

Chapter 7

PARTITIONING BETWEEN BULK PHASES: GENERAL ASPECTS AND MODELING APPROACHES

7.1 Introduction

Box 7.1 Partition Constants, Partition Coefficients, and Distribution Ratios: A Few Comments on Nomenclature

7.2 Molecular Interactions Governing Bulk Phase Partitioning of Organic Chemicals

Gas–Liquid Phase Partitioning

Box 7.2 Estimating Molar (Molecular) Volumes from Structures

Liquid Organic Phase–Water Partitioning

Some General Conclusions

7.3 Quantitative Approaches to Estimate Bulk Phase Partition Constants/Coefficients: Linear Free Energy Relationships (LFERs)

Fragment Contribution Methods

Single-Parameter Linear Free Energy Relationships (sp-LFERs)

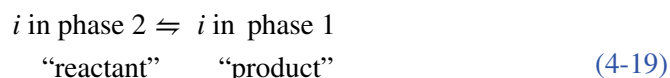
Poly-Parameter Linear Free Energy Relationships (pp-LFERs)

7.4 Questions

7.5 Bibliography

7.1 Introduction

In Section 4.2, we discussed the partitioning of a given chemical i between two bulk phases 1 and 2 (i.e., phases in which a compound may partition into as compared to adsorption onto a surface):



and we defined its *equilibrium partition constant*, K_{i12} , between the two phases as:

$$K_{i12} = \frac{\text{concentration of } i \text{ in phase 1}}{\text{concentration of } i \text{ in phase 2}} \quad (4-20)$$

When considering bulk phases other than well-defined solvents, such as natural organic matter or biota (Chapters 13 and 16), one often expresses the concentration of i in mol per mass (e.g., mol kg⁻¹) and not in mol per volume. If so, we refer to K_{i12} as a *partition coefficient* and not as a partition constant (see Box 7.1 for more details on nomenclature).

Box 7.1 Partition Constants, Partition Coefficients, and Distribution Ratios: A Few Comments on Nomenclature

In the literature, one sometimes encounters a certain confused use of the terms “partition constant,” “partition coefficient,” and “distribution ratio.” Throughout this book, we use these terms in the following way: we talk of a partition constant or a partition coefficient when only *one chemical species* is considered in each phase. The term *partition constant* is reserved for those cases where we deal with the equilibrium partitioning between two *well-defined* phases at given conditions and where we can be sure that the proportionality factor between the concentrations in the two phases is a concentration-independent constant at given conditions. Examples include the air–water partition constant (Chapter 9), the solvent–air and the solvent–water partition constants (Chapter 10), and the air–pure surface partition constant (Chapter 11). In all other cases where this proportionality factor describes structurally varying phases, such as organic matter, black carbon, or lipids, we talk about a *partition coefficient*. A prominent example is the natural organic matter–water partition coefficient that we discuss in Chapter 13.

Furthermore, the very general term “distribution *ratio*” is used for situations where we want to express the ratio of total concentrations of a given chemical in two phases. Examples include the equilibrium distribution ratio of organic acids or bases in air–water, organic solvent–water, or natural organic matter–water systems, where these compounds may be present as both neutral and charged species. Another case is the natural solid–water distribution ratio of a chemical where *various* different sorption mechanisms may be responsible for the presence of the compound in the solid phase. Finally, we should note that several other terms including “distribution constants,” “distribution coefficients,” and “accumulation factors” are often used in the literature to describe partitioning. We generally do not use these terms except for in our discussion on bioaccumulation, where we adopt the commonly used term “bioaccumulation factor” (BAF, Chapter 16).

If molar concentrations (mol L^{-1}) or the same mass concentration units (e.g., ng, μg , or mg per L) are used instead of mole fractions in each phase, as used in Chapter 4, K_{i12} is related to the free energy of transfer: $\Delta_{12}G_i$, by:

$$K_{i12} = \frac{\bar{V}_2}{\bar{V}_1} \cdot e^{-\Delta_{12}G_i/RT} \quad (4-29)$$

where \bar{V}_1 and \bar{V}_2 are the molar volumes of the two bulk phases (e.g., in mL mol^{-1} or L mol^{-1}). K_{i12} is then not dimensionless but is expressed in units of, e.g., L_2/L_1 or $\text{m}_2^3/\text{m}_1^3$. The ratio of the molar volumes (\bar{V}_2/\bar{V}_1) of the two bulk phases may have a noticeable effect on the absolute value of K_{i12} , particularly if the two phases have significantly different molar volumes. Such is the case for air–water partitioning at 25°C , as the molar volumes of air and water are 24.8 L mol^{-1} and 0.018 L mol^{-1} respectively. Hence, the air–water partition constant expressed in molar concentrations is 1378 ($= 24.8/0.018$) times smaller than the one expressed in partial pressure and mole fraction. However, since the molar volumes of most organic liquid phases (solvents) that we discuss do not vary much more than a factor of 2 or 3, the dissimilarities among $\Delta_{12}G_i$ are far more important than volume differences when comparing partition constants of organic compounds in various organic solvent–water and organic solvent–air systems.

Finally, we recall that thermodynamic properties, such as partition constants or reaction constants, are independent of the transfer or reaction pathway and only depend on the starting and ending conditions. Thus, one can use known partition constants to derive unknown partition constants by *thermodynamic cycles*. To illustrate, one can derive the organic solvent (ℓ)–air (a) partition constant of a compound i from the ratio of its organic solvent–water (w) and its air–water partition constants:

$$K_{i\ell a} = K_{i\ell w}/K_{iaw} \quad (7-1)$$

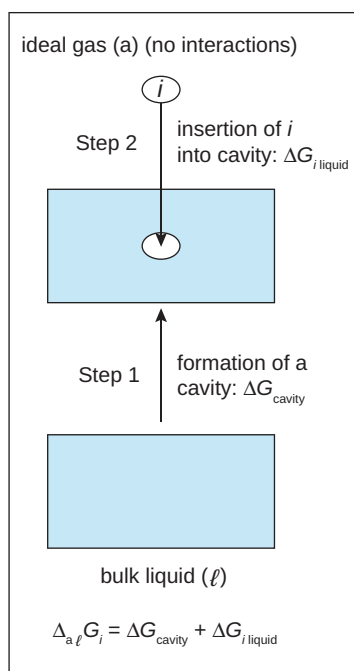
remembering that the organic solvent phase in $K_{i\ell w}$ is water-saturated and, therefore, so is the solvent phase in $K_{i\ell a}$. This point is in many cases unimportant, as dry and wet solvents usually have similar partition constants, but we do expand on this issue in Chapter 10 where we also discuss examples in which the water present in the organic solvent makes a difference.

7.2 Molecular Interactions Governing Bulk Phase Partitioning of Organic Chemicals

Irrespective of whether we consider organic chemicals as solutes or as solvents, we can classify them according to their ability to form hydrogen bonds (H-bonds) with apolar (no H-bonding), monopolar (either H-accepting or H-donating), and bipolar (both H-accepting and H-donating) compounds (Chapter 2, Box 2.2; see also examples given in Table 7.1). In this section, we use this simple classification to gain some qualitative insights into how intermolecular interactions within a given bulk phase plus those

Table 7.1 Classification of Organic Chemicals According to Their Interaction Abilities (see Fig. 2.11 for functional groups)

Compound	Interactions	Examples
Apolar	only van der Waals	alkanes, chlorobenzenes, PCBs
Monopolar	van der Waals + H-accepting (e-donating)	alkenes, alkynes, alkylaromatic compounds, ethers, ketones, esters, aldehydes
Monopolar	van der Waals + H-donating (e-accepting)	chloroform, dichloromethane
Bipolar	van der Waals + H-accepting + H-donating	primary amines, secondary amines, carboxylic acids, alcohols

**Figure 7.1** Partitioning of a compound *i* from an ideal gas phase (air, subscript "a") into a bulk liquid (subscript "ℓ").

between the bulk phase molecules and the molecules of a compound *i* determine the extent to which *i* partitions between two bulk phases.

