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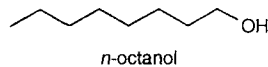
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6.1 Introduction

The transfer of chemicals between air and aqueous phases is one of the key processes affecting the fates of many organic compounds in the environment. Examples include exchanges of volatile and semivolatile compounds between air and rain or fog droplets, between the atmosphere and rivers, lakes, or the oceans, and between residual soil water and soil gases below ground. Additionally, we are sometimes interested in the transfers of organic chemicals from other bulk liquids to neighboring gas phases. An example involves the evaporation of benzene from gasoline. In all of these instances, we need to know the equilibrium distribution constant or coefficient of the substance partitioning between the liquid and gas phases of interest.

In light of our discussions of the molecular factors determining excess free energies of organic compounds in gas phases (Chapter 4) and in liquid phases (particularly in aqueous phases, Chapter 5), we are now in a good position to understand equilibrium partitioning of organic compounds between air and bulk liquids. In this chapter, we will focus on air–water partitioning (Section 6.4). But before we do this, we will first examine the equilibrium partitioning of organic compounds between air and various organic liquids (Section 6.3). In addition to having instances where such partitioning is important, we can use these partitioning data to further illustrate how chemical structure controls chemical behavior. By comparing air/liquid partition constants of model compounds interacting with solvents ranging from apolar (e.g., hexane, hexadecane) to bipolar (e.g., methanol, ethylene glycol), we can deepen our understanding of the molecular factors that govern partitioning processes involving bulk liquid organic phases. This will be of importance later in our discussions of partitioning processes involving natural organic phases, including natural organic matter (Chapter 9) as well as organic phases present in living organisms (Chapter 10).



At this point, we note that one particular organic solvent, *n*-octanol, is still widely used as a surrogate for many natural organic phases. The air–octanol partition constant (see below) and the octanol–water partition constant (Chapter 7) of a compound have been extremely popular parameters for relating partition coefficients involving natural organic phases by applying simple one-parameter LFERs (see examples given in Table 3.5). Hence, to put us in the position to critically analyze such LFERs, it is necessary that we learn more about the properties of this “famous” solvent.

We begin, however, our discussion of air/liquid phase partitioning by reiterating some general thermodynamic considerations that we will need throughout this chapter.

6.2 Thermodynamic Considerations

Raoult's Law

Assuming ideal gas behavior, the equilibrium partial pressure, p_i , of a compound above a liquid solution or liquid mixture is a direct measure of the fugacity, $\mathcal{F}_{i\ell}$, of that compound in the liquid phase (see Fig. 3.9 and Eq. 3-33).

Note that we make a distinction between a solution and a mixture. When we talk of a solution, we imply that the organic solute is not a major component of the bulk liquid. Therefore, that presence of a dissolved organic compound does not have a significant impact on the properties of the bulk liquid. In contrast, in a mixture we recognize that the major components contribute substantially to the overall nature of the medium. This is reflected in macroscopic properties like air–liquid surface tensions and in molecule-scale phenomena like solubilities of trace constituents.

In any case, we may write the equilibrium condition (Eq. 3-33):

$$\mathcal{F}_{i\ell} = p_i = \gamma_{i\ell} \cdot x_{i\ell} \cdot p_{iL}^* \quad (6-1)$$

Let us now consider two special cases. In the first case, we assume that the compound of interest forms an *ideal* solution or mixture with the solvent or the liquid mixture, respectively. In assuming this, we are asserting that the chemical enjoys the same set of intermolecular interactions and freedoms that it has when it was “dissolved in a liquid of itself” (reference state). This means that $\gamma_{i\ell}$ is equal to 1, and, therefore, for any solution or mixture composition, the fugacity (or the partial pressure of the compound i above the liquid) is simply given by:

$$\mathcal{F}_{i\ell} = p_i = x_{i\ell} \cdot p_{iL}^* \quad (6-2)$$

Eq. 6-2 is known as *Raoult's Law*.

In some cases of organic mixtures, we can apply Eq. 6-2 without too much inaccuracy; however, assuming that $\gamma_{i\ell}$ is equal to 1 can be quite inappropriate in many other cases (see Section 7.5).

