Chapter 10

ORGANIC LIQUID–AIR AND ORGANIC LIQUID–WATER PARTITIONING

Box 10.1 Estimating the Concentrations of Individual PCB Congeners
in Water in Equilibrium with an Aroclor Mixture

10.6 Questions and Problems

10.7 Bibliography

10.1   Introduction

We now extend our discussions of equilibrium bulk phase partitioning in Chapters 7 to 9 to include partitioning of organic compounds between different organic liquids and air or water. In Chapters 8 and 9, we have already introduced a special case of an organic liquid, that is, the pure liquid compound itself, which we also use as reference state in our thermodynamic treatment of partitioning equilibrium (see Section 4.2). In Section 10.2, we start out by considering some thermodynamic aspects of the partitioning of an organic compound between an organic solvent and air or an organic solvent and water. As a follow-up of our discussions in Chapter 7, we will compare some solvents that exhibit different solvent characteristics. Some emphasis will be given to 1-octanol (referred to as octanol), the most widely used solvent applied in sp-LFERs for predicting partitioning of organic chemicals in natural systems (see Section 7.3). Section 10.3 will then be devoted to a more detailed treatment of the octanol–water system, particularly to the estimation of octanol–water partition constants ($K_{i\text{ow}}$) using the fragment contribution approach. However, the main purpose of this section is not to provide another estimation method for the octanol–water partition constant. Instead, we want to visualize how structural subunits (atoms or fragments) affect the partitioning of an organic compound between water and an organic solvent, using octanol as model solvent. This visualization, which is complementary to our discussions on pp-LFERs that are based on characteristics of the entire compound, should provide the reader with important additional insights into how structural moieties determine the extent of partitioning of organic compounds.

In the last two sections of this chapter, we discuss two special cases of partitioning involving mixed phases. In Section 10.4, we discuss the effect of water-miscible cosolvents on aqueous activity coefficients, and, thus, on aqueous solubility and partitioning of compounds to a mixed organic solvent–water phase. Section 10.5 focuses on the dissolution of organic compounds into water from organic liquid mixtures, such as gasoline, diesel fuel, heating oil, chlorinated solvent mixtures, or PCBs. Here, we consider the case in which the organic chemical of interest is not present in dilute concentration in the organic liquid but forms a significant part of it.

## 10.2   Thermodynamic Considerations and Comparisons of Different Organic Solvents

Thermodynamic Considerations

In analogy to air–water partitioning (Eqs. 9-14 and 9-15), we can express the solvent (ℓ)–air partition constant, $K_{i\ell\text{a}}$, of a compound as:

$$K_{i\ell\text{a}} = \frac{C_{i\ell}}{C_{i\text{a}}} = \frac{1}{(p_{i\text{L}}^*/RT)\gamma_{i\ell}\bar{V}_\ell} \tag{10-1}$$

where $p_{i\text{L}}^*$ is the liquid vapor pressure of the compound, $\gamma_{i\ell}$ is its activity coefficient in the solvent, and $\bar{V}_\ell$ is the molar volume of the solvent. When one substitutes the subscript ℓ by w, Eq. 10-1 expresses the water–air constant, $K_{i\text{wa}}$, the reciprocal of

Figure 10.1 Plot of the logarithms of the octanol–water partition constants (log $K_{i\text{ow}}$) versus the aqueous activity coefficients (log γ_{iw}) for a variety of apolar, monopolar, and bipolar compounds. The diagonal lines indicate where the activity coefficients in octanol (γ_{io}) (calculated from Eq. 10-2) equal 0.1, 1, 10, or 100.
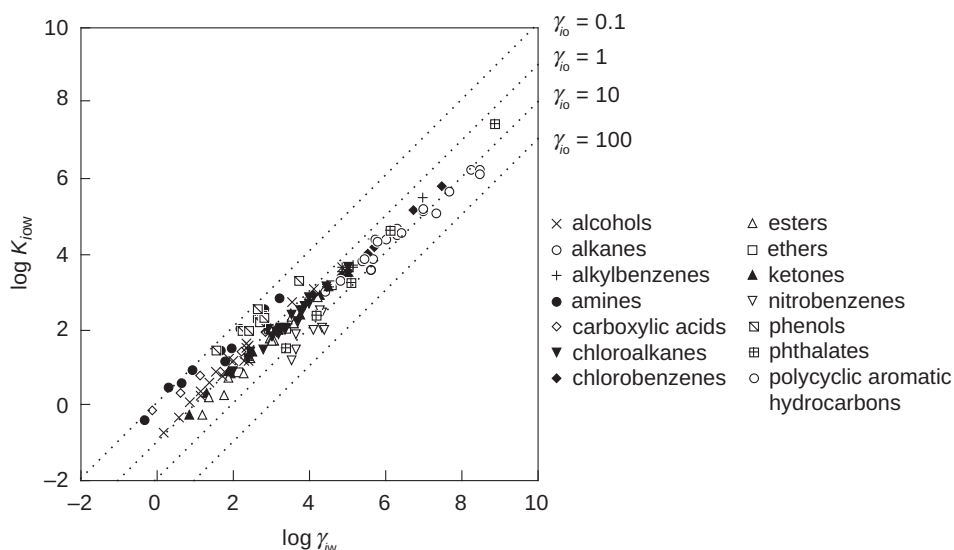
air–water constant in Eq. 9-15. Dividing $K_{i\ell\text{a}}$ by K_{iwa} then yields the solvent–water partition constant, $K_{i\ell\text{w}}$:

$$K_{i\ell\text{w}} = \frac{C_{i\ell}}{C_{iw}} = \frac{\gamma_{iw}\bar{V}_\text{w}}{\gamma_{i\ell}\bar{V}_\ell} \qquad (10\text{-}2)$$

The dominant factor determining the magnitude of any organic solvent–water partition constant is, for most compounds, the large aqueous activity coefficient, γ_{iw}. As an example, Fig. 10.1 illustrates the partition constant, log $K_{i\text{ow}}$ (Eq. 10-2, ℓ = o), for a large number of diverse organic compounds in the octanol–water system. Activity coefficients in octanol, γ_{io}, lie only between 0.1 (bipolar small molecules) and about 50 (large apolar and weakly polar compounds), whereas γ_{iw} values span a range of ten orders of magnitude (see also Table 9.1). Therefore, the tendency of the compound to leave the aqueous phase (its "hydrophobicity") primarily drives partitioning into an organic bulk phase.

When using the thermodynamic cycle to calculate a partition constant from two others, such as Eq. 10-2, one should distinguish, in principle, whether one considers the organic solvent "dry" (no water dissolved in the solvent) or "wet" (saturated with water). Hence, when using experimental solvent–air partition constants determined for dry solvents, we would get hypothetical dry solvent–water partition coefficients. Conversely, when using experimental solvent–water partition constants, we would derive water-saturated organic solvent–air partition constants.

Table 10.1 shows that, at water saturation, apolar or weakly polar organic solvents contain very small amounts of water. Therefore, the distinction between dry and wet

Table 10.1 Mole Fraction of Some Common Organic Solvents Saturated with Water[a]

| Organic Solvent "ℓ"	x_ℓ	Organic Solvent "ℓ"	x_ℓ
n-Pentane	0.9995	Chlorobenzene	0.9981
n-Hexane	0.9995	Nitrobenzene	0.9860
n-Heptane	0.9993	Aminobenzene	0.9787
n-Octane	0.9994		
n-Decane	0.9994	Diethylether	0.9501
n-Hexadecane	0.9994	Methoxybenzene	0.9924
		Ethyl acetate	0.8620
Trichloromethane	0.9948	Butyl acetate	0.9000
Tetrachloromethane	0.9993	2-Butanone	0.6580
Trichloroethene	0.9977	2-Pentanone	0.8600
Tetrachloroethene	0.9993	2-Hexanone	0.8930
Benzene	0.9975	1-Butanol	0.4980
Toluene	0.9976	1-Pentanol	0.6580
1,3-Dimethylbenzene	0.9978	1-Hexanol	0.7100
1,3,5-Trimethylbenzene	0.9978	1-Octanol	0.8060
n-Propylbenzene	0.9958		

[a]Data from Demond and Lindner (1993).

is generally not important. In contrast, some smaller, polar solvents contain significant amounts of water. In these cases, $\gamma_{i\ell,\mathrm{dry}}$ may be significantly different from $\gamma_{i\ell,\mathrm{wet}}$. Moreover, the molar volume of the solvent may be somewhat different, leading to differences in the corresponding partition constants (Abraham and Acree, 2008; Abraham et al., 2009). For example, in the case of octanol, at equilibrium, there will be roughly one water molecule per four octanol molecules in the organic phase ($x_\ell \cong 0.8$, Table 10.1). The molar volume of "dry" octanol ($\bar{V}_\ell = 0.16$ L mol^{-1}) is, therefore, about 20% larger than that of "wet" octanol ($\bar{V}_\ell \cong 0.13$ L mol^{-1}, see Section 10.3 for calculation of molar volumes of organic solvent–water mixtures). Conversely, only about one octanol molecule will be present per 10,000 water molecules in octanol–saturated water. Neither the aqueous activity coefficient of the compound nor the molar volume of the aqueous phase is, therefore, significantly impacted by such a small amount of octanol in the water.

LFERs for Evaluation and Prediction of Organic Solvent–Air and Organic Solvent–Water Partition Constants

As for many other two-phase systems, pp-LFERs have been developed for estimating solvent–air and solvent–water partition constants. Table 10.2 lists pp-LFERs for a few common organic liquids; additional pp-LFERs for other liquids are compiled in the UFZ-LSER database (Endo et al., 2014). With the exception of octanol, one equation is valid for both the wet and dry solvent, since these organic liquids contain only a small fraction of water at saturation (e.g., chloroform and olive oil: $x_\ell > 0.99$; diethylether: $x_\ell = 0.95$).

Table 10.2 pp-LFERs for Some Organic Solvent–Air ($\log K_{i\ell a} = v_{\ell a}V_i + l_{\ell a}L_i + s_{\ell a}S_i + a_{\ell a}A_i + b_{\ell a}B_i + c$) and Organic Solvent–Water ($\log K_{i\ell w} = v_{\ell w}V_i + l_{\ell w}L_i + s_{\ell w}S_i + a_{\ell w}A_i + b_{\ell w}B_i + c$) Systems at 25°C[a,b]

Solvent–air system solvents	Equation	$v_{\ell a}$	$l_{\ell a}$	$s_{\ell a}$	$a_{\ell a}$	$b_{\ell a}$	c
Diethylether (wet/dry)	10-3	+0.87	+0.74	+0.93	+3.21	0.00	+0.03
Chloroform (wet/dry)	10-4	+0.89	+0.69	+1.33	+0.28	+1.42	−0.01
Octanol (wet)	10-5	−0.04	+0.91	+0.66	+3.49	+1.42	−0.25
Octanol (dry)	10-6	+0.07	+0.90	+0.47	+3.52	+0.82	−0.14
Olive oil (wet/dry)	10-7	+0.35	+0.80	+1.01	+1.76	+0.01	−0.38
Water ($\ell = w$)	9-18	−2.55	+0.48	+2.07	+3.67	+4.87	−0.59

Solvent–water system solvents		$v_{\ell w}$	$l_{\ell w}$	$s_{\ell w}$	$a_{\ell w}$	$b_{\ell w}$	c
Diethylether (wet/dry)	10-8	+3.42	+0.26	−1.14	−0.46	−4.87	+0.62
Chloroform (wet/dry)	10-9	+3.44	+0.21	−0.70	−3.39	−3.38	+0.58
Octanol (wet)	10-10	+2.41	+0.43	−1.41	−0.18	−3.45	+0.34
Olive oil (wet/dry)	10-11	+2.90	+0.32	−1.06	−1.91	−4.87	+0.21

[a]Data from Goss (2005) and UFZ-LSER Database (Endo et al. 2014).
[b]ppLFER expressions contain solute descriptors for the size of the compound (V_i), the $\log K_{i\text{hexadecane–air}}$ (L_i), the H-donor property (A_i), the H-acceptor property (B_i), and a "dipolarity/polarizability" parameter (S_i), plus the complementary fitted system descriptors characterizing the bulk liquid phases involved (lower case letters).

$$
\begin{array}{l}
\text{—O—COR}_1 \\
\text{—O—COR}_2 \\
\text{—O—COR}_3
\end{array}
$$
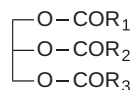
General structure of olive oil, R$_1$, R$_2$, R$_3$ = C$_{14}$, C$_{16}$, C$_{18}$ saturated or unsaturated chains (for details see Hui, 1996).