To attain these insights, we first consider the partitioning of an organic compound *i* between the gas phase (air) and a bulk liquid phase. We then discuss the partitioning of *i* between two liquid phases, one of which is water. For the gas phase, we assume ideal behavior, that is, we assume that no molecular interactions exist between the molecules. In the liquid phase, we assume that the compound is present in dilute solution. Therefore, we can presume that the compound's molecules never interact with one another, but only with the solvent, thus the partition constants are independent of concentration. This section closely follows the concepts originally outlined in Goss and Schwarzenbach (2003), where further details can be obtained.

Gas–Liquid Phase Partitioning

As illustrated in Fig. 7.1, when using a simple cavity model for gas–liquid partitioning, we only have to consider two free energy contributions: (1) the formation of the cavity in the liquid ($\Delta G_{\text{cavity}} > 0$, costing free energy), and (2) the free energy gained from the molecular interactions of the solute with the solvent molecules ($\Delta G_{\text{liquid}} < 0$) upon insertion of the solute into the cavity:

$$\Delta_{a\ell}G_i = \Delta G_{\text{cavity}} + \Delta G_{\text{liquid}} \quad (7-2)$$

ΔG_{cavity} is dependent on the size and the shape of the molecule to be inserted and on how strongly the bulk liquid phase molecules interact with each other, commonly referred to as cohesive energy (see Otto, 2013), especially if such interactions have to be disrupted when forming the cavity. ΔG_{cavity} is particularly large when dealing with bipolar solvents with small solvent molecules, with water being, by far, the most extreme case (see Chapter 9). The second term in Eq. 7-2, ΔG_{liquid} , depends on the strength of interactions of the inserted molecule with the liquid phase molecules surrounding the cavity. Insertion of $\Delta_{a\ell}G_i$ into Eq. 4-29 yields the air–liquid equilibrium partition constant (K_{fal}).

We can now divide both free energy terms in Eq. 7-2 into a van der Waals (vdW) component, which always occurs and includes London dispersive and, in most cases, also Debye and Keesom contributions (the latter two components being of secondary importance, for more details see Section 2.2), and into a hydrogen bonding (H-bonding) component:

$$\Delta_{\text{al}} G_i = \left(\Delta G_{\text{cavity}}^{\text{vdW}} + \Delta G_{\text{cavity}}^{\text{H}} \right) + \left(\Delta G_{\text{liquid}}^{\text{vdW}} + \Delta G_{\text{liquid}}^{\text{H}} \right) \quad (7-3)$$

We recall from Section 2.2 that vdW as well as H-bonding interactions are always attractive and that the former occur between all kinds of molecules. Hence, $\Delta G_{\text{cavity}}^{\text{vdW}}$ in Eq. 7-3 is always > 0 , and $\Delta G_{\text{liquid}}^{\text{vdW}}$ is always < 0 . For a simple but convenient visualization of vdW interactions, we can imagine all molecules to be covered by a “glue” that has a different “stickiness” on different types of compounds. The strength of vdW attractions between a molecule i and its interaction partners then depends on the stickiness of the glues and on the size of the contact area.

One should also recall from Chapter 4 that each free energy term is composed of an enthalpy and an entropy contribution (Section 4.1). When we talk about vdW and H-bonding interactions or use terms like “glue” or “vdW-stickiness” of molecules, we solely address the enthalpy contribution to free energy. Often, the contributions from enthalpy and entropy of partitioning of organic compounds are correlated. However, situations exist in which such a correlation does not hold, and we need to look at the entropy contribution to free energy to understand the differences in partitioning behavior among certain compound classes.

When considering partitioning of organic compounds between air and a bulk liquid phase, one can distinguish four different possible cases:

Case I: Only vdW interactions are important ($\Delta G_{\text{cavity}}^{\text{H}} = 0$; $\Delta G_{\text{liquid}}^{\text{H}} = 0$),

Case II: H-bonding affects only cavity formation ($\Delta G_{\text{liquid}}^{\text{H}} = 0$),

Case III: H-bonding affects only interactions between i and the bulk liquid phase ($\Delta G_{\text{cavity}}^{\text{H}} = 0$), and

Case IV: H-bonding affects both cavity formation and interactions between i and the bulk liquid phase (all terms in Eq. 7.3 are important).

In the following discussion, we briefly address each of these cases with the aim to learn how the various terms in Eq. 7-3 govern the overall partitioning of apolar, monopolar, and bipolar chemicals between air and liquid phases of different polarities.

Case I. For the first case, when only vdW interactions are important, we consider the partitioning of *any organic compound* between air and *any apolar liquid* phase. Here, the apolar phase is *n*-hexadecane, or simply hexadecane. In Fig. 7.2a, the logarithms of hexadecane–air partition constants ($\log K_{\text{hexadecane–air}}$), of several classes of