Henry's Law and the Henry's Law Constant

In this chapter we will focus on another special case, that is, the case in which we assume that $\gamma_{i\ell}$ is different from 1 *but is constant over the concentration range considered*. This situation is primarily met when we are dealing with dilute solutions. As we have seen for the solvent water (Table 5.2), for many organic compounds of interest to us, γ_{iw} does not vary much with concentration, even up to saturated solutions. Hence, for our treatment of air–water partitioning, as well as for our examples of air/organic solvent partitioning at dilute conditions, we will assume that $\gamma_{i\ell}$ is constant. This allows us to modify Eq. 6-1 to a form known as *Henry's Law*:

$$\mathcal{F}_{i\ell} = p_i = \gamma_{i\ell} \cdot p_{iL}^* \cdot x_{i\ell} = K'_{iH}(\ell) \cdot x_{i\ell} \quad (6-3)$$

$$K'_{iH}(\ell) = \frac{p_i}{x_{i\ell}} = \gamma_{i\ell} \cdot p_{iL}^* = \text{constant} \quad (6-4)$$

where $K'_{iH}(\ell)$ is the *Henry's Law Constant* of solute i for the solvent ℓ . Note that we use the superscript prime to indicate that the equilibrium partition constant is expressed on a partial pressure and mole fraction basis, as was originally done by Henry (Atkins, 1998). Hence when we give a numerical value for $K'_{iH}(\ell)$, we have to express it as fraction of the standard pressure (which is 1 bar).

In the environmental chemistry literature, it is common to refer to “the” Henry’s Law constant of a given compound when the solvent in question is water. In the following, we will adopt this nomenclature and denote the air–water partition constant as defined by Eq. 6-4 simply as K'_{iH} (i.e., we omit to indicate the solvent).

Two other common ways of expressing air–liquid equilibrium partitioning are to use molar concentrations for i (i.e., $\text{mol} \cdot \text{L}^{-1}$), either only in the liquid or in both the liquid and the gas phase. In the first case, we simply have to convert mole fractions to molar concentrations (Eq. 3-43):

$$K_{iH}(\ell) = \frac{p_i}{C_{i\ell}} = K'_{iH}(\ell) \cdot \bar{V}_\ell = \gamma_{i\ell} \cdot p_{iL}^* \cdot \bar{V}_\ell \quad (6-5)$$

where \bar{V}_ℓ is the molar volume of the bulk liquid (e.g., in $\text{L} \cdot \text{mol}^{-1}$), and $K_{iH}(\ell)$ (no prime superscript) now has units like $(\text{bar} \cdot \text{L} \cdot \text{mol}^{-1})$ or $(\text{Pa} \cdot \text{L} \cdot \text{mol}^{-1})$. Note again that when pure water is the solvent, we denote $K_{iH}(\ell)$ simply as K_{iH} . Furthermore, we should point out that, particularly in the engineering literature but also in many handbooks, K_{iH} values are often given in units of $(\text{Pa} \cdot \text{m}^3 \text{mol}^{-1})$. In this case, the liquid phase concentration is in units of $(\text{mol} \cdot \text{m}^{-3})$. No matter in what units we express this parameter, it always reflects the same relative concentrations of the partitioning chemical in the gaseous and liquid phases.

For practical applications, such as for assessing the equilibrium distribution of a given compound in a multiphase system, it is most convenient to use a “dimensionless” air–solvent partition constant. This form uses molar concentrations in both phases. In this case, we denote the air–liquid partition constant as $K_{ia\ell}$. Since $C_{ia} = p_i / RT$ (Section 3.2), we then obtain:

$$K_{ia\ell} = \frac{C_{ia}}{C_{i\ell}} = K_{iH}(\ell) / RT = \gamma_{i\ell} \cdot \bar{V}_\ell \cdot p_{iL}^* / RT \quad (6-6)$$

If $K_{ia\ell}$ and p_{iL}^* are known for a given compound, that chemical’s activity coefficient (and thus its excess free energy via Eq. 3-37) in the liquid phase can be calculated:

$$\gamma_{i\ell} = K_{ia\ell} \cdot \frac{RT}{\bar{V}_\ell \cdot p_{iL}^*} \quad (6-7)$$

Note that many of the activity coefficients of organic compounds in dilute aqueous solution, γ_{iw}^∞ , that we used in Chapter 5 were derived from experimental air–water partition constants (K_{iaw}) using Eq. 6-7. Finally, we should point out that in the literature, similar to air–solid surface partitioning (Section 11.1), partition constants are quite often reported as the reciprocal quantity of the *air–solvent* partition constants as defined above, that is, as *solvent–air* partition constants. However, it does not really matter in what form such constants are given, as long as we pay

careful attention to how they are defined, the temperature at which they are given and the units of concentration that are used.