First, let us directly compare the different solvent characteristics by inspecting the pp-LFERs for solvent–air partitioning. For example, the monopolar solvents diethylether (H-acceptor) and chloroform (H-donor), which exhibit very similar molar volumes and vdW properties, only significantly differ, as expected, in their $a_{\ell a}$ and $b_{\ell a}$ system descriptors (Eqs. 10-3 and 10-4). The solvent–air partition constants of apolar compounds in the two monopolar solvents or any apolar solvent are thus very similar. In contrast to monopolar solvents, the bipolar solvent octanol differs significantly in the $v_{\ell a}$ system descriptor, which encompasses the larger free energy contribution of cavity formation, and in the $a_{\ell a}$ or $b_{\ell a}$ descriptors (Eqs. 10-5 and 10-6). We can also see that the water present in wet octanol has an influence primarily on the $b_{\ell a}$ descriptor, making wet octanol a somewhat better H-donor. However, as is evident from Fig. 10.2, for the majority of our test set of apolar, monopolar, and bipolar compounds (introduced in Chapter 7, in the following referred to as "test set"), the differences between the wet octanol–air and the dry octanol–air partition constants are within a factor of two. Therefore, if no experimental dry octanol–air partition constants are available, the estimated wet octanol–air partition constants are very reasonable surrogates. Finally, comparison of the two monopolar H-accepting solvents diethylether (Eq. 10-3) and olive oil (Eq. 10-7, structure in margin) shows that olive oil has a significantly smaller $a_{\ell a}$ descriptor, which is due to its 2.5 times smaller carbon to oxygen ratio.

As already pointed out in Chapter 7 (Section 7.3), a common approach used to predict partition coefficients between natural organic matter or biological media and air or water is based on sp-LFERs using octanol as reference solvent:

$$\log K_{i\ell a} = a \log K_{ioa} + b \tag{10-12}$$

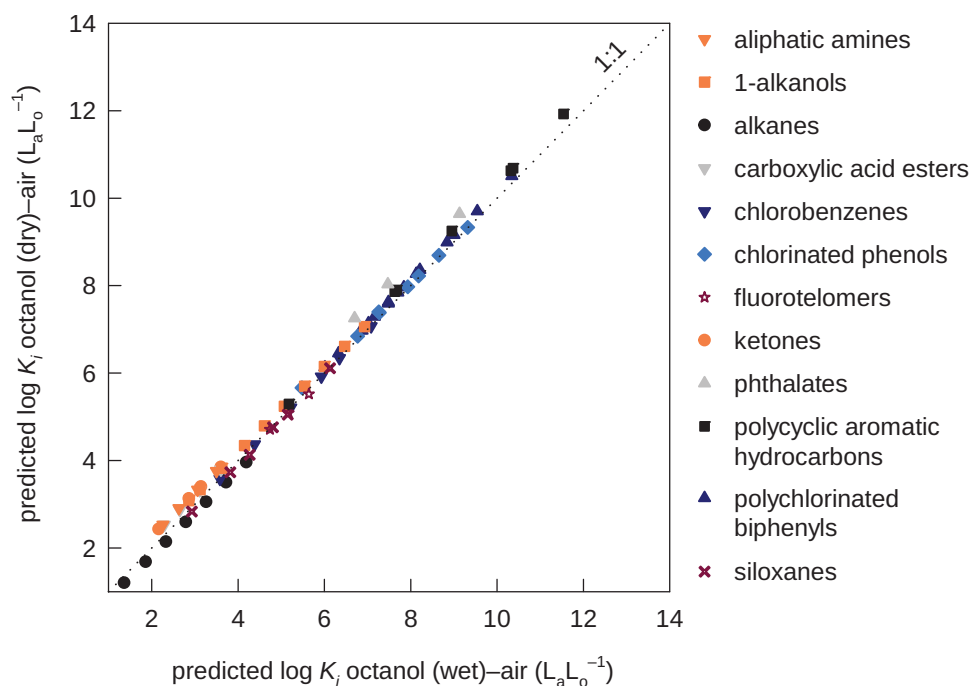$$\log K_{i\ell w} = c \log K_{iow} + d \tag{10-13}$$

Figure 10.2 Dry versus wet octanol–air partition constants for our test set. The values have been calculated using Eqs.10-6 and 10.5, respectively.

The underlying idea is that octanol offers solutes a similar set of intermolecular interactions as they would experience in organic matter or biological media. Therefore, one might expect the free energies of partitioning into like media (e.g., octanol and biological media) from air or water to correlate with one another. Using olive oil as an example of a biological material, the calculated logarithms of the olive oil–air (Eq. 10-7) and olive oil–water (Eq. 10-11) partition constants of our test set are plotted against the corresponding calculated logarithms of the octanol–air (Eq. 10-6) and octanol–water (Eq. 10-10) partition constants, respectively, in Figs. 10.3*a* and *b*. Similar to our findings in Chapter 7 when plotting the logarithms of hexadecane–air versus octanol–air as well as the hexadecane–water versus octanol–water partition constants (Fig. 7.3), no single sp-LFER of the type in Eqs. 10-12 and 10-13 is capable of fitting the entire data set. Good linear relationships can, however, be found for subsets of compounds, in particular for structurally related compounds, such as homologous series of alkanes, aliphatic ketones, esters, amines, alcohols, siloxanes, and fluorotelomers. Hence, we point out again that an sp-LFER of the type Eqs. 10-12 and 10-13 using octanol (or any other organic liquid) as a reference solvent needs to be applied with caution, especially if the training set of solutes exhibits different intermolecular interactions than the compounds of interest. However, when used properly, they can be quite useful, as we see in Chapters 13 and 16.

Effect of Temperature on the Organic Solvent–Air and Organic Solvent–Water Partition Constants

As discussed in Chapter 4 (Eq. 4-33), for a narrow temperature range (e.g., the ambient temperature range, –20 to 40°C), the temperature dependence of the organic
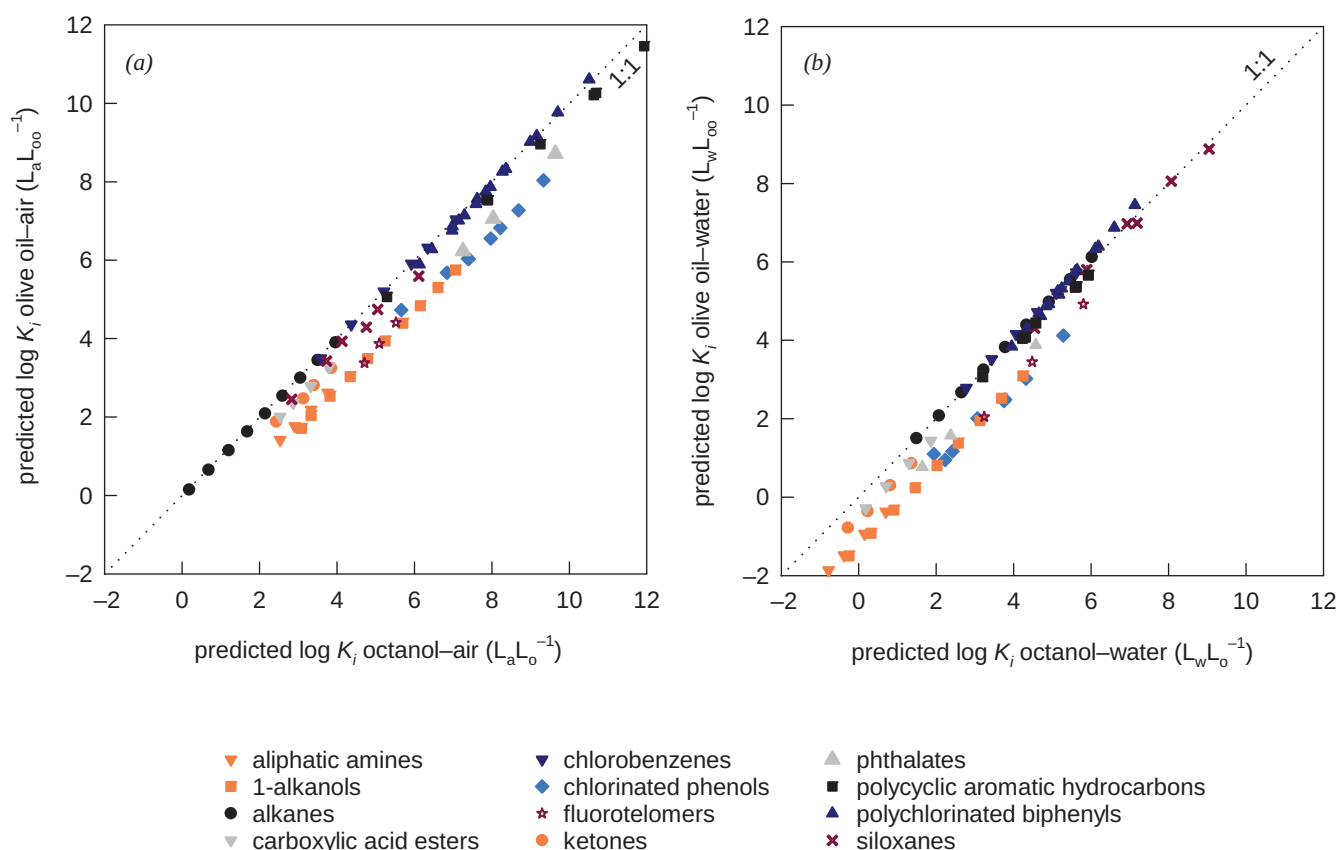
aliphatic amines   ▼ **chlorobenzenes**   ▲ **phthalates**
1-alkanols   ◆ **chlorinated phenols**   ■ **polycyclic aromatic hydrocarbons**
● **alkanes**   ✶ **fluorotelomers**   ▲ **polychlorinated biphenyls**
▼ **carboxylic acid esters**   ● **ketones**   ✕ **siloxanes**

Figure 10.3 Calculated (a) olive oil–air (Eq. 10-7) versus octanol–air (Eq. 10-6) and (b) olive oil–water (Eq. 10-11) versus octanol–water (Eq. 10-10) partition constants for our test set.