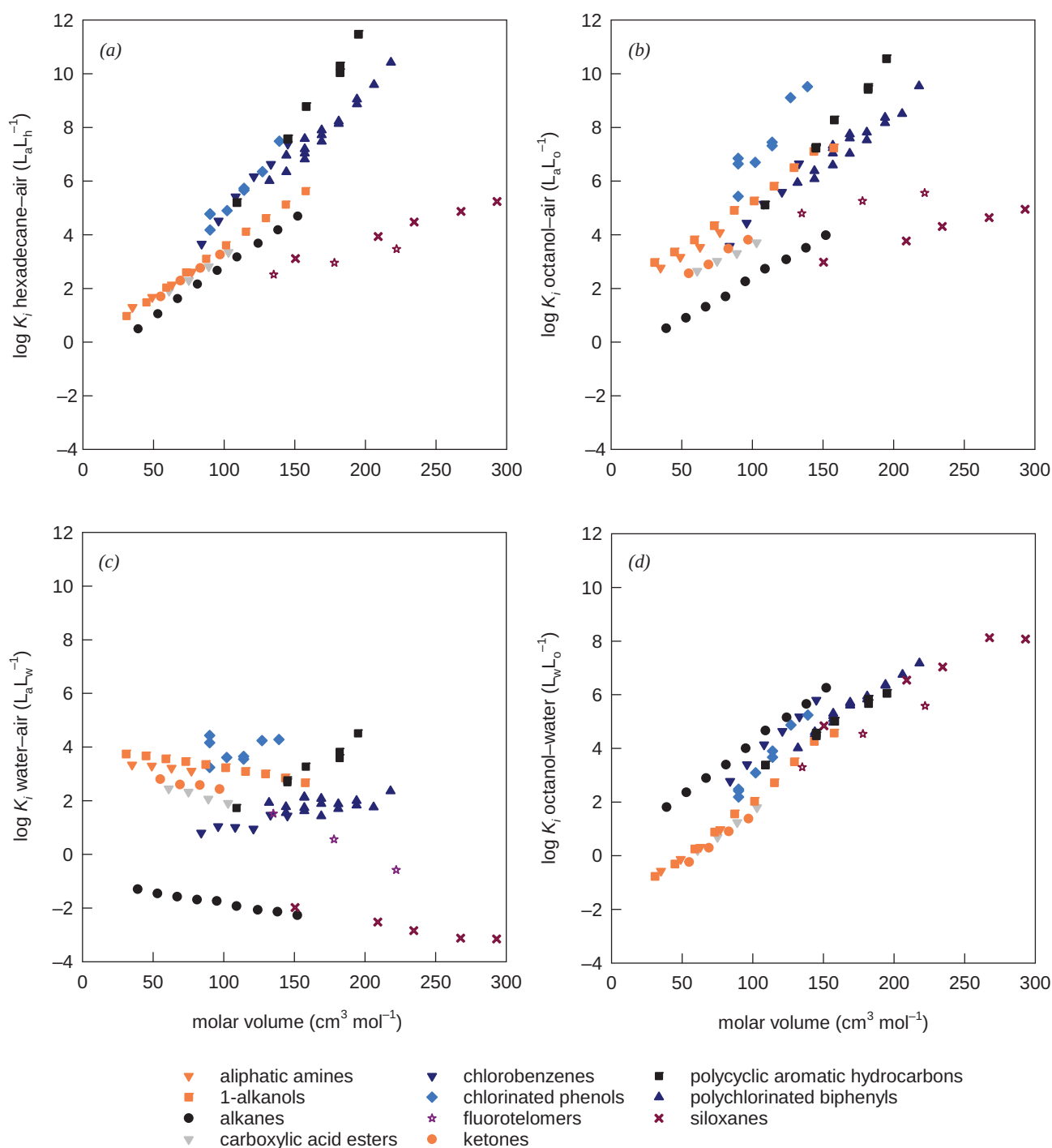


Figure 7.2 Plots of the logarithms of the hexadecane–air (a), octanol–air (b), water–air (c), and octanol–water (d) partition constants of series of apolar, monopolar, and bipolar compounds (our “test set”) versus their molar volumes, V_i .

apolar, monopolar, and bipolar compounds are plotted against the size of the compounds expressed by their molar volumes, V_i , calculated by the McGowan method (see Box 7.2). We use these compounds, which we refer to as “our test set,” in Parts II and III to visualize relationships between different properties and parameters. Some important general observations, which also hold for partitioning to any other apolar liquid phase, can be made from hexadecane–air partitioning (Fig. 7.2a):

Box 7.2 Estimating Molar (Molecular) Volumes from Structures

A very common way of expressing the bulk size of 1 mole of molecules of a given compound is to use the “molar volume,” V_i (mL mol^{-1}), of the compound. As discussed in Chapter 4, we can derive V_i from the molar mass (g mol^{-1}) and the liquid density (g mL^{-1}) of the compound at a given temperature. This way of defining V_i does have certain disadvantages when we want to use it to describe the size of a compound, as in Fig. 7.2. First, because the liquid density is a bulk property, for polar compounds (e.g., alcohols) that have a network-like hydrogen-bond structure between molecules, the calculated V_i value reflects not only the *intrinsic molecular volume* but also the bulk structure. Second, adjustments have to be made when dealing with compounds that are solids. Therefore, various methods for estimating V_i values from the structure of a compound have been developed (for an overview see Yalkowski and Banerjee, 1992; Mackay et al., 1992–1997). Although each of these methods yields different absolute V_i values, the various data sets correlate reasonably well with each other (Mackay et al., 1992–1997). Notably, McGowan and coworkers proposed a simple method that works almost as well as the more sophisticated approaches (McGowan and Mellors, 1986; Abraham and McGowan, 1987). In this method, each element is assigned a characteristic atomic volume (see the following table), and the total volume is calculated by summing up all atomic volumes and by subtracting $6.56 \text{ cm}^3 \text{ mol}^{-1}$ for each bond, no matter whether single, double, or triple. As an example, V_i for benzene is calculated as $V_i = (6)(16.35) + (6)(8.71) - (12)(6.56) = 71.6 \text{ cm}^3 \text{ mol}^{-1}$, illustrating the simplicity of the calculation. Of course, by this method, identical V_i values are obtained for structural isomers, which is sufficient as a first approximation for many applications.

Characteristic Atomic Volumes ($\text{cm}^3 \text{ mol}^{-1}$)^a

C 16.35	H 8.71	O 12.43	N 14.39	P 24.87	F 12.48
Cl 20.95	Br 26.21	I 34.53	S 22.91	Si 26.83	

^a Data from Abraham and McGowan (1987) and Goss et al. (2006) for the fluorine increment.

(1) Except for some small molecules such as methane or ethane, generally, organic compounds partition favorably from air into an *apolar* liquid such as hexadecane ($K_{i\text{hexadecane-air}} > 1$). The reason is, if only vdW forces play a role, the gain in free energy from insertion of the compound in the cavity is larger than the free energy that has to be spent to form the cavity.

(2) $K_{i\text{hexadecane-air}}$ values of compounds with similar size may be orders of magnitude different among various compound classes. For example, the polycyclic aromatic hydrocarbon (PAH), phenanthrene ($V_i = 145 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 7.68$), partitions nearly three orders of magnitude more favorably from air into hexadecane as compared to an alkane of similar size, decane ($V_i = 152 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 4.69$), and more than five orders of magnitude more favorably than hexamethyldisiloxane ($V_i = 150 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 3.12$) or perfluorobutylethanol ($V_i = 135 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 2.52$). In general, rigid aromatic compounds, such as PAHs, exhibit significantly higher $K_{i\text{hexadecane-air}}$ values as compared to aliphatic compounds of similar size, regardless of whether they contain a polar functional group or not. These higher values are, on the one hand, due to the ability of aromatic compounds to undergo somewhat more intense vdW interactions than aliphatic compounds, thanks to their higher “vdW-stickiness.” This ability is

even more pronounced when comparing them to polyfluorinated aliphatic compounds (i.e., fluorotelomers) and siloxanes (Fig. 7.2), which both exhibit unusually small “vdW-stickiness” (see also Chapter 3 for general characteristics of these compounds). On the other hand, the more rigid aromatic compounds also exhibit a smaller loss in entropy when being transferred from the gas phase into a bulk liquid phase as compared to the much more flexible alkanes, fluorotelomers, and siloxanes, which lose more freedom of motion. Therefore, when comparing phenanthrene with decane, perfluorobutylethanol, or hexamethylsiloxane, the differences in the entropy losses due to partitioning also contribute to the observed disparities in their $K_{i\text{hexadecane-air}}$ values.


(3) Within a set of structurally closely related compounds, such as homologues or congeners, a linear correlation between $\log K_{i\text{hexadecane-air}}$ and V_i is observed. The slopes of these correlations (increase of $\log K_{i\text{hexadecane-air}}$ per increase in V_i) are smallest for siloxanes and fluorotelomers. These small slopes can be rationalized primarily by their unusually low vdW interaction capabilities, which do not increase significantly with size as compared to other compound classes. The slope is highest for the planar PAHs because they exhibit a significant increase in “vdW-stickiness” per unit increase in size and display an entropy loss much less dependent on size, as compared to the more flexible aliphatic or alicyclic compounds. For example, our companion PAHs, phenanthrene and benzo(a)pyrene, exhibit a difference in V_i of $43 \text{ cm}^3 \text{ mol}^{-1}$, which translates into a variation in $K_{i\text{hexadecane-air}}$ of four orders of magnitude. Conversely, for siloxanes or fluorotelomers, the same difference in V_i leads to a variation of less than one order of magnitude in $K_{i\text{hexadecane-air}}$.