Effect of Temperature on Air–Liquid Partitioning

Temperature influences air–bulk liquid partitioning of a compound i chiefly in two ways: (1) by its effect on the activity coefficient of the compound in the liquid phase and (2) by its effect on the compound’s liquid vapor pressure. In the cases where Henry’s law applies (Eq. 6-4), for a narrow temperature range, we may write the familiar relationship (Section 3.4):

$$\ln K'_{iH}(\ell) = -\frac{\Delta_{al}H_i}{R} \cdot \frac{1}{T} + \text{constant} \quad (6-8)$$

where $\Delta_{al}H_i$ is the standard enthalpy of transfer of i from the liquid to the gas phase. This enthalpy change is given by the difference between the excess enthalpy of the compound in the gas phase ($H_{ig}^E \equiv \Delta_{vap}H_i$) and in the liquid phase (H_{il}^E):

$$\Delta_{al}H_i = \Delta_{vap}H_i - H_{il}^E \quad (6-9)$$

Hence, if no experimental value for $\Delta_{al}H_i$ is available (i.e., from measurements of $K'_{iH}(\ell)$ at different temperatures), it can be obtained from experimental (or estimated) $\Delta_{vap}H_i$ and H_{il}^E values. Finally, we should note that Eq. 6-8 applies in a strict sense only if we express the amount of the compound in the gas and liquid phase as partial pressure and mole fraction, respectively. However, if we assume that the molar volume of the liquid, \bar{V}_ℓ , is not significantly affected by temperature changes, we may also apply Eq. 6-8 to describe the temperature dependence of $K_{iH}(\ell)$ (Eq. 6-5) with a constant term that is given by “constant + $\ln \bar{V}_\ell$.” Furthermore, if we express the amount of the compound in the gas phase in molar concentrations (Eq. 6-6), then we have to add the term RT_{av} to $\Delta_{al}H_i$ where T_{av} (in K) is the average temperature of the temperature range considered (see Section 3.4):

$$\ln K_{ial} = -\frac{\Delta_{al}H_i + RT_{av}}{R} \cdot \frac{1}{T} + \text{constant} \quad (6-10)$$

6.3 Air–Organic Solvent Partitioning

Air–Organic Solvent and Other Partition Constants

Now we turn our attention to the equilibrium constants, K_{ial} , that quantify the partitioning of organic compounds between air and various liquids of very diverse solvent characteristics. As discussed in Chapter 3, the air–liquid partitioning behaviors of organic compounds differ greatly when comparing an apolar organic solvent like n -hexadecane with the polar solvent water (Fig. 3.6). This stems from the differences in *solute:solvent* and *solvent:solvent* molecular interactions, and we have introduced a mathematical model to sum the effects of these interaction energies (Eqs. 4-26 and 5-21).

Since thermodynamic properties are independent of the reaction pathway and only depend on the starting and ending conditions, we know that the partitioning of

organic chemicals between air and liquids can be related to other equilibrium processes (Fig. 6.1). For example, there is a direct relationship between a chemical's air–organic solvent partition constant ($K_{ia\ell}$), its partitioning between air and water (K_{iaw}), and its organic solvent–water partition constant ($K_{i\ell w}$), provided that we consider only the water-saturated (i.e. “wet”) organic phase:

$$K_{ia\ell} \left(= \frac{C_{ia}}{C_{i\ell}} \right) = \frac{K_{iaw} (= C_{ia} / C_{iw})}{K_{i\ell w} (= C_{i\ell} / C_{iw})} \quad (6-11)$$

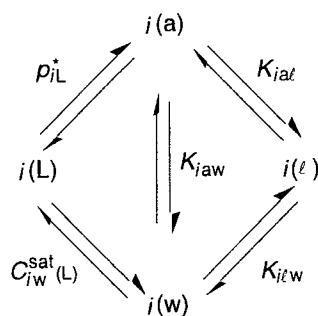


Figure 6.1 Partitioning processes for a chemical, i , considered in Chapters 3 to 7. a = air (gas phase), ℓ = water-immiscible organic solvent, L = pure liquid organic compound, and w = aqueous phase.