solvent–air (Eq. 10-14) and organic solvent–water (Eq. 10-15) partition constants is given by the familiar *van't Hoff* relationships:

$$\ln K_{i\ell a} = -\frac{\Delta_{\ell a} H_i}{R} \cdot \frac{1}{T} + \text{constant} \tag{10-14}$$

$$\ln K_{i\ell w} = -\frac{\Delta_{\ell w} H_i}{R} \cdot \frac{1}{T} + \text{constant} \tag{10-15}$$

We also recall from Chapter 4 that, if one of the phases considered is the gas phase and the partition constant is expressed in molar concentrations, due to the temperature dependence of the molar volume of gases, $\Delta_{\ell a} H_i$ has to be replaced by $\Delta_{\ell a} H_i + RT_{av}$ where T_{av} is the average temperature (in K) of the temperature range considered (Atkinson and Curthoys, 1978). However, because RT_{av} is equal to only about 2.5 kJ mol^{-1}, we neglect this term, just like we did when discussing air–water partitioning (Eq. 9-25). Finally, using the thermodynamic cycle, we can relate the enthalpies in Eqs. 10-14 and 10-15 with the enthalpy of water–air exchange, $\Delta_{wa} H_i$ (see Table 9.2 for some examples; note that the table gives $\Delta_{aw} H_i = -\Delta_{wa} H_i$ values) by:

$$\Delta_{\ell w} H_i = \Delta_{\ell a} H_i - \Delta_{wa} H_i \tag{10-16}$$

For ℓ = octanol and ℓ = hexadecane, Table 10.3 summarizes the $\Delta_{\ell a} H_i$ and $\Delta_{\ell w} H_i$ values of some apolar, monopolar, and bipolar compounds, together with their enthalpies

Table 10.3 Examples of Experimental or Calculated Enthalpies of Condensation, Water–Air Partitioning, Octanol–Air and Octanol–Water Partitioning, and Hexadecane–Air and Hexadecane–Water Partitioning

	Solvent system					
Solute Compound	pure liquid–air[a] $\Delta_{cond}H_i$ (kJ mol^{-1})	water–air[a] $\Delta_{wa}H_i$ (kJ mol^{-1})	octanol–air[b] $\Delta_{oa}H_i$ (kJ mol^{-1})	hexadecane–air[c] $\Delta_{ha}H_i$ (kJ mol^{-1})	octanol–water[b] $\Delta_{ow}H_i$ (kJ mol^{-1})	hexadecane–water[d] $\Delta_{hw}H_i$ (kJ mol^{-1})
n-Hexane	−32	−32	−30	−32	2	1
MTBE	−30	−49	−28	−28	16	21
PCE	−40	−42	−38	−38	4	4
Benzene	−34	−32	−31	−31	1	1
Phenol	−58	−58	−65	−40	−7	18
1-Hexanol	−62	−67	−61	−40	6	27
Phenanthrene	−69	−54	−75	−77	−21	−23
Pyrene	−74	−59	−76	−85	−17	−26
Lindane (γ-HCH)	−70	−54	−74	−74	−20	−20
PCB 153	−90	−70	−88	−96	−18	−26
D5	−60	−80	−58	−69	22	11

[a]Data from Table 9.2. [b]Data from Beyer et al. (2002) and Mintz et al. (2007) or calculated using Eq. 10-17. [c]Calculated using pp-LFER for $\Delta_{ha}H_i$ published by Mintz et al. (2008). [d]Calculated using Eq. 10-16.

of condensation (negative enthalpies of vaporization) and of air–water partitioning at 25°C. For octanol–air partitioning, some of the $\Delta_{oa}H_i$ values have been calculated using the pp-LFER published by Mintz et al. (2008):

$$\Delta_{oa}H_i(\text{kJ mol}^{-1}) = +1.6V_i - 9.7L_i + 6.0S_i - 53.7A_i - 9.2B_i - 6.7$$
$$\text{(number of chemicals} = 138; r^2 = 0.99; \text{S.D.} = 2.6) \quad (10\text{-}17)$$

From Table 10.3, we can draw some general conclusions. First, for all compounds, the enthalpy of octanol–air partitioning is quite similar to the enthalpy of condensation. The same holds for partitioning between the apolar solvent hexadecane and air, with the exception that bipolar compounds exhibit somewhat smaller enthalpies because they cannot undergo H-bonding in the apolar solvent. Therefore, $K_{i\ell a}$ is very sensitive to temperature (recall from Chapter 4 (Table 4.3) that a $\Delta_a H_i$ value of 50 kJ mol^{-1} means a factor of two change in $K_{i\ell a}$ per 10 degree change in temperature and a factor of 4 if $\Delta_{\ell a} H_i$ is 100 kJ mol^{-1}). We also highlight that, because all these enthalpies are negative, an increase in temperature favors the gas phase; that is, $K_{i\ell a}$ decreases with increasing temperature.

In contrast to solvent–air partitioning, partitioning between organic solvents and water is significantly less temperature dependent. That is, the corresponding enthalpies are much smaller (Table 10.3), which is not surprising since the enthalpy of partitioning is given by the difference of the excess enthalpies of the compound in the organic solvent and water, $\Delta_{\ell w}H_i = H_{i\ell}^E - H_{iw}^E$. Typically, $H_{i\ell}^E$ for organic compounds in organic solvents is small and does not exceed ± 10 kJ mol^{-1}; the excess enthalpy of a compound

in a solvent is given by $H_{i\ell}^{\text{E}} = \Delta_{\ell a}H_i - \Delta_{\text{cond}}H_i$, and the liquid–air term is commonly close to the condensation term. Also, the excess enthalpies in water are fairly small (Table 9.2), leading to H_{iw}^{E} values that are not much larger than $\pm$ 20 to 30 kJ mol^{-1}, meaning less than a factor of 1.5 change in $K_{i\ell w}$ per 10 degree change in temperature. Finally, if needed, to estimate the enthalpy for octanol–water partitioning, we may derive a pp-LFER combining Eq. 10-17 and the pp-LFER reported for air–water partitioning (Chapter 9, Eq. 9-27) using the thermodynamic cycle (Eq. 10-16):

$$\Delta_{\text{ow}}H_i(\text{kJ mol}^{-1}) = +18.9V_i - 8.3L_i + 5.3S_i - 20.1A_i + 34.3B_i + 1.7 \quad \text{(10-18)}$$

10.3 The Octanol–Water System: The Atom/Fragment Contribution Method for Estimation of the Octanol–Water Partition Constant

The classical fragment or group contribution method for estimating log $K_{i\text{ow}}$ was originally introduced by Rekker and co-workers (Rekker, 1977) and Hansch and Leo (Hansch and Leo, 1979; Hansch and Leo, 1995; Hansch et al., 1995). A computerized version of this method (known as the CLOGP program; note that P is often used to denote $K_{i\text{ow}}$) was initially established by Chou and Jurs, (1979) and later modified and extended by Hansch and Leo (1995). The method estimates log $K_{i\text{ow}}$ by using single atom "fundamental" fragments consisting of isolated types of carbons, hydrogen, and various heteroatoms, plus some multiple atom "fundamental" fragments (e.g., –OH, –COOH, –NH$_2$, –CN, –NO$_2$). These fundamental fragments were derived from a limited number of rather simple compounds assuming that one can cut up molecules into parts that interact somewhat independently with the surrounding media. The values of each fragment are summed together to estimate a log $K_{i\text{ow}}$. Since the extent of these interactions are not independent in more complex molecules due to stereochemical factors or inductive effects, the method also uses a large number of correction factors for unsaturation and conjugation, branching, multiple halogenation, proximity of polar groups, and more (Hansch et al., 1995).

Meylan and Howard (1995) also developed a simple atom/fragment contribution method derived from multiple linear regressions of experimental log $K_{i\text{ow}}$ values. To estimate the log $K_{i\text{ow}}$ of a given compound at 25°C, one simply adds up the fragment coefficients, f_k, and correction factors, c_j, according to the equation:

$$\log K_{i\text{ow}} = \sum_k n_k \cdot f_k + \sum_k n_j \cdot c_j + 0.23 \quad \text{(10-19)}$$

where n_k and n_j are the frequency of each type of fragment or specific interaction, respectively, occurring in the compound of interest. Tables 10.4 and 10.5 give selected values of fragment coefficients and correction factors; for a more comprehensive collection, see Meylan and Howard (1995). An updated collection is used in the KOWWIN program (v1.66: $n(f_k) = 186$, $n(c_j) = 322$) in EPI Suite (Estimation Programs Interface Suite; U.S. EPA, (2012).

Table 10.4 Selected Atom/Fragment Coefficients, f_k, for log K_{iow} Estimation at 25°C (Eqs. 10-19 and 10-20)[a]

Atom/Fragment[b]	f_k	Atom/Fragment[b]	f_k
Carbon		*Carbonyls*	
−CH$_3$	0.55	al–CHO	−0.94
−CH$_2$−	0.49	ar–CHO	−0.28
−CH<	0.36	al–CO–al	−1.56
>C<	0.27	ol–CO–al	−1.27
=CH$_2$	0.52	ar–CO–al	−0.87
=CH– or =C<	0.38	ar–CO–a—r	−0.20
C$_{ar}$	0.29	al–COO– (ester)	−0.95
		ar–COO– (ester)	−0.71
Halogens		al–CON< (amide)	−0.52
al–F	0.00	ar–CON< (amide)	0.16
ar–F	0.20	>N–COO– (carbamate)	0.13
al–Cl	0.31	>N–CO–N< (urea)	1.05
ol–Cl	0.49	al–COOH	−0.69
ar–Cl	0.64	ar–COOH	−0.12
al–Br	0.40		
ar–Br	0.89	*Nitrogen Containing Groups*	
al–I	0.81	al–NH$_2$	−1.41
ar–I	1.17	al–NH–	−1.50
		al–N<	−1.83
Aliphatic Oxygen		ar–NH$_2$, ar–NH–, ar–N<	−0.92
al–O–al	−1.26	al–NO$_2$	−0.81
al–O–ar	−0.47	ar–NO$_2$	−0.18
ar–O–ar	0.29	ar–N=N–ar	0.35
al–OH	−1.41	al–C≡N	−0.92
ol–OH	−0.89	ar–C≡N	−0.45
ar–OH	−0.48		
al–O–(P)	−0.02	*Sulfur Containing Groups*	
ar–O–(P)	0.53	al–S–al	−0.40
		ar–S–al	0.05
Heteroatoms in Aromatic Systems		al–SO–al	−2.55
		ar–SO–al	−2.11
Oxygen	−0.04	al–SO$_2$–al	−2.43
Nitrogen in five-member ring	−0.53	ar–SO$_2$–al	−1.98
Nitrogen in six-member ring	−0.73	al–SO$_2$N<	−0.44
Nitrogen in fused ring	0.00	ar–SO$_2$N<	−0.21
Sulfur	0.41	ar–SO$_3$H	−3.16
Phosphorus		*Silicon Containing Groups*	
→P=O	−2.42	al–Si–al	0.30
→P=S	−0.66	ar–Si– or O–Si–	0.68

[a]Data from Meylan and Howard (1995); total $n(f_k)$ = 130.
[b]al: aliphatic attachment, ol: olefinic attachment; ar: aromatic attachment.