(4) Large rigid organic compounds, particularly those exhibiting a strong “vdW-stickiness,” partition very strongly from air into hexadecane. Examples include two companion compounds, benzo(a)pyrene ($V_i = 195 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 11.74$) and PCB 153 ($V_i = 206 \text{ cm}^3 \text{ mol}^{-1}$, $\log K_{i\text{hexadecane-air}} = 9.59$). Therefore, we can already see why such compounds have a high tendency to partition from air to apolar or weakly monopolar biological materials in the environment, such as waxes or lipids (see Chapter 16).

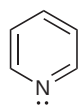
Case II. To illustrate the case when H-bonding affects only cavity formation, we consider the partitioning of apolar compounds between air and a bipolar liquid phase. Compared to partitioning to an apolar phase, the partition constant of a given compound can be expected to be smaller since the energy of cavity formation is higher and no additional energy is gained from polar interactions when inserting the apolar compound. Table 7.2 summarizes the solvent–air partition constants of the apolar compound *n*-octane in water and various apolar and bipolar organic liquids. As is evident, the partition constant of *n*-octane decreases significantly with increasing cohesive energy of the liquid organic phase. However, as compared to partitioning into water, *n*-octane still partitions more than four orders of magnitude better into the strongly bipolar solvent, 1,2-ethanediol, highlighting the extraordinary cohesive energy of water.

Case III. An example of the case when H-bonding affects only interactions of *i* and the bulk phase molecules is the transfer of a monopolar compound from air into a monopolar liquid phase of opposite polarity. Here, $\Delta G_{\text{cavity}}^{\text{H}} = 0$ and energy is gained from additional H-bonding upon insertion of the compound into the cavity. In this

Table 7.2 Liquid Phase–Air Partition Constants of *n*-Octane for Various Organic Liquids and Water at 25°C

Liquid	Formula	Cohesive Energy ^a	$K_{\text{liquid-air}}$
Heptane	C ₇ H ₁₆		8600
Hexadecane	C ₁₆ H ₃₄		5000
Butanol	C ₄ H ₉ OH		2300
1,3-Propanediol	C ₃ H ₆ (OH) ₂		80
1,2-Ethandiol	C ₂ H ₄ (OH) ₂		13
Water	HOH		0.008

^a The cohesive energy of the organic solvents increases with increasing number of bipolar OH-groups per carbon atom.



pyridine

case, larger $K_{i/la}$ values can be expected as compared to partitioning of the compound into an apolar phase. Also, the activity coefficient of the compound, γ_{il} , is smaller than one (Section 4.2). For example, the partition constant of the H-acceptor pyridine (a widely used solvent and precursor substance for syntheses in chemical industry; structure in margin) between the H-donating solvent chloroform (CHCl₃) and air is about 50 times larger as its hexadecane–air partition constant.

Case IV: We conclude our qualitative discussion of air–bulk liquid partitioning by considering two examples that encompass all possible energetic combinations in Eq. 7-3, the partitioning of any kind of compound between air and a bipolar liquid. We examine the bipolar phases of *n*-octanol, referred to as octanol, which has a moderate $\Delta G_{\text{cavity}}^H$ term, and water, which exerts extraordinarily high cohesive energy, i.e., a large $\Delta G_{\text{cavity}}^H$. Figures 7.2*b* and 7.2*c* display the logarithms of the octanol–air and water–air constants versus V_i of the same classes of apolar, monopolar, and bipolar compounds as seen in Fig. 7.2*a*.

Comparison of hexadecane–air and octanol–air partitioning (Figs. 7.2*a* and *b*) shows that, for the various compound classes, very similar slopes are found when plotting the logarithms of the partition constants versus V_i . This correspondence in slopes suggests that the vdW terms in Eq. 7-3 are quite similar for partitioning from air to these two organic liquids (Goss and Schwarzenbach, 1998). However, for some compound classes, the absolute values of the partition constants are significantly different between the two systems, primarily reflecting the differences in $\Delta G_{\text{liquid}}^H$ contributions for different polar functional groups. For example, the $K_{\text{hexadecane-air}}$ values of aliphatic compounds, including apolar alkanes, monopolar ketones and carboxylic acid esters, and bipolar amines and alcohols, are all in the same order of magnitude, whereas the octanol–air partition constants, K_{ioa} , are spread over three orders of magnitude. Qualitatively, we can see that the bipolar OH- and NH₂-groups increase the magnitude of K_{ioa} relative to $K_{\text{hexadecane-air}}$ more strongly than the monopolar keto- or carboxylic ester groups. The reason is that bipolar compounds undergo much stronger H-bonding with the OH-groups of octanol as compared to the monopolar compounds. The effect of H-bonding can also be nicely seen when comparing the partition constants of the apolar chlorinated benzenes and the bipolar chlorinated phenols, which

are very similar in the hexadecane–air system but are almost two orders of magnitude different in the octanol–air system.

Figure 7.2c illustrates that quite a different dependency on size is obtained for water–air partitioning than in the octanol–air system. Here, except for PAHs, an increase in size of structurally related compounds has little or even slightly disfavoring effects on partitioning into the liquid phase. In the case of PAHs, the observed increase in $K_{i\text{water-air}}$ can again be rationalized by the fact that vdW interaction abilities increase significantly with increasing size, while the entropy losses of these rigid compounds upon transfer from the gas phase do not. We discuss these entropic aspects in more detail in Chapter 9.

Liquid Organic Phase–Water Partitioning

We can now use the insights gained from the previous discussion on air–bulk liquid phase partitioning to evaluate the partitioning of organic chemicals between water and a bulk organic liquid. For partitioning between two bulk liquids 1 and 2, we can rewrite Eq. 7.3 as:

$$\Delta_{12}G_i = \left(\Delta_{12}\Delta G_{\text{cavity}}^{\text{vdW}} + \Delta_{12}\Delta G_{\text{cavity}}^{\text{H}} \right) + \left(\Delta_{12}\Delta G_{\text{liquid}}^{\text{vdW}} + \Delta_{12}\Delta G_{\text{liquid}}^{\text{H}} \right) \quad (7-4)$$

where $\Delta_{12}\Delta G = \Delta_{1a}G - \Delta_{2a}G$. According to the thermodynamic cycle, Eq. 7-4 is the difference between two equations of the type Eq. 7-3 written for the respective bulk liquid–air systems. To solve the equation, we just have to consider the differences in the free energies for cavity formation ($\Delta\Delta G_{\text{cavity}}$) and insertion of the compound ($\Delta\Delta G_{\text{liquid}}$), respectively, in the two bulk liquids. As in Eq. 7-1, we can then relate the organic liquid–water partition constant to the corresponding organic liquid–air and water–air partition constants. Using octanol (o) as model organic phase, we obtain:

$$K_{iow} = K_{ioa}/K_{iwa} \quad (7-5)$$

By plotting K_{iow} versus size (Fig. 7.2d), we see organic chemicals of increasing size increasingly favor partitioning into the octanol phase, which is similar to octanol–air partitioning (Fig. 7.2b). In fact, the slopes of the lines correlating structurally closely related compounds are very similar in both systems. This finding is expected from Eq. 7-5, since K_{ioa} increases significantly with size (Fig. 7.2b) whereas K_{iwa} is much less size dependent (Fig. 7.2c). However, comparison of Figs. 7.2b and d also reveals some important differences. Comparing the absolute values of the partition constants for the various groups of compounds, one sees that polar compounds exhibit much higher octanol–air than octanol–water partition constants. For example, the K_{ioa} values of alkyl alcohols are more than two orders of magnitude higher than the corresponding K_{iow} values. The contrary is found for apolar compounds, such as alkanes, for which K_{iow} is about two orders of magnitude larger than K_{ioa} . This difference is due to the large free energy costs for cavity formation in water being partly compensated by inserting polar, particularly bipolar, molecules exhibiting strong H-bonding properties but not by inserting compounds that can only undergo vdW interactions.