This brings up an important question. To what extent is the $K_{ia\ell}$ value that has been determined experimentally using the “dry” organic solvents different from the value calculated from the air–water and organic solvent–water partition constants (Eq. 6-11)? Several methods yield such equilibrium constants, including use of head space analysis (Park et al., 1987), chromatographic techniques (Gruber et al., 1997), generator columns (Harner and Mackay, 1995; Harner and Bidleman, 1998a), or a fugacity meter (Kömp and McLachlan, 1997a). In order to answer this question, we have to evaluate how the cross “contaminations” of the organic solvent with water and of the water with organic solvent affect the activity coefficients of the compound of interest in both the organic and aqueous phases. Also, these solvent modifications may affect the molar volumes of the liquids. For pure nonpolar organic solvents that are only sparingly soluble in water and contain only very little water at saturation (e.g., $x_L > 0.99$, Table 5.1), we may justifiably neglect such molar volume effects. However, for more polar solvents the situation is not so clear. For example, if we use n -octanol as the organic solvent, there will be roughly one water molecule for every four octanol molecules in the organic phase at equilibrium with water ($x_L \cong 0.8$, Table 5.1). This means that the molar volume of “dry” octanol ($\bar{V}_\ell = 0.16 \text{ L} \cdot \text{mol}^{-1}$) is about 20% larger than that of “wet” octanol ($\bar{V}_\ell \cong 0.13 \text{ L} \cdot \text{mol}^{-1}$). In contrast, there will be only about one octanol molecule for every 10,000 water molecules in octanol-saturated water. This has no significant impact on the molar volume of the aqueous phase.

Furthermore, for most compounds of interest to us, the octanol molecules present as cosolutes in the aqueous phase will have only a minor effect on the other organic compounds' activity coefficients. Also, the activity coefficients of a series of apolar, monopolar, and bipolar compounds in wet versus dry octanol shows that, in most cases, $\gamma_{i\ell}$ values changes by less than a factor of 2 to 3 when water is present in wet octanol (Dallas and Carr, 1992; Sherman et al., 1996; Kömp and McLachlan, 1997a). Hence, as a first approximation, for nonpolar solvents, for n -octanol, and possibly for other solvents exhibiting polar groups, we may use Eq. 6-11 as a first approximation to estimate air–“dry” organic solvent partition constants for organic compounds as illustrated in Fig. 6.2. Conversely, experimental $K_{ia\ell}$ data may be used to estimate K_{iaw} or $K_{i\ell w}$, if one or the other of these two constants is known.

Comparison of Different Organic Solvents

Let us now evaluate how the $K_{ia\ell}$ values of different compounds are affected by the chemical nature of the organic solvent. To this end, we consider a set of five model compounds (Fig. 6.3) exhibiting very different structures that enable them to

Figure 6.2 Experimentally determined air–“dry octanol” partition constants versus calculated (Eq. 6-11) air–“wet octanol” partition constants. Data from Harner and Mackay (1995), Gruber et al. (1997), Harner and Bidleman (1998a,b), Abraham et al. (2001).