Table 10.5 Examples of Correction Factors, c_j, for log K_{iow} Estimation at 25°C (Eqs. 10-19 and 10-20)[a]

Functional Group[b]	c_j	Functional Group[b]	c_j
Factors Involving Aromatic Ring Substituent Positions			
o–OH/–COOH	1.19	o–N</two ar N	1.28
o–OH/o–COO–(ester)	1.26	o–CH$_3$/–CON<(amide)	−0.74
o–N/–CON<(amide)	0.62	$2 \times o$–CH$_3$/–CON<(amide)	−1.13
o–OR/ar N	0.45	p–N/–OH	−0.35
o–OR/two ar N	0.90	o,m,p–NO$_2$/–OH or –N<	0.58
o–N</ar N	0.64	p–OH/–COO–(ester)	0.65
Miscellaneous Factors			
More than 1 aliphatic –COOH	−0.59	Symmetric triazine ring	0.89
More than 1 aliphatic –OH	0.41	Fused aliphatic ring connection	−0.34
–Amino acid	−2.02		

[a]Data from Meylan and Howard (1995); total $n(c_j) = 235$.
[b]o = *ortho*, m = *meta*, p = *para* substitution. ar: aromatic attachment.

The magnitudes of the individual atom/fragment coefficients give us a feeling for the contribution of each type of substructural unit (e.g., a functional group) to the overall log K_{iow} of a compound. We can assume the contribution of a given subunit is primarily due to its effect on the aqueous activity coefficient of the compound, γ_{iw}, and to a lesser extent on γ_{io} (Eq. 10-2 with ℓ = o; see Fig. 10.1). Let us now inspect a few atom/fragment coefficients (Table 10.4) and try to visualize how these structural subunits are reflected in the pp-LFER discussed earlier in Section 10.1 (Eq. 10-10):

$$\log K_{iow} = 2.41V_i + 0.43L_i - 1.41S_i - 0.18A_i - 3.45B_i + 0.34 \quad \text{(10-10)}$$

First, we note that any aliphatic, olefinic, or aromatic carbon atom has a positive fragment coefficient and, therefore, increases log K_{iow}. This reflects the local incompatibility of such apolar fragments with water as compared to with octanol. For aliphatic carbons, the coefficient decreases with increased branching. This can be rationalized by the smaller contact area of a branched versus non-branched carbon atom (less hydrogens), resulting in reduced "costs" of cavity formation (i.e., smaller V_i). Furthermore, because of the higher polarizability of π-electrons, olefinic and, particularly, aromatic carbon atoms have a smaller fragment coefficient as compared to the corresponding aliphatic carbon. Higher polarizability is also reflected in the higher S_i values of aromatic compounds, which favors the aqueous phase, as compared to saturated hydrocarbons ($S_{i\text{alkanes}} = 0$).

Inspection of the halogen atom fragment coefficients shows that, except for aliphatically bound fluorine, all halogens significantly increase log K_{iow}. This *hydrophobic* effect of the halogens increases, as expected, with the size of the halogens (i.e., increase in V_i and L_i; I > Br > Cl > F). The fragment coefficients are even more pronounced for halogens bound to aromatic carbon as the interactions of the nonbonded electrons of the halogens with the π-electron system (i.e., by resonance, see Chapter 2) causes a decrease in their polarity (i.e., smaller relative contribution to S_i).

Indeed, these characteristics of aromatically bound halogens, particularly of chlorine and bromine, render polychlorinated (e.g, PCBs) or polybrominated (e.g., PBDEs) aromatic compounds highly hydrophobic (see Chapter 3 for more examples).

With respect to the functional groups containing oxygen, nitrogen, sulfur, and phosphorus, in most cases, such polar groups decrease log $K_{i\text{ow}}$, primarily due to hydrogen bonding (reflected in B_i). In general, this *hydrophilic* effect is more pronounced if the polar group is aliphatically bound. Again, interactions of non-bonded or π-electrons of the functional group with the aromatic π-electron system causes a decrease in polarity and explains the diminished hydrophilic effect. As illustrated by comparing the fragment coefficient of ar–O–ar (+0.29) with al–O–al (–1.26), the effect on log $K_{i\text{ow}}$ can be quite significant.

As illustrated by the examples in Table 10.5, application of correction factors is necessary in those cases in which electronic and/or steric interactions of functional groups within a molecule influence the solvation of the compound. A positive correction factor is required if the interaction decreases the overall H-donor and/or H-acceptor capability of the compound. For example, *ortho*-substitutions in aromatic systems leading to *intramolecular* H-bonding (e.g., –COOH/–OH; –COOR/–OH; –OH/–OH) or substitutions in any position that decreases the electron density at a polar group (e.g., –OH or –N< with –NO$_2$) require a positive correction factor. Negative correction factors have to be applied for *ortho*-substitutions in aromatic systems that cause a disturbance of the resonance of a polar group with the aromatic system (the attachment has a more aliphatic character, e.g., –CH$_3$/–CONH$_2$) or for the presence of several polar groups leading to a higher overall polarity of the molecule.

Finally, if the log $K_{i\text{ow}}$ value of a structurally related compound is known, Eq. 10-19 is simplified, and the accuracy of the result is improved using:

$$\log K_{i\text{ow}} = \log K_{i\text{ow}}(\text{related compound}) - \underbrace{\sum_k n_k \cdot f_k}_{\substack{\text{fragments} \\ \text{removed}}} + \underbrace{\sum_k n_k \cdot f_k}_{\text{added}} - \underbrace{\sum_j n_j \cdot c_j}_{\substack{\text{corrections} \\ \text{removed}}} + \underbrace{\sum_j n_j \cdot c_j}_{\text{added}}$$

(10-20)

10.4 Partitioning Involving Organic Solvent–Water Mixtures

So far, we have only considered situations in which an organic compound partitions from water into a *water-immiscible* organic liquid. In this section, we focus on the effect of highly water-soluble organic compounds (i.e., *organic cosolvents*) that *may change the solvation properties* of an "aqueous" phase. We encounter such situations in industrial wastewaters or at waste disposal sites where leachates may contain a high portion of organic solvents. Furthermore, one of the remediation techniques for contaminated soils is to "wash" the soil with mixtures of water and water-miscible cosolvents (e.g., Augustijn et al., 1994; Ghosh et al., 1997). From an analytical point of view, knowledge of how cosolvents influence the activity coefficient of a given organic compound in organic solvent–water mixtures is central for choosing appropriate mobile phases in reversed-phase liquid chromatography.

Finally, in pharmaceutical sciences, knowledge of cosolvent solubilization of poorly water-soluble drugs is needed to incorporate the required dose in the smallest volume of solution as possible (Millard et al., 2002).

We start our discussion with some comments on the experimental data available on the effects of cosolvents on the aqueous solubility and aqueous activity coefficient of organic solutes. First, the majority of the systematic studies on this topic have focused on the effects of *completely water-miscible organic solvents* (CMOSs, e.g., methanol, ethanol, propanol, acetone, dioxane, acetonitrile, dimethylsulfoxide, dimethylformamide, or glycerol) and on the *solubility* of sparingly soluble organic *solids*. A large portion of the available data has been collected for drugs and published in the pharmaceutical literature. With respect to more environmentally relevant compounds, most investigations have been conducted quite some time ago and have been confined primarily to PAHs (Morris et al., 1988; Dickhut et al., 1989; Li et al., 1996; Fan and Jafvert, 1997) and PCBs (Li and Andren, 1994). Few studies have investigated the impact of CMOSs on the solubility (Groves, 1988) or on the activity coefficient in dilute solution (Munz and Roberts, 1986; Jayasinghe et al., 1992) of *liquid* organic compounds. Solubility experiments involving organic liquids are more difficult to interpret because of the partitioning of the organic cosolvents into the liquid organic phase, which may lead to significant changes in its composition (Groves, 1988). In certain cases, the composition of the liquid phase may even affect the crystal structure of a solid compound, thus complicating the interpretation of solubility data (Khossravi and Connors, 1992). Finally, only very limited data are available on the effect of *partially miscible organic solvents* (PMOSs, e.g., *n*-alcohols with $n > 3$), ethers, halogenated C_1– and C_2–compounds, substituted benzenes) on the aqueous solubility or aqueous activity coefficient of organic pollutants in the presence (Pinal et al., 1990 and 1991) or in the absence (Li and Andren, 1994; Coyle et al., 1997) of a CMOS. Thus, our discussion is devoted to water–CMOS systems.

Let us first look at some qualitative aspects of how CMOSs affect the activity coefficient and, thus, the solubility and partitioning behavior of a given organic solute in a water/CMOS mixture. In general, the activity coefficient of an organic solute in a water/CMOS mixture, $\gamma_{iw,\mathrm{CMOS}}$, decreases (i.e., solubility increases) in an *exponential way* with increasing volume fraction of CMOS, $f_{v,\mathrm{CMOS}}$ (see Fig. 10.4). A notable exception are highly polar compounds, such as certain drugs, which are equally or even more soluble in water as compared to an organic solvent (e.g., Machatha and Yalkowsky, 2005). In the following, we do not distinguish between $\gamma_{iw,\mathrm{CMOS}}$ values at saturated and dilute solute solutions. We also recall that $\gamma_{iw}/\gamma_{iw,\mathrm{CSOM}}$ represents the inverse ratio of the mole fraction solubilities of the compound in the water/CMOS mixture and in water, $x^{\mathrm{sat}}_{iw,\mathrm{CSOM}}/x^{\mathrm{sat}}_{iw}$ (see Eq. 9-5).

For the *cosolvent effect* to be significant (> factor 2), the cosolvent volume fraction needs to be greater than 5 to 10%, depending on the solvent. Below 1%, the effect can be neglected, even for very hydrophobic compounds. Therefore, when conducting experiments, we do not have to worry about significant changes in the activities of organic solutes in an aqueous phase when adding a small amount of a CMOS, as is, for example, common practice when spiking an aqueous solution with a sparingly soluble organic compound dissolved in an organic solvent such as methanol.
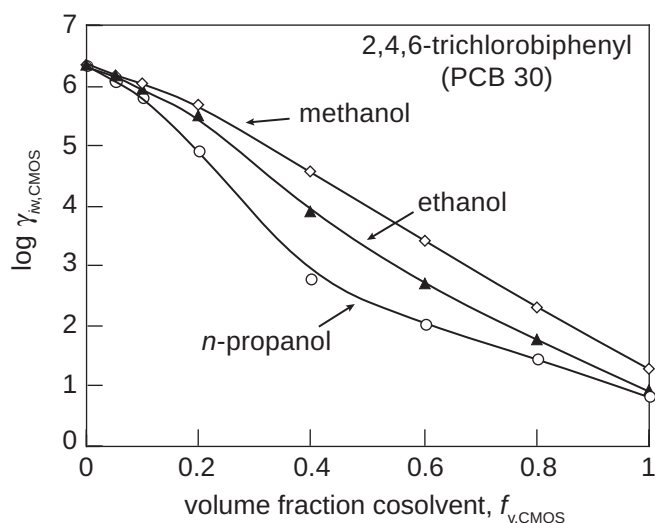
Figure 10.4 Effect of different CMOSs (methanol, ethanol, and propanol) on the activity coefficient, $\gamma_{iw,CMOS}$, of 2,4,6-trichlorobiphenyl (PCB 30) in water/CMOS mixtures. Data from Li and Andren (1994).