Some General Conclusions

In summary, from our discussions thus far, we have gained important insights into how molecular interactions determine the extent to which a neutral organic chemical partitions between two bulk phases. In particular, we have seen that:

- (1) With few exceptions, organic compounds generally favor bulk organic phases over air or water. The extent of partitioning is determined by the molecular size, entropic contributions, and the vdW and H-bonding properties of the compound, as well as by the characteristics of the bulk phases involved (i.e., apolar, monopolar, and bipolar). Depending on the properties of the bulk phase(s) considered, compounds exhibiting the same size but belonging to different compound classes may exhibit substantially different partition constants.
- (2) For both air–organic bulk phase and organic bulk phase–water partitioning of a series of structurally closely related compounds (e.g., homologues, congeners), a linear correlation between the free energy of transfer, and thus the logarithm of the corresponding partition constant or coefficient, and the size of the molecule is observed. The slopes of these correlations depend to a great extent on the vdW interaction abilities of the compounds as well as on entropic aspects. For organic phase–air partitioning, the slopes are largest for PAHs and polychlorinated and polybrominated aromatic compounds (data not shown) and smallest for siloxanes and fluorotelomers (Figs. 7.2*d* and *b*). For organic phase–water partitioning, the slopes tend to be more similar for the different compound classes (see Fig. 7.2*d*), which is a result of compensating vdW and, in some cases, H-bonding interactions occurring in both phases. Also, entropy contributions are significantly smaller if both phases are liquids, which is particularly important when considering rigid compounds such as the PAHs.

7.3

Quantitative Approaches to Estimate Bulk Phase Partition Constants/Coefficients: Linear Free Energy Relationships (LFERs)

For many environmentally relevant matrices, experimental partition constants or coefficients required to assess quantitatively the partitioning behavior of a given compound are often not available and, therefore, have to be estimated. Examples include the partitioning from water or air to natural organic matter; to biological materials such as lipids, proteins, lignin or cellulose; or to mineral oxides or black carbon surfaces (see Part III). In the following section, we introduce some general approaches for predicting partition constants for such matrices. In all of these approaches, one tries to express the free energy of transfer, $\Delta_{12}G_i$, of a given compound in the system of interest by one or several other known free energy terms in a way that they are linearly related to $\Delta_{12}G_i$. Such approaches are, therefore, commonly referred to as linear free energy relationships (LFERs). They are useful for predictive purposes and also helpful for checking reported experimental data for consistency (i.e., to detect experimental errors or to discover unexpected partitioning behavior of a given compound).

Fragment Contribution Methods

A common approach that is particularly suited to computer-assisted evaluations takes advantage of the assumption that the interactions of molecules with their surroundings can be estimated by summing the interactions of each of the structures' parts. Hence, to estimate partition constants of a compound in a given two-phase system one assumes that the free energy of transfer term for the whole molecule ($\Delta_{12}G_i$) can be expressed by a linear combination of terms that describe the free energy of transfer of parts of the molecule:

$$\Delta_{12}G_i = \sum_{\text{parts}} \Delta_{12}G_{\text{part of } i} + \text{special interaction terms} \quad (7-6)$$

Expressed in terms of partition constants, Eq. 7-6 becomes:

$$\log K_{i12} = \sum_{\text{parts}} \Delta \log K_{\text{part of } i12} + \text{special interaction terms} \quad (7-7)$$

In the extreme case, each part is an atom of the molecule. The special interaction terms are necessary to describe *intramolecular* interactions and stereochemical aspects between different parts of the molecule that cannot be accounted for when considering the free energy of transfer of the isolated parts. Obviously, this type of approach, dubbed the *fragment contribution approach*, has the advantage that it allows one to estimate a partition constant based solely on the compound's structure. For our purposes, this approach is of interest because it provides valuable insights into how parts of a molecule contribute to the overall partition constant. Good predictions can be anticipated particularly in cases where the partition constant of a structurally closely related compound is known, and, thus, only the contributions of the parts that are different between the two compounds have to be modified. In recent years, quite sophisticated computer models based on the fragment contribution approach have become available, including Absolv (ACD/Labs), SPARC (SPARC Performs Automated Reasoning in Chemistry; see Hilal et al., 2007), and EPI Suite (Estimation Programs Interface Suite; U.S. EPA, 2012). The most widely used application based on this approach is the structural group contribution method used for estimating octanol–water partition constants (see Chapter 10, Section 10.3).

Single-Parameter Linear Free Energy Relationships (sp-LFERs)

The most simple and widely used approach to predict partition constants is the single-parameter linear free energy relationship (sp-LFER), in which a linear relationship is assumed between the free energies of transfer of a series of compounds in two different two-phase systems:

$$\Delta_{12}G_i = a' \Delta_{34}G_i + b' \quad (7-8)$$

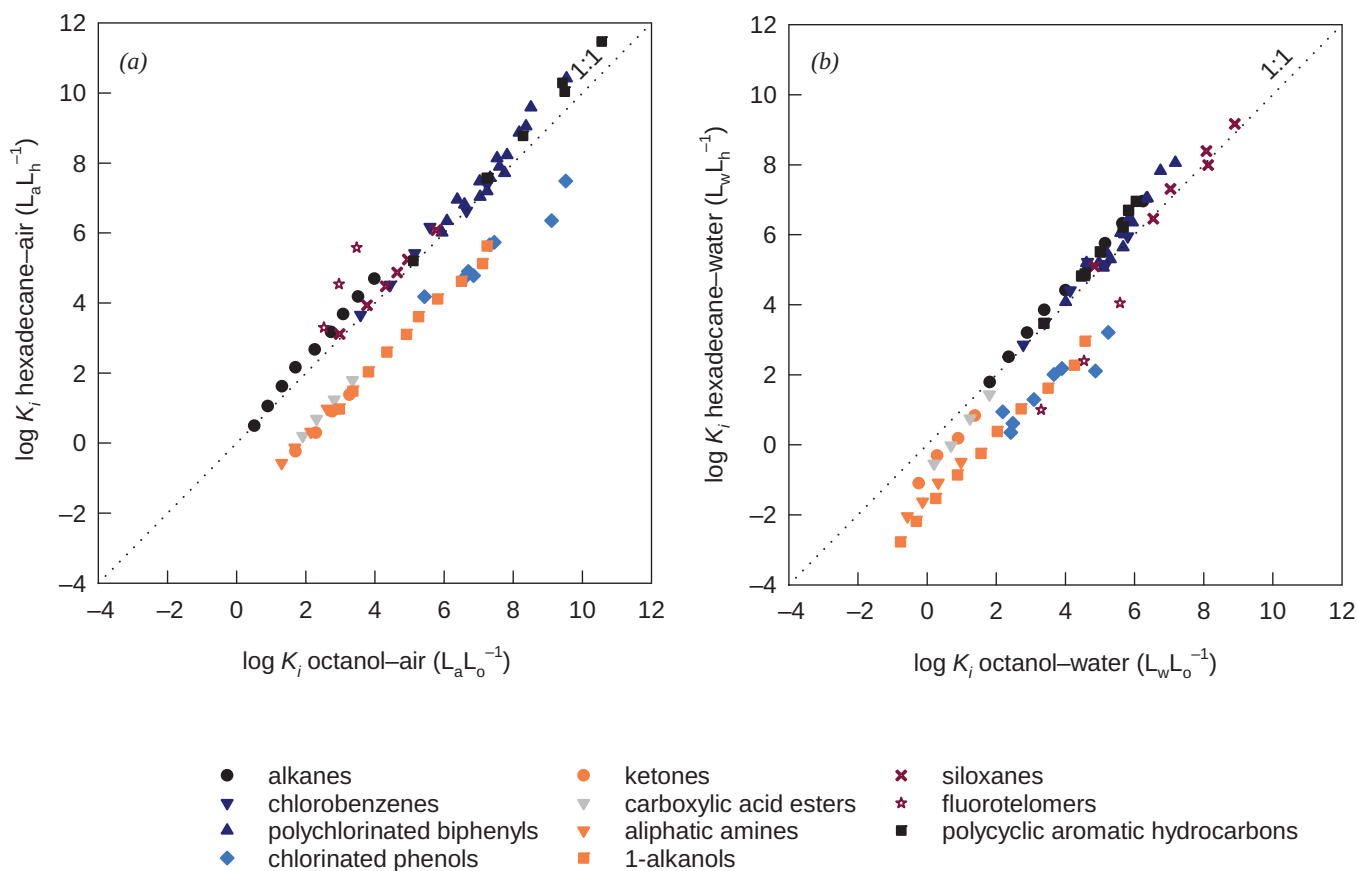
where usually one of the phases is the same in the two systems (e.g., 2 = 4 = water or air, 1 and 3 are two different organic phases). In terms of partition constants or coefficients, Eq. 7-8 can then be written as:

$$\log K_{i12} = a \log K_{i32} + b \quad (7-9)$$

The slope, a , and the constant, b , in Eq. 7-9 are then determined by a linear regression analysis of a set of compounds with known partition constants or coefficients in both systems.

Such sp-LFERs work reasonably well if certain criteria are fulfilled. First, a sp-LFER should only be applied to compounds undergoing similar intermolecular interactions during partitioning as the compounds for which the sp-LFER was derived. This means, for example, one should not expect to assemble a sp-LFER using a set of apolar compounds to predict behaviors of bipolar compounds. Also, the phases 1 and 3 (Eq. 7-9) should be comparable in terms of possible molecular interactions. As an illustration of the importance of these criteria, Fig. 7.3 shows plots of the logarithms of the hexadecane–air versus the octanol–air (K_{ioa}) partition constants (Fig. 7.3a) and the logarithms of the hexadecane–water versus octanol–water (K_{iow}) partition constants (Fig. 7.3b) for different compound classes. As is evident from Fig. 7.3, in

Figure 7.3 Plot of the logarithms of (a) the hexadecane–air ($K_{i\text{hexadecane-air}}$) versus the octanol–air (K_{ioa}) partition constants, and (b) the logarithms of the hexadecane–water ($K_{i\text{hexadecane-water}}$) versus octanol–water (K_{iow}) partition constants at 25°C for our test set.



both cases, no single sp-LFER of the type Eq. 7-9 can fit the whole data set. Good linear relationships can, however, be found for structurally closely related subsets of compounds, such as homologues series of alkanes, aliphatic ketones, esters, amines, 1-alkanols, siloxanes, and fluorotelomers. Highlighting the importance of molecular interactions, the linear relationships seen in Fig. 7.3 are quite different for bipolar compounds capable of H-bonding interactions, such as alcohols, as for apolar compounds only capable of vdW interactions in both phases, such as the *n*-alkanes. Therefore, sp-LFERs of the type seen in Eq. 7-9 need to be applied with necessary caution, but when used properly, they can successfully predict partition constants or coefficients of compounds from known partition constants or coefficients in one of the systems considered. Common applications include the prediction of natural organic matter–air and natural organic matter–water or biological media–air and biological media–water partition coefficients from octanol–air or octanol–water partition constants, respectively, which are discussed in Chapters 13 and 16.

Poly-Parameter Linear Free Energy Relationships (pp-LFERs)

A more generally applicable, yet still simple to use, set of tools for prediction of bulk phase partition constants are the poly-parameter linear free energy relationships (pp-LFERs), sometimes also referred to as the linear solvation energy relationships (LSERs). The goal of this approach is to capture the structural variety of organic compounds and bulk phase characteristics affecting intermolecular interactions in one single equation. The basic concept is to express $\Delta_{12}G_i$ in Eqs. 7-3 or 7-4 by a linear combination of free energy terms explicitly describing cavity formation as well as vdW and H-bonding interactions between the solute and solvent molecules. Kamlet and Taft and later Abraham and co-workers introduced this rather simple approach some decades ago (Kamlet and Taft, 1979; Taft et al., 1985; Abraham, 1993), and it has since been used successfully in numerous applications in analytical and environmental chemistry (see Endo and Goss, 2014a). The Abraham model comprises the following five terms for quantifying the logarithms of liquid–air (Eq. 7-10) and organic liquid–water (Eq. 7-11) partition constants (see Abraham et al., 2004):

$$\log K_{i\ell a} = l_{\ell a}L_i + e_{\ell a}E_i + s_{\ell a}S_i + a_{\ell a}A_i + b_{\ell a}B_i + c \quad (7-10)$$

$$\log K_{i\ell w} = v_{\ell w}V_i + e_{\ell w}E_i + s_{\ell w}S_i + a_{\ell w}A_i + b_{\ell w}B_i + c \quad (7-11)$$

As proposed by Goss (2005), a very similar approach can be used to describe partitioning between any bulk phase involving air, water, and organic liquids:

$$\log K_{i12} = v_{12}V_i + l_{12}L_i + s_{12}S_i + a_{12}A_i + b_{12}B_i + c \quad (7-12)$$

The capital letters in Eqs. 7-10 to 7-12 are compound (solute) descriptors of *i* that are relevant for the partitioning process: the size of the compound (V_i), parameters expressing the compound's "vdW-stickiness" (the excess molar refraction (E_i) or the $\log K_{i\text{hexadecane-air}}$ (L_i), the latter also incorporating the size), H-donor (or electron acceptor) property (A_i), H-acceptor (or electron donor) property (B_i), and a "dipolarity/polarizability" parameter (S_i), which describes the ability of the compound to undergo polar interactions that are not covered by the other parameters. Often, these

solute descriptors are referred to as “Abraham parameters” or LSER parameters. Finally, we should point out that these descriptors describe only enthalpic aspects of partitioning with the exception of the L_i term, which, as we have discussed earlier in Section 7.2, also contains an entropic contribution. The incorporation of entropic considerations is particularly important for systems where one of the phases is a gas, which is why Eq. 7-10 also uses L instead of V .

The small letters in Eqs. 7-10 to 7-12 are the complementary system descriptors characterizing the bulk liquid phases involved. Hence, the first two terms in Eqs. 7-10 to 7-12 (vV , eE or lL) represent the differences between the two bulk phases with respect to the free energy contributions of cavity formation and of the vdW interactions upon introduction of the compound in the cavity. The other three terms (sS , aA , and bB) describe the differences of all polar interactions of the solute with the liquid phase molecules in the two phases. The system descriptors are derived from a multiple linear regression using known partition constants and solute descriptors of a large number (> 50) of chemicals. Because the obtained system descriptors hinge critically on the compounds used for calibration, the selected compounds should represent as wide a structural variability as possible with descriptors that are not cross-correlated. As we see throughout Parts II and III, this requirement is fortunately met for many published pp-LFERs of interest to us.