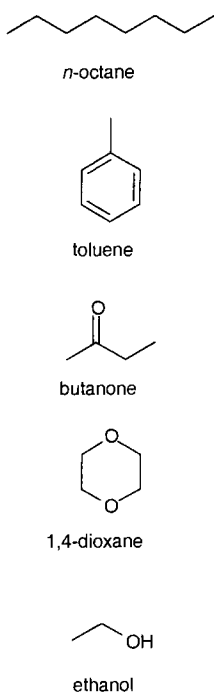
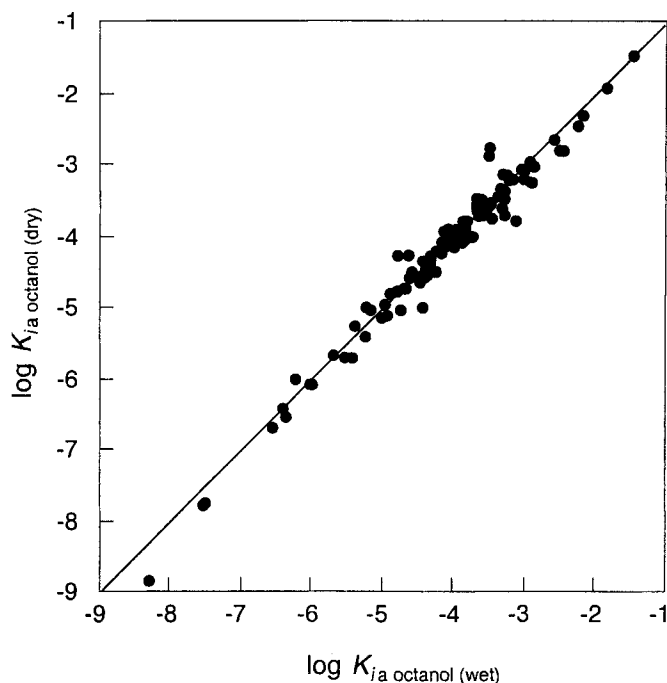


Figure 6.3 Structures of the model compounds used for evaluating partitioning in various air–solvent systems.

participate to varying degrees in dispersive, dipole:dipole, dipole:induced dipole, H-donor, and H-acceptor interactions (Tables 4.3 and 5.4). For these compounds, the $K_{ia\ell}$ values have been determined for six organic solvents that differ quite substantially in “polarity” (Table 6.1; Park et al., 1987). Note that the parameters π_i , α_i , and β_i used to characterize *solutes* cannot be directly used to describe *solvent* properties. Nevertheless, they provide a qualitative measure of the interactions that molecules of a given organic solvent may undergo. Thus, the solvent hexadecane and toluene can be classified as apolar and weakly monopolar, respectively. Dichloromethane represents a solvent with some H-donor character, in addition to participating in dispersive and polar/polarizable interactions. And *n*-octanol, methanol, and ethylene glycol are H-donor as well as H-acceptor solvents of increasing polarity. Also note that these solvents exhibit quite different molar volumes (e.g., $\bar{V}_{\text{hexadecane}} = 0.293 \text{ L}\cdot\text{mol}^{-1}$, $\bar{V}_{\text{methanol}} = 0.040 \text{ L}\cdot\text{mol}^{-1}$). This has a significant influence on the absolute values of the corresponding $K_{ia\ell}$ ’s of a given compound in the various solvents (Eq. 6-6). Nevertheless, for visualizing the effects of solvation of the compounds in the various solvents, we can use these air–solvent partition constants instead of the corresponding $K_{iH}(\ell)$ values (Eq. 6-4), which would be directly related to the $\Delta_{a\ell}G_i$ values.

In the air–organic solvent combinations considered in Table 6.1, all of these compounds partition favorably into the organic phase (i.e., $K_{ia\ell} \ll 1$). This is even true for the partitioning of the bipolar chemical, ethanol, into the apolar solvent, hexadecane. Even more importantly, it is true for the apolar solute, *n*-octane, dissolving into the highly bipolar solvent, ethylene glycol. Note that this glycol derivative represents one of the most “water-like” organic solvents (Table 5.8). The latter finding illustrates again the unique properties of the solvent water, since in water, the activity coefficient of *n*-octane is about 10^7 (Chapter 5) as compared to

Table 6.1 Measured Air–Solvent Partition Constants ($K_{i,air}$) and Calculated Activity Coefficients ($\gamma_{i,l}$, Eq. 6-7) at 25°C of Five Model Compounds Exhibiting Different H-Donor, H-Acceptor, and Polarity/Polarizability Properties for Some Organic Solvents