The magnitude of the cosolvent effect, as well as its dependence on the amount of cosolvent present, is a function of both the type of cosolvent (see examples given in Fig. 10.4 and in Table 10.6) and the type of organic solute considered (see Fig. 10.5). In general, CMOSs are relatively small molecules with strong H-acceptor and/or H-donor properties. When mixed with water, they are able to break up some of the hydrogen bonds between the water molecules and thus form a new H-bonded "mixed solvent" that changes its nature as a function of the properties and the relative amount of the cosolvent. We can see in Table 10.6 that, qualitatively, the more "water-like" solvents such as glycerol, ethylene glycol, and methanol have a much smaller impact on the activity coefficient of an organic solute as compared to organic solvents for which hydrogen bonding plus vdW interactions are important for partitioning. For example, the activity coefficient of naphthalene decreases by a factor of about 5 when going from pure water to a 40% glycerol/60% water mixture, while the effect is about 10 or 20 times larger when ethanol or acetone, respectively, are the cosolvents. The
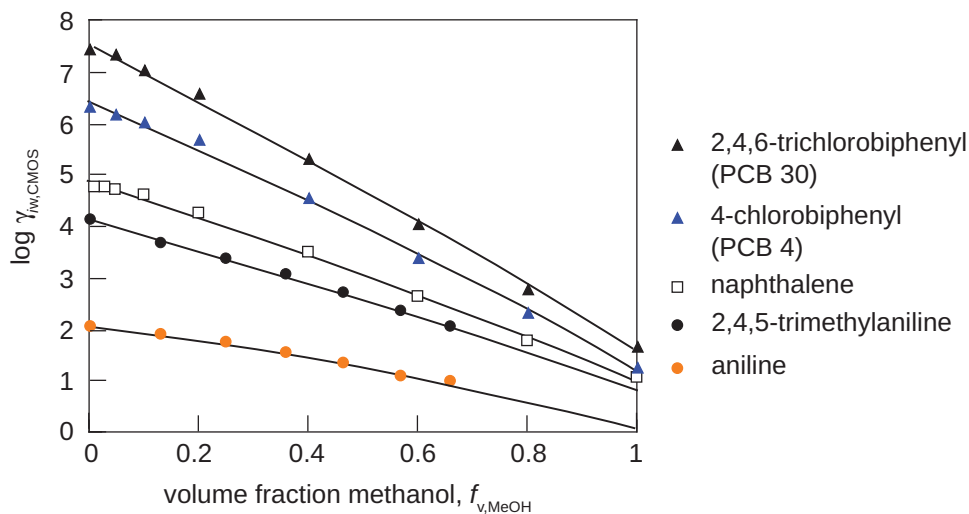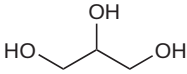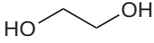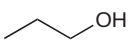
Figure 10.5 Illustration of the effect of a CMOS (methanol) on the activity coefficient of organic compounds in different water–methanol mixtures. Data calculated from measurements in Dickhut et al. (1989); Jayasinghe et al. (1992); Li and Andren (1994); Fan and Jafvert (1997).

Table 10.6 Effect of Various CMOSs on the Activity Coefficient, $\gamma_{iw,CMOS}$, of Naphthalene at Two Different CMOS/Water Ratios ($f_{v,CMOS} = 0.2$ and 0.4)

Cosolvent	Structure	Solubility Parameter δ (MPa$^{1/2}$)[b]	Naphthalene Activity Coefficient[a] $\gamma_{iw}/\gamma_{iw,CMOS} = x_{iw,CMOS}/x_{iw}$	
			$f_{v,CMOS} = 0.2$ (σ_i^c)[c]	$f_{v,CMOS} = 0.4$
Glycerol	OH, HO, OH	36.2	2.5 (2.0)	5.5
Ethylene glycol	HO, OH	34.9	3 (2.4)	9
Methanol	H_3C-OH	29.7	3.5 (2.7)	14
Dimethylsulfoxide (DMSO)	O, S	26.7	5.5 (3.7)	36
Ethanol	OH	26.1	7 (4.2)	48
Propanol	OH	24.9	17 (6.2)	180
Acetonitrile	$H_3C-C\equiv N$	24.8	14 (5.7)	140
Dimethylformamide	O, N, H	24.8	15 (5.9)	130
1,4-Dioxane	O, O	20.7	14 (5.7)	180
Acetone	O	19.7	20 (6.5)	270

[a]Data from Dickhut et al. (1989); Li et al. (1996); Fan and Jafvert (1997). [b]Hildebrand solubility parameter from Barton (1991) in units of megapascal$^{1/2}$. [c]Cosolvency power, σ_i^c, for the range $0 < f_{v,solv} < 0.2$; see Eq. 10-22.

Hildebrand solubility parameter, δ, given in Table 10.6, is a measure of the cohesive forces among the molecules in the pure solvent, ℓ; it is defined as the square root of the cohesive energy density (Barton, 1991):

$$\delta = \left(\frac{\Delta_{vap}H_\ell - RT}{\bar{V}_\ell} \right)^{1/2} \tag{10-21}$$

The solvents exhibiting higher cohesive forces in their pure liquid (larger δ) tend to have a smaller cosolvent effect in water.

Generally, the cosolvent effect is largest for large apolar solutes like PCBs and smallest for small, polar solutes line aniline (Fig. 10.5). Since the changes in excess

enthalpy and entropy with changing cosolvent–water composition are not generally linearly correlated with each other, a strictly linear relationship between excess free energy (or $\log \gamma_{iw,CSOM}$) and $f_{v,CSOM}$ cannot be expected over the whole water/CMOS mixture range (see Figs. 10.4 and 10.5). Considering the rather complex factors that determine the excess free energy of an organic solute in a CMOS/water mixture, it is not surprising that any simple quantitative models developed for describing cosolvent effects all have somewhat limited predictive capabilities. Such models are, however, quite well-suited for fitting experimental data and for estimating activity coefficients of structurally closely related compounds in a given water/CMOS system for which experimental data are available. As we subsequently discuss, an alternative to these classical experimental approaches is to use pp-LFERs to describe activity coefficients in water/CMOS mixtures.

For a discussion of the various approaches taken to quantify cosolvent effects, we refer to the literature (e.g., Li and Andren, 1995; Li et al., 1996; Fan and Jafvert, 1997; Millard et al., 2002; Machatha and Yalkowski, 2005). For our purposes, as a first approximation, we adopt the simplest empirical approach where we assume a *log-linear* relationship between activity coefficient (or mole fraction solubility) of a given compound and volume fraction of the CMOS for a restricted cosolvent range. For example, for the cosolvent range $f_{v,CSOM}^1 \leq f_{v,CSOM} \leq f_{v,CSOM}^2$ we may write:

$$\log \gamma_{iw,CSOM}(f_{v,CSOM}) = \log \gamma_{iw,CSOM}(f_{v,CSOM}^1) - \sigma_i^c \left[f_{v,CSOM} - f_{v,CSOM}^1 \right] \quad (10\text{-}22)$$

with the cosolvency power $\sigma_i^c = [\log \gamma_{iw,CSOM}(f_{v,CSOM}^1) - \log \gamma_{iw,CSOM}(f_{v,CSOM}^2)]/[f_{v,CSOM}^1 - f_{v,CSOM}^2]$.

If we consider a $f_{v,CSOM}$ range starting with pure water, that is, $f_{v,CSOM}^1 = 0$, $\gamma_{iw,CSOM}(f_{v,CSOM}^1) = \gamma_{iw}$, and $\sigma_i^c = [\log \gamma_{iw,CSOM}(f_{v,CSOM}^2) - \log \gamma_{iw}]/f_{v,CSOM}^2$, Eq. 10-22 can also be written as:

$$\gamma_{iw,CSOM}(f_{v,CSOM}) = \gamma_{iw} 10^{-\sigma_i^c \cdot f_{v,CSOM}} \quad (10\text{-}23)$$

This approach is very similar to the one used for describing the effect of salt on the aqueous activity coefficient (Eq. 9-28) and *thus also on the effect of salt on the organic solvent-water partition constant*, only with the opposite sign in the exponent. Finally, for calculating molar volumes of CMOS/water mixtures, we use Amagat's Law (Eq. 4-27), with the mole fractions of two solvents in a binary mixture (subscripts 1 and 2) related to the volume fractions by:

$$x_1 = \frac{1}{1 + \dfrac{1 - f_{v1}}{f_{v1}} \cdot \dfrac{\overline{V}_1}{\overline{V}_2}} \quad \text{and} \quad x_2 = 1 - x_1 \quad (10\text{-}24)$$

As previously mentioned, an alternative to the classic log-linear approach is to apply pp-LFERs to estimate activity coefficients in water/CMOS mixtures. Abraham and Acree (2011) have determined the solubilities of 73 organic compounds in water and

Table 10.7 pp-LFERs Describing the Effect of the Cosolvent Ethanol on the Activity Coefficient of Organic Solutes in Ethanol/Water Mixtures ($\log \dfrac{\gamma_{iw}}{\gamma_{iw,\text{ETOH}}} = v_{w,\text{ETOH}}V_i + e_{w,\text{ETOH}}E_i + s_{w,\text{ETOH}}S_i + a_{w,\text{ETOH}}A_i + b_{w,\text{ETOH}}B_i + c$) at 25°C[a]

$f_{v,\text{ETOH}}$	$\overline{V}_{w,\text{ETOH}}$ (L mol^{-1})	$v_{w,\text{ETOH}}$	$e_{w,\text{ETOH}}$	$s_{w,\text{ETOH}}$	$a_{w,\text{ETOH}}$	$b_{w,\text{ETOH}}$	c^b
0.1	0.019	+0.45	−0.02	0.00	+0.07	−0.37	−0.23
0.2	0.021	+0.92	+0.04	−0.04	+0.10	−0.82	−0.18
0.3	0.023	+1.41	+0.11	−0.10	+0.13	−1.32	−0.16
0.4	0.025	+1.92	+0.13	−0.16	+0.17	−1.81	−0.08
0.5	0.027	+2.42	+0.12	−0.25	+0.25	−2.28	+0.04
0.6	0.031	+2.81	+0.14	−0.33	+0.29	−2.68	+0.20
0.7	0.035	+3.10	+0.09	−0.37	+0.31	−2.94	+0.35
0.8	0.040	+3.32	+0.18	−0.47	+0.26	−3.21	+0.52
0.9	0.048	+3.55	+0.21	−0.58	+0.26	−3.45	+0.67
1.0	0.058	+3.86	+0.47	−1.04	+0.33	−3.60	+0.73

[a]Data from Abraham and Acree (2011).
[b]Note: the constants deviate from the original published equation by the term $\log \overline{V}_{w,\text{ETOH}}/\overline{V}_w$.

in ten different ethanol/water mixtures ranging from pure ethanol (volume fraction of ethanol, $f_{v,\text{EtOH}} = 1$) down to 10% ethanol/90% water ($f_{v,\text{EtOH}} = 0.1$). We use the ethanol/water system as an example as it has been extensively investigated because of its importance in the pharmaceutical industry. Using these solubilities, Abraham and Acree (2011) derived the ten pp-LFERs given in Table 10.7 for quantifying "partition constants" between the ten ethanol/water mixtures and water. We note that they used the E-term (excess molar refraction) instead of the L-term ($\log K_{i\text{hexadecane–air}}$) (Eq. 7-11 instead of Eq. 7-12). We recall that the standard free energy of transferring a solute from pure water (w) to another liquid (ℓ) is given by:

$$\Delta_{w,\ell}G_i = -2.302RT \log \gamma_{iw}/\gamma_{i\ell} \tag{10-25}$$

where, in this case, $\gamma_{i\ell}$ is $\gamma_{iw,\text{ETOH}}(f_{v,\text{ETOH}})$.