Among the compound descriptors, some can be independently determined, while others cannot. The size parameter, V_i , can be calculated from the molecular structure (Box 7.2). For scaling reasons, the V_i term is expressed as the volume calculated by the McGowan method (Box 7.2) *divided by 100*. Nevertheless, we use the same notation, V_i . As for the vdW parameters, L_i can be experimentally determined (e.g., Li et al., 2000; Stenzel et al., 2012), and E_i is related to the refractive index (Abraham et al., 1990). The other three polar parameters (S_i , A_i , B_i) cannot be independently determined but can be derived from partition constants measured in a number of well-defined air–solvent or water–solvent systems (e.g., Stenzel et al., 2013a) or from retention data in chromatographic systems using various stationary phases (e.g., Abraham et al., 2004; Poole et al., 2009; Stenzel et al., 2013b). The different solvents or stationary phases are chosen to exhibit characteristically different intermolecular interaction properties. An extensive review of this topic has been recently published by Poole et al. (2013). Currently, complete sets of compound descriptors are publicly available for about 3700 chemicals, compiled and publicly available on the UFZ-LSER database (Endo et al., 2014: [http://www.ufz.de/index.php?en=31698&contentonly=1&lserd_data\[mvc\]=Public/start](http://www.ufz.de/index.php?en=31698&contentonly=1&lserd_data[mvc]=Public/start)). As an illustration of the variety of descriptor values, Table 7.3 summarizes the compound descriptors for our companion compounds. More data can also be found in Appendix C.

As we already pointed out in earlier discussions in Chapter 2 and in Section 7.2, inspection of Table 7.3, and of the much larger data set given in Appendix C, shows that compounds with one or more O or N atoms are strong H-acceptors, and, if they have a H-atom attached to these atoms, they are also strong H-donors. Furthermore, we note again that most monopolar compounds are H-acceptors ($A_i = 0$), a notable exception being CHCl_3 . The dipolar/polarizability parameter S_i assumes high values

Table 7.3 Solute Descriptors (Abraham parameters) for our Companion Compounds (see structures in Table 3.1)

Compound (<i>i</i>)	McGowan molar volume (cm ³ mol ⁻¹)/100 <i>V_i</i>	log <i>K_i</i> _{hexadecane–air} at 25°C <i>L_i</i>	Excess molar Refraction <i>E_i</i>	Dipolarity/ polarizability constant <i>S_i</i>	H-donating parameter <i>A_i</i>	H-accepting parameter <i>B_i</i>
Methyl bromide	0.42	1.63	0.37	0.43	0.00	0.10
PCE	0.84	3.58	0.64	0.44	0.00	0.00
MTBE	0.87	2.38	0.02	0.21	0.00	0.59
Benzene	0.72	2.79	0.61	0.52	0.00	0.14
Phenol	0.78	3.77	0.81	0.89	0.60	0.30
Lindane	1.58	7.57	1.45	1.28	0.00	0.50
Aniline	0.82	3.93	0.96	0.96	0.26	0.41
<i>n</i> -Hexane	0.95	2.67	0.00	0.00	0.00	0.00
TNT	1.38	7.27	1.57	1.78	0.11	0.48
Atrazine	1.62	7.78	1.22	1.29	0.17	1.01
D5	2.93	5.24	−0.70	−0.10	0.00	0.50
PCB 153	2.06	9.59	2.17	1.74	0.00	0.11
PBDE 99	2.26	11.71		1.51	0.00	0.44
Triclosan	1.87	8.96	1.85	1.81	0.92	0.30
DDT	2.22	10.02	1.81	1.76	0.00	0.16
Phenanthrene	1.45	7.58	1.94	1.25	0.00	0.24
Benzo(a)pyrene	1.95	11.47	3.63	1.82	0.00	0.31

(> 0.5) primarily for compounds exhibiting delocalized π -electron systems, in particular aromatic compounds. Also, the presence of chlorine, bromine, or nitro substituents leads to an increased S_i value. We look further into these parameters in the following chapters, when we apply pp-LFERs to various partitioning processes. In most cases, we use Eq. 7-12, which yields comparable, and in some cases even better, results as Eqs. 7-10 and 7-11 (Goss, 2005; Endo and Goss, 2014b). Equation 7-12 has the advantage that only one equation has to be used for describing partitioning from both air and water. Also, even more importantly, Eq. 7-12 allows the direct application of the thermodynamic cycle (e.g. Eq. 7-1) to derive an equation for a two-phase system for which no or little experimental data is available. For example, a pp-LFER for organic phase–air partitioning can be derived from the corresponding pp-LFERs for organic phase–water and air–water partitioning respectively.

We conclude this chapter with an illustrative application of a pp-LFER. We consider the octanol–water system for which the following two equations have been derived from experimental K_{iow} values of a large set of compounds representing a wide structural diversity (Goss, 2005):

$$\log K_{iow} = 2.41 V_i + 0.43 L_i - 1.41 S_i - 0.18 A_i - 3.45 B_i + 0.34 \quad (7-13)$$

(number of chemicals = 314; $r^2 = 0.99$; S.D. = 0.15)

and using E_i instead of L_i (Eq. 7-11) yields:

$$\log K_{iow} = 3.88 V_i + 0.57 E_i - 1.06 S_i - 0.05 A_i - 3.45 B_i + 0.03 \quad (7-14)$$

(number of chemicals = 314; $r^2 = 0.99$; S.D. = 0.15)

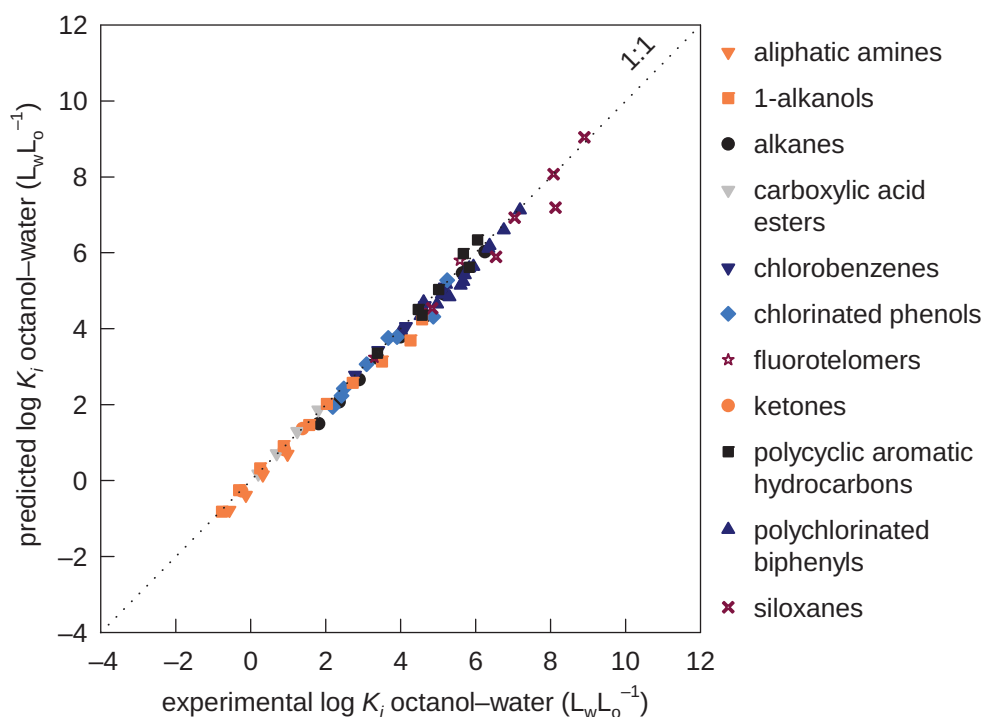


Figure 7.4 Predicted (using Eq. 7-13) versus experimental K_{iow} values of our test set.