Compound i ^b	$\log p_{i,l}^*/\text{Pa}$	Solvent l : $\log K_{i,air}$ ($\gamma_{i,l}$ in parentheses) ^a					
		Hexadecane (apolar)	Toluene (monopolar, H-A)	Dichloromethane (bipolar, primarily H-D)	<i>n</i> -Octanol (bipolar)	Methanol (bipolar)	Ethylene glycol (bipolar)
<i>n</i> -Octane	3.27	-3.7 (0.92)	-3.9 (1.7)	-3.7 (4.1)	-3.4 (3.2)	-2.9 (46)	-1.1 (1800)
Toluene	3.58	-3.4 (0.96)	-3.8 (1.0)	-4.0 (0.96)	-3.3 (2.0)	-3.2 (10)	-2.4 (52)
Butanone	4.10	-2.3 (3.2)	-3.1 (1.4)	-3.9 (0.44)	-2.8 (2.1)	-3.3 (2.5)	-2.6 (8.4)
1,4-Dioxane	3.69	-2.9 (2.4)	-3.6 (1.2)	-4.3 (0.42)	-3.2 (2.1)	-3.6 (3.4)	-3.3 (4.9)
Ethanol	3.90	-1.5 (35)	-2.3 (15)	-2.7 (9.2)	-3.2 (1.1)	-3.9 (1.01)	-3.5 (1.9)

^a Data from Park et al. (1987). ^b The structures are given in Fig. 6.3.

only 1800 in ethylene glycol. In general, with few exceptions (e.g., ethanol), we may assume that the activity coefficient of most organic compounds in an organic solvent will be much smaller than their γ_{iw} values. In many cases, $\gamma_{i\ell}$ is less than 100 or even less than 10. Consequently, compounds with very small liquid–vapor pressures will also exhibit very small $K_{ia\ell}$ values. This is, of course, not a surprising result because p_{iL}^* is itself an air–organic solvent partition constant. Hence, like vapor pressure, the air–organic solvent partition constants may vary by many orders of magnitude within a compound class. This contrasts the air–water partition constants for the same sets of compounds. Such chemically related groups of compounds commonly have K_{iaw} values that span a much more narrow range (Section 6.4). Finally, we should note that these findings also indicate that, in the environment, we may anticipate that most of the chemicals of interest to us will partition favorably from the air into condensed natural organic phases (see Chapters 10 and 11).

LFERs Relating Partition Constants in Different Air–Solvent Systems

Another important lesson that we can learn from the data presented in Table 6.1 is that the activity coefficient of an organic compound in an organic solvent depends strongly on the prospective involvements of both the partitioning compound *and* the solvent for dispersive, dipolar, H-donor, and H-acceptor intermolecular interactions. This implies that we may need to represent the properties of both the solute and the solvent when we seek to correlate air–liquid partition constants of structurally diverse substances. Thus, if the types of intermolecular interactions of a variety of solutes interacting with two chemically distinct solvents 1 and 2 are very different, a one-parameter LFER for all compounds, i , of the form:

$$\log K_{ia1} = a \cdot \log K_{ia2} + b \quad (6-12)$$

is inadequate to correlate partition constants (Fig. 6.4). For example, hexadecane interacts only via vdW forces with all partitioning substances. Thus, solute interactions with this hydrocarbon and the corresponding $K_{ia\ell}$ values will reflect only these energies. Another solvent like octanol may, however, participate in various combinations of dispersive, polar, H-acceptor, and H-donor interactions with solutes of diverse structures. Thus the $K_{ia\ell}$ values for octanol may involve a sum of effects. These sums of intermolecular attractions may not correlate with the vdW-alone interactions that hexadecane can offer.

Recalling our earlier discussions of one-parameter LFERs (Section 5.3), we should be able to predict when we can anticipate that Eq. 6-12 is applicable to a given set of compounds and solvents. Obviously, if we consider two apolar solvents (e.g., cyclohexane and hexadecane) where chiefly dispersive interactions predominate between these solvents and all solute molecules, then we can expect to find an LFER encompassing apolar, monopolar, and bipolar compounds (e.g., Fig. 6.5). Furthermore, we can also anticipate success developing an LFER when combining different types of compounds partitioning into two closely related polar solvents (e.g., methanol and ethanol). In this case, we can assume that the contributions to the excess free energies of solution in both solvents are due to very similar polar interactions in the two solvents (e.g., Fig. 6.6). Finally, if two solvents are considered that exhibit rather different abilities to interact through polar mechanisms,

Figure 6.4 Plots of $\log K_{ia\ell}$ versus $\log K_{ia\text{octanol}}$ for the model compounds and solvents listed in Table 6.1. Data for 25°C. Note the different scales on the x- and y-axes.