Inspection of Table 10.7 shows that two terms in the pp-LFERs are dominating the overall effect of the cosolvent ethanol on the activity coefficient of the compound: the volume term ($v_{w,\text{ETOH}}$) representing the difference in cavity formation costs as well as the size term in the dispersive vdW interactions and the H-donor term ($b_{w,\text{ETOH}}$) expressing the difference in the H-donor properties between water and the ethanol/water mixture. We already made a similar observation when discussing the partitioning of organic compounds between another bipolar solvent, octanol, and water (Eq. 10-10). As a consequence, we may expect large cosolvent effects for large, apolar compounds and much smaller effects for small, polar compounds. We already noted these effects when discussing Fig. 10.5, and Fig. 10.6 shows predicted log $\gamma_{iw}/\gamma_{iw,\text{ETOH}}$ values of some of our companion compounds. We can also see that for a restricted cosolvent range, particularly between 0 and 50% EtOH, a log-linear relationship (Eq. 10-22) describes the dependency of log $\gamma_{iw}/\gamma_{iw,\text{ETOH}}$ on $f_{v,\text{EtOH}}$ reasonably well.
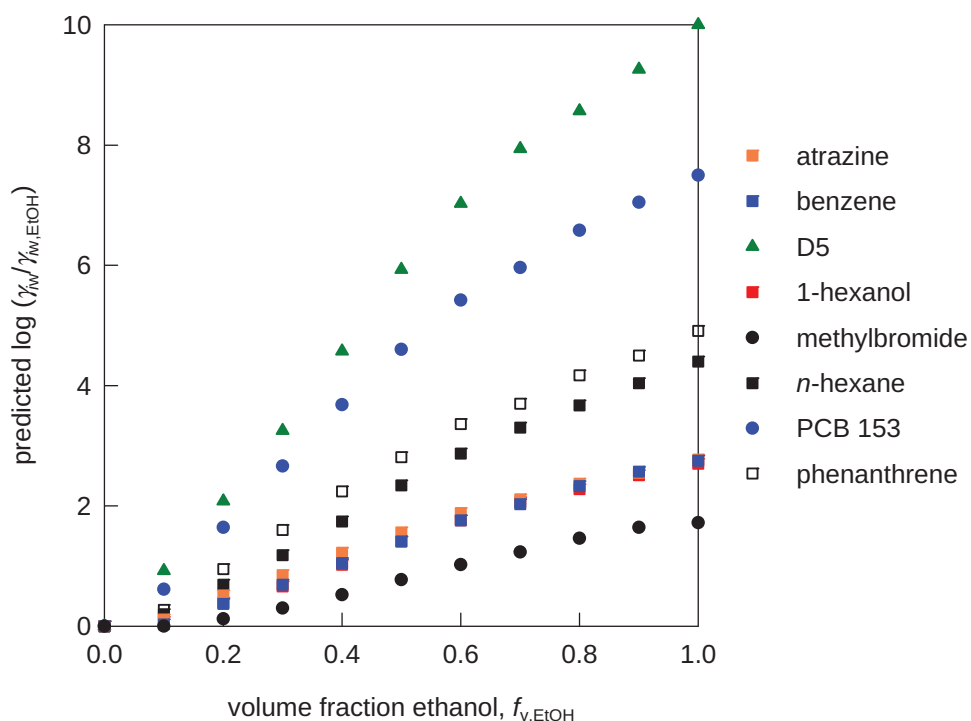
Figure 10.6 Calculated $\log \gamma_{iw} / \gamma_{iw,ETOH}$ plotted as a function of the ethanol fraction for several of our companion compounds, using the equations given in Table 10.7.

In conclusion, any partition constant or coefficient between air or another (organic) bulk phase, including the pure compound and water, $K_{i\text{bulkw}}$, is modified by a cosolvent present in the aqueous phase by:

$$K_{i\text{bulkw,CSOM}}(f_{v,\text{CSOM}}) = K_{i\text{bulkw}} \frac{\gamma_{iw,\text{CSOM}}}{\gamma_{iw}} \qquad (10\text{-}26)$$

We neglect the change in molar volume due to added cosolvent as it is minimal as compared to the change in the activity coefficient. For example, when considering a 50% ethanol/50% water mixture, the bulk phase–ethanol/water partition coefficient of PCB 153 would be about 50,000 times smaller as compared to the bulk phase–water coefficient (see $\log \gamma_{iw} / \gamma_{iw,\text{ETOH}}$ in Fig. 10.6).

10.5 Evaporation and Dissolution of Organic Compounds from Organic Liquid Mixtures–Equilibrium Considerations

Liquid organic mixtures are commonly divided into so-called light non-aqueous phase liquids ("LNAPLs", e.g., gasoline, diesel fuel, and heating oil) or dense non-aqueous phase liquids (DNAPLs", e.g., coal tars, creosotes, chlorinated solvent mixtures, and PCBs). The density distinction is made when considering dissolution into water, because if the liquid mixture's density is greater than that of water, then the mixture tends to "fall" through water bodies and reside at loci like bedrock underlying aquifers or river bottoms. In contrast, LNAPLs float on water tables or at the air–water interface. To assess such environmental contamination, we need to know how

organic compounds present in liquid organic mixtures partition into air (evaporation) or into an aqueous phase (dissolution).

In this section, we discuss the factors that determine the concentration of a given component of a LNAPL or DNAPL in an adjacent gaseous or aqueous phase that is *in equilibrium* with the organic mixture. Therefore, we consider a "snapshot" of the situation where we assume a constant composition of the liquid organic mixture. In reality, when exposed continuously to air or "clean" water, the composition of a LNAPL or DNAPL may change significantly with time, as more volatile or water-soluble compounds, respectively, become depleted (e.g., Lemkau et al., 2010). Depending on the contact time and contact area between the organic phase and air or water, equilibrium may not be established. Thus, a mass transfer approach has to be taken to describe the evaporation or dissolution process. However, even for modeling the evaporation or dissolution kinetics, the equilibrium partitioning of a given compound needs to be known to quantify the mass transfer gradient (see Part IV).

Evaporation

We recall from Chapter 4 (Eq. 4-14) that, when assuming ideal gas behavior, the partial pressure of a compound above a liquid mixture (subscript "mix") is given by:

$$p_i = \gamma_{i\text{mix}} x_{i\text{mix}} p_{i\text{L}}^* \qquad (10\text{-}27)$$

Let us now evaluate in which cases we may, as a first approximation, assume that Raoult's Law ($\gamma_{i\text{mix}} = 1$) is valid. From our earlier discussions concerning the molecular factors causing deviations from ideal behavior (Section 4.2), we would expect $\gamma_{i\text{mix}}$ values not too different from 1 when either apolar compounds or monopolar compounds are in mixtures in which the major components undergo primarily vdW interactions, with the added restriction for monopolar compounds that no major constituents have complementary polarity. As confirmed by experimental data and by model calculations (e.g., Peters et al., 1999a), examples meeting the above criteria include aliphatic hydrocarbons and BTEX compounds present in most gasolines and in other fuels (Cline et al., 1991; de Hemptinne et al., 1998; Heermann and Powers, 1998; Garg and Rixey, 1999); the components of mixtures of chlorinated solvents (Broholm and Feenstra, 1995); PAHs present in diesel fuels, coal tars, and creosotes (Lane and Loehr, 1992; Lee et al., 1992a, b); and PCB congeners present in pure PCB mixtures (e.g., Aroclor 1242) or in hydraulic oils consisting of other types of compounds (e.g., trialkylphenylphosphates; Luthy et al., 1997). In all these cases, the $\gamma_{i\text{mix}}$ values determined were found to meet the Raoult's law criteria within less than a factor of 2 to 3, and, therefore, for practical purposes, $\gamma_{i\text{mix}}$ can be set to 1.

Dissolution Into Water

As a starting point for describing the equilibrium partitioning of a given compound, *i*, between a liquid organic mixture and an aqueous phase (subscript "w"), we rearrange Eq. 10-2:

$$C_{i\text{w}} \gamma_{i\text{w}} \bar{V}_{\text{w}} = C_{i\text{mix}} \gamma_{i\text{mix}} \bar{V}_{\text{mix}} \qquad (10\text{-}28)$$

With $x_{i\text{mix}} = C_{i\text{mix}} \bar{V}_{\text{mix}}$, we obtain:

$$C_{i\text{w}} = \frac{x_{i\text{mix}} \gamma_{i\text{mix}}}{\gamma_{i\text{w}} \bar{V}_{\text{w}}} \tag{10-29}$$

Hence, in order to calculate the aqueous concentration of compound i at equilibrium, one needs to know its mole fraction in the mixture, $x_{i\text{mix}}$ (or $C_{i\text{mix}}$ and $\bar{V}_{\text{mix}}$), as well as its activity coefficients in the organic ($\gamma_{i\text{mix}}$) and the aqueous ($\gamma_{i\text{w}}$) phases. Very often when dealing with complex mixtures, $\bar{V}_{\text{mix}}$ is not known and has to be estimated. As a first approximation, this can be done from the density of the liquid mixture, ρ_{mix}, and by assuming an average molar mass, $\bar{M}_{\text{mix}}$, of the mixture components:

$$\bar{V}_{\text{mix}} \cong \frac{\bar{M}_{\text{mix}}}{\rho_{\text{mix}}} \tag{10-30}$$

For example, the average molar masses of gasoline and coal tar have been estimated as 105 g mol^{-1} and 150 g mol^{-1}, respectively (Cline et al., 1991; Picel et al., 1988).