Comparison of the two equations shows that when using E_i instead of L_i , the system descriptor for the V_i term has become more prominent, because it is the only term that describes the size of the molecule. In Eq. 7-13, the L_i term represents cavity formation as well as dispersive vdW interactions. Furthermore, the H-bonding terms are virtually identical, which can be expected since substitution of L_i by E_i has an influence only on how the dispersive vdW interactions are described. Finally, since S_i and E_i are not completely unrelated, the relative magnitudes of the S_i term in the two equations cannot be easily interpreted.

In Fig. 7.4, the $\log K_{iow}$ values calculated from Eq. 7-13 for the set of compounds already used in Figs. 7.2 and 7.3 are plotted against their experimental $\log K_{iow}$ values. As is evident, compared to sp-LFERs, this conceptually simple pp-LFER is a powerful tool to predict octanol–water partition constants of a very diverse set of apolar, monopolar, and bipolar compounds. A comparable result is obtained when using Eq. 7-14 instead of Eq. 7-13 (data not shown). Predictions within a factor of 2 to 3 (0.3 to 0.5 log units) are possible (see examples in Table 7.4). Eq. 7-13 also allows us to evaluate, at least semi-quantitatively, the relative contributions of the various free energy terms to the overall free energy of partitioning. In this case, we consider partitioning between two liquid phases, and the coefficients (system descriptors) in Eq. 7-13 represent the differences in the free energy terms between the two solvents, that is, the difference in cavity formation energies and the differences in free energy gains when introducing the organic molecule in the cavity, as expressed in Eq. 7-4.

Inspection of Eq. 7-13 and Table 7.4 shows that the first two terms favor partitioning into octanol, a finding attributable primarily to the hydrophobic effect (see

Table 7.4 Contribution of the Different Terms in Eq. 7-13 to the Overall Octanol–Water Partition Constant of Some Selected Compounds ^a

Compound	log K_{iow} exp.	log K_{iow} calc.	+2.41 V_i	+0.43 L_i	−1.41 S_i	−0.18 A_i	−3.45 B_i	+0.34
MTBE	0.94	1.13	+2.10	+1.02	−0.30	0.00	−2.04	+0.34
Benzene	2.17	2.06	+1.74	+1.20	−0.73	0.00	−0.48	+0.34
<i>n</i> -Hexane	4.00	3.78	+2.29	+1.15	0.00	0.00	0.00	+0.34
Atrazine	2.65	2.26	+3.90	+3.35	−1.82	−0.03	−3.48	+0.34
8:2 FTOH	5.58	5.80	+5.35	+1.49	−0.20	−0.11	−1.07	+0.34
D5	8.08	8.07	+7.06	+2.25	+0.14	0.00	−1.73	+0.34
PCB 153	6.75	6.60	+4.96	+4.12	−2.45	0.00	−0.38	+0.34
PBDE 99	7.32	7.17	+5.45	+5.04	−2.13	0.00	−1.52	+0.34
Triclosan	4.78	4.95	+4.51	+3.85	−2.55	−0.17	−1.04	+0.34
Benzo(a)pyrene	6.05	6.34	+4.70	+4.93	−2.57	0.00	−1.07	+0.34

^a The solute parameters of the compounds are given in Table 7.3.

Chapter 10). In particular, the volume term (vV_i) reflects the large difference in cohesion energies between octanol and water. Since S_i , A_i , and B_i are all zero or positive (exception: the S_i values of the siloxanes are slightly negative), the three “polar” terms are either not relevant or favor the aqueous phase. A striking feature of Eq. 7-13 is that the coefficients (system descriptors) of the terms describing H-bonding are very different (−0.18 versus −3.45). This distinction indicates that, relative to octanol, the H-donor properties of water are much more important than its H-acceptor properties when partitioning an organic molecule between these two liquids. Hence, the polar terms (sS , aA , and bB) are particularly important for compounds exhibiting high S_i and/or B_i values. For example, when comparing the various terms for the three gasoline components MTBE, benzene, and *n*-hexane, we can see that they exhibit very similar size and vdW terms (vV and lL), but differ significantly in the polar terms. As a result, the K_{iow} of MTBE is three orders of magnitude smaller than that of *n*-hexane, which is primarily due to the strong H-accepting properties of MTBE. The two orders of magnitude smaller K_{iow} of benzene as compared to *n*-hexane is a result of benzene’s moderate polarizability/dipolarity and weak hydrogen accepting properties. A somewhat unexpected finding is that the herbicide atrazine, and other triazines, have strong H-accepting properties but low H-donating properties, although they contain two N-H groups (Abraham et al., 2007).

7.4 Questions

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.

Q7.1

What are the prerequisites for a proper application of the thermodynamic cycle to calculate a partition constant from two other partition constants, such as, for example, the octanol–air partition constant from the octanol–water and air–water partition

constants? Can you think of an example where the thermodynamic cycle may not be applied at all?

Q 7.2

What is the difference between a partition constant, a partition coefficient, and a distribution ratio?

Q 7.3

Explain the different free energy terms considered when applying the simple cavity model to describe (a) bulk liquid–air partitioning, and (b) partitioning between two bulk liquids. Which thermodynamics entities do you always have to keep in mind when talking about free energy contributions?

Q 7.4

Estimate the molar volumes in $\text{cm}^3 \text{mol}^{-1}$ of the following companion compounds using the McGowan method described in Box 7.2: methyl-*t*-butyl ether (MTBE), γ -HCH (lindane), atrazine, decamethylcyclopentasiloxane (D5), and phenanthrene.

Q 7.5

Assign the following equilibrium solvent–air partitioning processes of the following compounds to the appropriate case (cases I to IV) defined when discussing Eq. 7-3.

	solvent	solute
(a)	dichloromethane	methyl- <i>t</i> -butyl ether
(b)	tetrachloroethene	perfluorooctylethanol (8:2 FTOH)
(c)	diethyl ether	17 α -ethinylestradiol
(d)	octanol	PCB 153
(e)	ethanol	atrazine
(f)	toluene	PBDE 99
(g)	hexane	triclosan
(h)	chloroform	4-nonylphenol
(i)	ethyl acetate	phenanthrene
(j)	water	<i>n</i> -decane

Q 7.6

Explain the following observations made when inspecting Fig. 7.2:

(a) The organic solvent–air partition constants increase with size of the compound (Figs. 7.2*a* and *b*), whereas for the water–air partition constants (Fig. 7.2*c*) a much smaller, and in some cases even negative, trend is observed.

(b) The organic solvent–air partition constants of the fluorotelomer alcohols and of the siloxanes increase much less with size as compared to all other compound classes (Figs. 7.2*a* and *b*).

(c) The difference between the hexadecane–air partition constants (Fig. 7.2a) of a homologues series of alkanes and the corresponding 1-alkanols is rather small, whereas for the octanol–air partition constants (Fig. 7.2b), this difference is more than two orders of magnitude.

(d) The octanol–air partition constants of the 1-alkanols are more than two orders of magnitude larger than those of the n-alkanes (Fig. 7.2b), exactly the opposite is true for the octanol–water partition constants (Fig. 7.2d).

Q7.7

What is the basic concept of a linear free-energy relationships (LFERs) for estimating partition constants? What are the main differences between the fragment contribution method, single-parameter LFER, and poly-parameter LFER? List advantages and disadvantages of each of these three approaches.

Q7.8

Discuss the role of the compound descriptors used in the pp-LFERs Eqs. 7-10 to 7-12, and given for the companion compounds in Table 7.3. Which ones can be determined independently and which have to be derived experimentally?

Q7.9

How are the system parameters (small letters in Eqs. 7-10 to 7-12) determined for a given system? What determines the applicability range of a thus derived pp-LFER?

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