAPL itself (Tadros 2004). The very small droplet size (50–200 nm in the case of a nano-emulsion) causes a large reduction in the force of gravity, enabling the system to remain dispersed and preventing a coalescence process. In a laboratory experiment mimicking the contamination of a coastal freshwater aquifer by hydrocarbon-polluted seawater, Dror et al. (2003) report hydrocarbon concentrations in the source saltwater that are higher than the intrinsic solubilities of the contaminants, due to the formation of droplets. Contaminant concentrations in the adjacent freshwater also were higher than the intrinsic aqueous solubilities. The experiments also demonstrated the stability of hydrocarbon–water emulsions as they are transported through a porous sand layer.

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