Let us now consider the various factors that may influence the equilibrium partitioning of an organic compound between a liquid organic mixture and water. First, the organic mixture may originally contain a significant amount of a highly water-soluble compound, which can cause a cosolvent effect in the water phase, as discussed in Section 10.3. Prominent examples include the oxygenated compounds such as methyl-t-butyl ether (MBTE), methanol, or ethanol that are added to gasoline (Cline et al., 1991; Poulsen et al., 1992; Heermann and Powers, 1998). We recall from Section 10.4 that we can neglect the cosolvent effect in the water if the volume fraction of the organic solvent does not exceed 0.01 (1%). However, in some countries, such polar compounds may make up 10 to 20 % of the gasoline. In these cases, cosolvent effects in the "aqueous" phase (now water-CMOS phase) may be significant (e.g., Heermann and Powers, 1998). In the following, we will focus on those cases for which we may assume that the effect on the *aqueous* activity coefficient of a given compound by other dissolved mixture constituents is minimal. Furthermore, we also neglect the effect of salts on $\gamma_{i\text{w}}$ (which has the opposite effect of a cosolvent, see Section 9.4, Eq. 9-28); we would need to consider salting-out when dealing with the pollution of the marine environment or groundwater brines. Thus, if we assume that $\gamma_{i\text{w}} \approx \gamma_{i\text{w}}^{\text{sat}}$ (Section 9.1, Table 9.1), we may substitute the term $\gamma_{i\text{w}} \bar{V}_{\text{w}}$ in Eq. 10-28 by the inverse of the *liquid* aqueous solubility, $1/C_{i\text{w}}^{\text{sat}}$ (L), of the compound:

$$C_{i\text{w}} = C_{i\text{mix}} \bar{V}_{\text{mix}} \gamma_{i\text{mix}} C_{i\text{w}}^{\text{sat}}(\text{L}) \tag{10-31}$$

With $x_{i\text{mix}} = C_{i\text{mix}} \bar{V}_{\text{mix}}$, we obtain:

$$C_{i\text{w}} = x_{i\text{mix}} \gamma_{i\text{mix}} C_{i\text{w}}^{\text{sat}}(\text{L}) \tag{10-32}$$

By rearranging Eq. 10-31, we may then also express the liquid organic mixture–water partition coefficient, $K_{i\text{mixw}} = C_{i\text{mix}}/C_{i\text{w}}$, as:

$$K_{i\text{mixw}} = \frac{1}{\bar{V}_{\text{mix}} \gamma_{i\text{mix}} C_{i\text{w}}^{\text{sat}}(\text{L})} \tag{10-33}$$

As previously mentioned, we usually apply Raoult's Law and assume $\gamma_{i\text{mix}}$ is 1. Box 10.1 provides an illustrative application of Eq. 10-32. We should note, however, that particularly for bipolar compounds, such as certain minor constituents in gasoline (e.g., phenolic compounds and aromatic amines), larger deviations from ideal behavior have to be expected. In addition, in mixtures containing large quantities of polar compounds, the activity coefficients of the various mixture compounds may change with time, if these polar constituents are depleted during the dissolution process. Furthermore, changes in the molar volume of the mixture as a consequence of the preferential dissolution of the more water-soluble components may have to

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Box 10.1   Estimating the Concentrations of Individual PCB Congeners in Water in Equilibrium with an Aroclor Mixture

Aroclor 1242 is a commercial PCB mixture with an average chlorine content of 42%, an average molar mass $\bar{M}_{\text{Aroclor}}$, of about 265 g mol^{-1} and a density, ρ_{Aroclor}, of 1.39 g cm^{-3}. Luthy et al. (1997) have determined the composition of a pure Aroclor 1242 mixture, and they have measured the aqueous concentrations of some individual congeners at 25°C in equilibrium with the Aroclor 1242 mixture. Among the congeners investigated was 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), which was determined to be present in the Aroclor 1242 mixture at about 3.2 mass percent (i.e., mass fraction $m_{i\text{Aroclor}} = 0.032$ g$_i$ g$_{\text{Aroclor}}^{-1}$). The measured aqueous concentration for this compound was 1.11 µg L^{-1}. Is this concentration reasonable? What aqueous PCB 52 concentration would you have predicted from the above information, when assuming that Raoult's Law is valid?

Convert the mass fraction ($m_{i\text{Aroclor}} = 0.032$) of PCB 52 in the Aroclor 1242 mixture into the mole fraction by using the average molar mass, $\bar{M}_{\text{Arcolor}}$, of 265 g mol^{-1}:

$$x_{i\text{Aroclor}} = m_{i\text{Aroclor}} \frac{\bar{M}_{\text{Aroclor}}}{M_i} = (0.032)\frac{(265)}{(292)} = 0.029$$

Estimate the liquid aqueous solubility of PCB 52 from its aqueous solubility using T_{m} (Eqs. 9-10 and 8-24). The resulting $C_{iw}^{\text{sat}}(\text{L})$ value is 3.5×10^{-7} mol L^{-1}. Insert this value, together with the previously calculated $x_{i\text{Aroclor}}$ value and $\gamma_{i\text{Aroclor}} = 1$, into Eq. 10-32 to get the estimated aqueous concentration of PCB 52:

$$C_{iw} = (0.029)(1)(3.5 \times 10^{-7} \text{ mol L}^{-1}) = 1.0 \times 10^{-8} \text{ mol L}^{-1}$$

or about 3 µg L^{-1}. This value is three times higher than the measured one, but it is within the same order of magnitude. Since apolar PCB 52 probably has an $\gamma_{i\text{Aroclor}}$ value near 1, the discrepancy is more likely due to uncertainties in the measured mole fraction in the Aroclor.
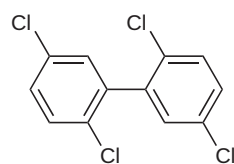
$M_i = 292$ g cm^{-3}
$T_{\text{m}} = 86.5°C$
$C_{iw}^{\text{sat}}(\text{s}) = 10^{-7}$ mol L^{-1}

2,2′,5,5′-tetrachlorobiphenyl
(PCB 52)

be considered. Finally, we should be aware that the preferential dissolution of more soluble compounds in a mixture leads to a higher concentration of the less soluble compounds, and thus to increasing concentrations, in the aqueous phase. The same holds for the preferential evaporation of more volatile compounds leading to higher partial pressures of the less volatile constituents. These issues have to be taken into account when evaluating the long-term dynamics of complex organic mixtures in the environment (e.g., Mackay et al., 1996; Peters et al., 1999b; Arey et al., 2007).

10.6   Questions and Problems

Special note: Problem solutions are available on the book's website. Solutions to problems marked with an asterisk are available for everyone. Unmarked problems have solutions only available to teachers, practitioners, and others with special permission.

Questions

Q 10.1

Give several reasons why it is important to an environmental scientist to be able to predict the partitioning behavior of a given compound between organic solvents and air or water.

Q 10.2

Imagine a hypothetical compound for which $\Delta_{\ell w} G_i$ is equal to zero $(G_{i\ell}^{E} = G_{iw}^{E})$ in each of the solvent–water systems: trichloromethane (chloroform)–water, n-octanol–water, and n-hexadecane–water. A colleague of yours claims that the $K_{i\ell w}$ $(= C_{i\ell}/C_{iw})$ values of such a compound are 0.22, 0.11, and 0.06, respectively, for the three solvent–water systems. Another colleague disagrees and claims that the $K_{i\ell w}$ values are all equal to 1. Who is right and why?

Q 10.3

What are the dominant factors determining the magnitude of organic solvent–air and organic solvent–water partitioning of the majority of organic compounds of environmental concern? In which cases would you expect significant differences between "wet" and "dry" solvents?
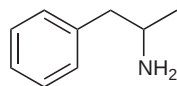
i = amphetamine
(2-aminopropylbenzene)

Q 10.4

The $K_{i\ell w}$ values of the stimulant amphetamine (see structure in margin) for the solvents trichloromethane (chloroform, log K_{icw} = 2.20), n-octanol (log K_{iow} = 1.80), and n-heptane (log K_{ihw} = 0.40) differ quite substantially. Explain why these values differ.

Q 10.5

Why in many cases is the effect of temperature on organic solvent–water partitioning of organic compounds not very significant in contrast to organic solvent–air partitioning? What maximum $|\Delta_{\ell w} H_i|$ values would you expect? Give examples of solutes and organic solvents for which you would expect (a) a substantial positive (i.e., > 10 kJ mol^{-1}) and (b) a substantial negative (i.e., < −10 kJ mol^{-1}) $\Delta_{\ell w} H_i$ value?

Q 10.6

How do dissolved salts in the aqueous phase affect the organic solvent–water partition constant, $K_{i\ell w}$? Write an analogues quantitative expression as derived for air–water partitioning (Chapter 9, Section 9.4).

Q 10.7

What are the major difficulties of any atom/fragment contribution method for estimation of solvent–water partition constants from structure?

Q 10.8

Which compound and cosolvent characteristics determine the effect of a cosolvent on the activity coefficient of the compound in an organic solvent–water mixture? In which cases is the effect particularly large?

Q 10.9

The air–water partition constant of decamethylcyclopentasiloxane (D5) is about 25 times larger than the one for *n*-hexane (see Appendix C). A colleague claims that when comparing the partition constant of the two compounds between air and a 30% ethanol/water mixture, the situation is very different, in that the air–ethanol/water mixture partition constant of *n*-hexane is now about a factor of 5 larger than that of D5. Is your colleague correct? Why or why not?

Q 10.10

What are the major factors determining the aqueous concentration of a constituent of a liquid organic mixture (LNAPL, DNAPL) that is in equilibrium with an aqueous phase? Explain Raoult's Law and give some practical examples of (a) cases in which you can apply it to estimate the concentration of a given LNAPL or DNAPL constituent in water that is in equilibrium with the organic liquid, and (b) cases in which Raoult's Law does not hold.

Q 10.11

When flushing a gasoline contaminated soil in a laboratory column with clean water, Mackay et al., (1996) observed that after 5 pore volumes (i.e., after 5 times replacing the water in the column), the benzene concentration in the effluent decreased from 370 to about 75 $\mu g\, L^{-1}$, while the 1,2-dimethylbenzene (*o*-xylene) concentration increased from 1200 to 1400 $\mu g\, L^{-1}$. Explain these findings.

Problems

P 10.1[*] ***How Much is the Olive Oil on your Balcony Contaminated by Air Pollutants***

You live in a town where air pollution, primarily from traffic, is quite substantial. From a recent article in the local newspaper, you learn that the benzene concentration in your area's air may reach up to 10 parts per billion on a volume base (i.e., 10 ppbv). You wonder to what extent the olive oil that you use for your salad, which you left in an open bottle on the table on your balcony, is contaminated with this rather toxic compound. Calculate the maximum concentration of benzene in the olive oil assuming

an average temperature of 15°C and a total pressure of 1 bar. Use the ideal gas law to convert ppbv to molar concentrations.

What is the situation with respect to another notorious air pollutant, benzo(a)pyrene, that is present at an average gaseous concentration of about 10 pg m^{-3} ? Comment on the results by comparing the calculated concentrations with the WHO drinking water standards for benzene and benzo(a)pyrene, which are 10 µg L^{-1} and 0.7 µg L^{-1} respectively.

Hint: Use Eq. 10-7 to estimate the olive oil–air partition constants and make some assumptions on the temperature dependence of these constants.

P 10.2* *A Small Accident in Your Kitchen*

In your kitchen ($T = 25°C$) you drop a small bottle with 20 mL of the solvent 1,1,1-trichloroethane (methyl chloroform), which you use for cleaning purposes. The bottle breaks and the solvent starts to evaporate. The doors and the windows are closed. On your stove sits an open pan containing 2 L of cold olive oil. Furthermore, on the floor there is a large bucket filled with 50 L of water. The air volume of the kitchen is 30 m^3. Calculate the concentration of methyl chloroform in the air, the water in the bucket, and in the olive oil at equilibrium. Assume that the adsorption of methyl chloroform to any other phases/surfaces present in the kitchen can be neglected. Comment on any other assumptions that you can make.

P 10.3 *Extraction of Neutral Organic Pollutants from Water Samples*

For analyzing organic pollutants in water samples, compounds are commonly concentrated by adsorption, purging with gas bubbles, or extraction with an organic solvent. You have the job to determine the concentration of 1-naphthol in contaminated groundwater by using gas chromatography. You want to extract 20 mL water samples with a convenient solvent. In the literature (Hansch and Leo, 1979), you find the following log $K_{i\ell w}$ values for 1-naphthol for a series of solvents:

Solvent ℓ	log $K_{i\ell w}$
n-hexane	0.52
benzene	1.89
trichloromethane (chloroform)	1.82
ethyl acetate (acetic acid ethyl ester)	2.60
n-octanol	2.90

Are you surprised to find such large differences in the $K_{i\ell w}$ values of 1-naphtol for the various solvents? If not, try to explain these differences. You decide to use ethyl acetate as the solvent for the extraction. Why would you not pick *n*-octanol?

Now you wonder how much ethyl acetate you should use. Calculate the volume of ethyl acetate that you need at minimum if you want to extract at least 99% of the total 1-naphthol present in the water sample. Are you happy with this concentration step? A colleague tells you that it would be much wiser to extract the sample twice with the goal to get 90% of the total compound each time out of the water (which would also amount to 99%), and then pool the two extracts. How much total ethyl acetate would you need in this case?

1-naphthol
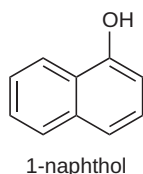
Finally, another colleague suggests you add 3.56 g NaCl to the 20 mL sample in order to improve the extraction efficiency. How much less ethyl acetate would be required in the presence of the salt ($K_i^s = 0.21$, Table 9.4)? Is there any other effect that the addition of NaCl would have on the extraction, and is this effect favorable for the analytical procedure chosen?

P 10.4 *Extraction of Organic Acids and Bases from Water Samples*

i = 2,4,6-trichlorophenol
(2,4,6-TCP)

log K_{ibw} = 3.60
pK_{ia} = 6.15

You have the job of determining the concentrations of 2,4,6-trichlorophenol (2,4,6-TCP) and 4-ethyl-2,6-dimethylpyridine (EDMP) in wastewater samples from an industrial site. You decide to extract the compounds first into an organic solvent, and then analyze them by liquid chromatography. From the $K_{i\ell w}$ values reported for the two compounds for various solvent–water systems, you conclude that there seems to be no single solvent that is optimally suited to extract the two compounds simultaneously. Would this be wise anyway? If there were such a solvent, at what pH would you carry out the extraction? What would be the problem? Regardless, you decide to extract first 2,4,6-TCP with butyl acetate (subscript b) and then EDMP with trichloromethane (chloroform, subscript c). Give the pH-conditions at which you perform the extractions and calculate how much solvent you need at a minimum in each case if you want to extract at least 98% of the compounds present in a 100 mL water sample.
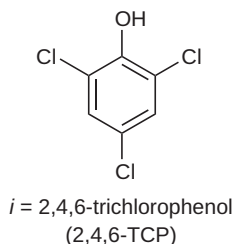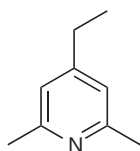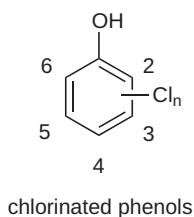
P 10.5 *Evaluating Partition Constants of Chlorinated Phenols in Two Different Organic Solvent–Water Systems*

i = 4-ethyl-2,6-dimethyl pyridine
(EDMP)

log K_{icw} = 3.70
pK_{ia} = 7.43

Kishino and Kobayashi (1994) determined the *n*-octane–water ($K_{i\text{octanew}}$) and *n*-octanol–water ($K_{i\text{ow}}$) partition constants of a series of chlorinated phenols. Plot the log $K_{i\text{octanew}}$ values versus the log $K_{i\text{ow}}$ values of the 13 compounds. Inspect the data and try to derive meaningful sp-LFERs of the type Eq. 10-13 for subsets of compounds. Discuss your findings in terms of the molecular interactions that govern the partitioning of the chlorinated phenols in the two different solvent–water systems.

chlorinated phenols

Partitioning constants for chlorinated phenols

Compound	log $K_{i\text{octanew}}$	log $K_{i\text{ow}}$[a]
1 Phenol	−0.99	1.57
2 2-Chlorophenol	0.74	2.29
3 3-Chlorophenol	−0.31	2.64
4 4-Chlorophenol	−0.41	2.53
5 2,3-Dichlorophenol	1.27	3.26
6 2,4-Dichlorophenol	1.21	3.20
7 2,5-Dichloropehol	1.31	3.36
8 2,6-Dichlorophenol	1.48	2.92
9 3,5-Dichlorophenol	0.41	3.60
10 2,4,5-Trichlorophenol	1.76	4.02
11 2,4,6-Trichlorophenol	2.05	3.67
12 2,3,4,6-Tetrachlorophenol	2.58	4.24
13 Pentachlorophenol	3.18	5.02

[a]Values given in the Appendix may differ somewhat from the ones determined by Kishino and Kobayashi (1994).

P 10.6* *Estimating Octanol–Water Partition Constants Using the Atom/Fragment Contribution Method*

Estimate the K_{iow} values at 25°C of (a) ethyl acetate, (b) 2,3,7,8-tetrachlorodibenzo-dioxin, (c) the herbicide 2-s-butyl-4,6-dinitrophenol (Dinoseb), (d) the insecticide parathion, and (e) the hormone testosterone using solely the fragment coefficients and correction factors given in Tables 10.4 and 10.5 (Eq.10-19). Compare the estimated values with the experimental K_{iow} values that you can find in Appendix C. Comment on the results.

ethyl acetate   2,3,7,8-tetrachlorobenzodioxin
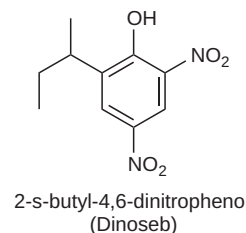
2-s-butyl-4,6-dinitrophenol
(Dinoseb)
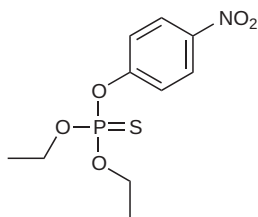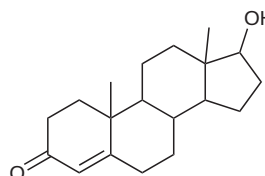
parathion   testosterone

P 10.7 *Estimating Octanol–Water Partition Constants from Known Values of Structurally Closely Related Compounds Using the Atom/Fragment Contribution Method*

Estimate the K_{iow} values of the following four compounds by using the K_{iow} value of a structurally related compound (Eq. 10-20) that you choose from Appendix C. Are the estimates different than the indicated experimental K_{iow} values? If so, why?
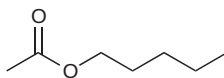
n-pentyl acetate
(exp. log K_{iow} = 2.23)
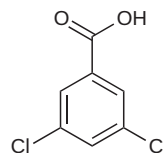
3,5-dichloro benzoic acid
(exp. log K_{iow} = 3.00)
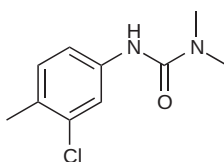
chlortoluron
(exp. log K_{iow} = 2.41)
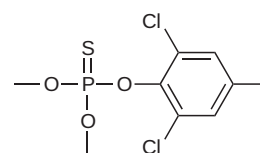
toldofus-methyl
(exp. log K_{iow} = 4.56)
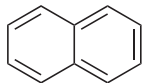
P 10.8 *Estimating the Solubilities and the Activity Coefficients of Organic Pollutants in Organic Solvent (CMOS)/Water Mixtures*

Estimate the solubility and the activity coefficient of naphthalene in a 30% methanol/70% water (v:v) mixture at 25°C.

$$C_{iw}^{sat}(25°C) = 2.5 \times 10^{-4} \text{ mol L}^{-1}$$
$$T_m = 80.2°C$$
$$\gamma_{iw}^{sat}(25°C) = 6.7 \times 10^4$$
(see Table 9.1)

naphthalene

P 10.9 *Assessing the Dissolution Behavior of Gasoline Components*

Gasoline is a mixture of primarily aliphatic (>50%) and aromatic (~30%) hydrocarbons with an average molar mass, $\bar{M}_{gas}$, of about 105 g mol^{-1} and a density of about 0.75 g cm^{-3} (Cline et al., 1991). In addition, it contains a variety of additives, including oxygenates, anti-oxidants, corrosion inhibitors, detergents, anti-freezing agents, and dyes (see Chapter 3). You are asked to investigate a gasoline spill underneath a gas station. Compounds that are among those of great concern with respect to groundwater pollution are benzene and 3,4-dimethylaniline (DMA). You know that the spilled gasoline contains 2 volume percent benzene and 10 mg L^{-1} DMA. Furthermore, in the literature, you find experimental gasoline–water partition coefficients (Eq. 10-33) of 300 L$_w$L^{-1} gasoline for benzene (Cline et al., 1991) and 30 L$_w$L^{-1} gasoline for DMA (Schmidt et al., 2002; at pH 8 where DMA is present primarily as neutral species). These coefficients have been determined for other brands of gasoline. With this information, answer the following questions:

(a) Using the gasoline–water partition coefficients reported in the literature, calculate the activity coefficients of benzene and DMA in the gasoline mixture of interest. Which of the two values do you trust more?

(b) What benzene and DMA concentration would you expect in groundwater that is in equilibrium with a large pool of the spilled gasoline at 25°C (i.e., assume that the gasoline composition is not altered significantly by the dissolution of the components in the aqueous phase)?

(c) In the aqueous phase that is in equilibrium with the spilled gasoline, you measure a naphthalene concentration of 1 mg L^{-1}. How much naphthalene does the gasoline contain? Comment on any assumptions that you make.

Hint: To estimate the mole fraction of a given gasoline component from its volume fraction, use Eq. 10-24 by assuming a binary mixture of the component with a solvent that has the average molar volume of the whole gasoline mixture.

P 10.10 *Estimating the Concentrations of Individual PCB Congeners in Water that is in Equilibrium with an Aroclor/Hydraulic Oil Mixture.*

Aroclor 1242 is a commercial PCB mixture with an average chlorine content of 42%, an average molar mass $\bar{M}_{Aroclor}$, of about 265 g mol^{-1} and a density, $\rho_{Aroclor}$, of
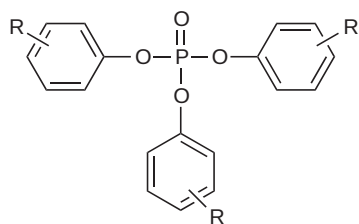
Fyrquel 220 hydraulic oil
(R is primarily *n*-butyl)

1.39 g cm^{-3}. Luthy et al., (1997) have determined the composition of a pure Aroclor 1242 mixture, and they have measured the aqueous concentrations of some individual congeners at 25°C in equilibrium with the real Aroclor 1242 mixture (see Box 10.1) and a mixture of 5% (v/v) Aroclor 1242 in a hydraulic oil (Fyrquel 220) consisting of trialkyl-phenyl phosphates (see structure in margin), with an average molar mass, $\bar{M}_{Aroclor}$, of about 380 g mol^{-1} and a density, $\rho_{Fyrquel}$, of 1.14 g cm^{-3} at 25°C. Among the congeners investigated was 2,2′,5,5′-tetrachlorobiphenyl (PCB 52), which was determined to be present in the Aroclor 1242 mixture at about 3.2 mass percent (i.e., mass fraction $m_{i\,Aroclor} = 0.032$ g$_i$ g$^{-1}_{Aroclor}$). The measured aqueous concentrations for this compound in equilibrium with Fyrquel was 0.10 µg L^{-1}. Is this concentration reasonable? What aqueous PCB 52 concentrations would you have predicted from the preceding information, when assuming that Raoult's Law is valid?

10.7   Bibliography

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