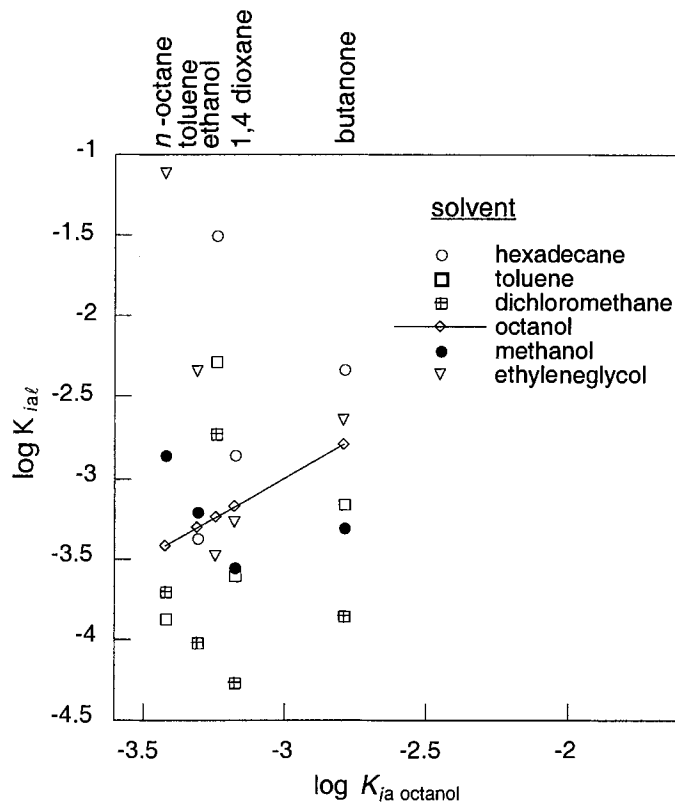
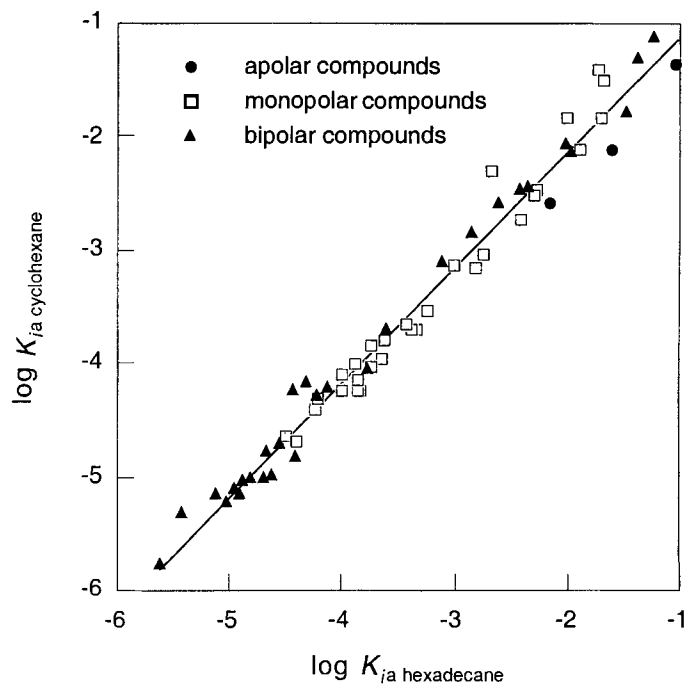


Figure 6.5 Plot of the decadic logarithms of the air–cyclohexane versus the air–hexadecane partition constants of a series of apolar, monopolar, and bipolar compounds. Data from Abraham et al. (1994b).



we can expect LFERs to hold only for strictly apolar compounds or for closely related sets of polar compounds. Let us, for example, consider air–olive oil partitioning versus air–octanol partitioning of a range of compounds. The polar groups in olive

Figure 6.6 Plots of the decadic logarithms of the air–methanol partition coefficients versus the air–ethanol partition constants of a series of apolar, monopolar, and bipolar compounds. Data from Tiegs et al. (1986) and Abraham et al. (1998 and 1999).

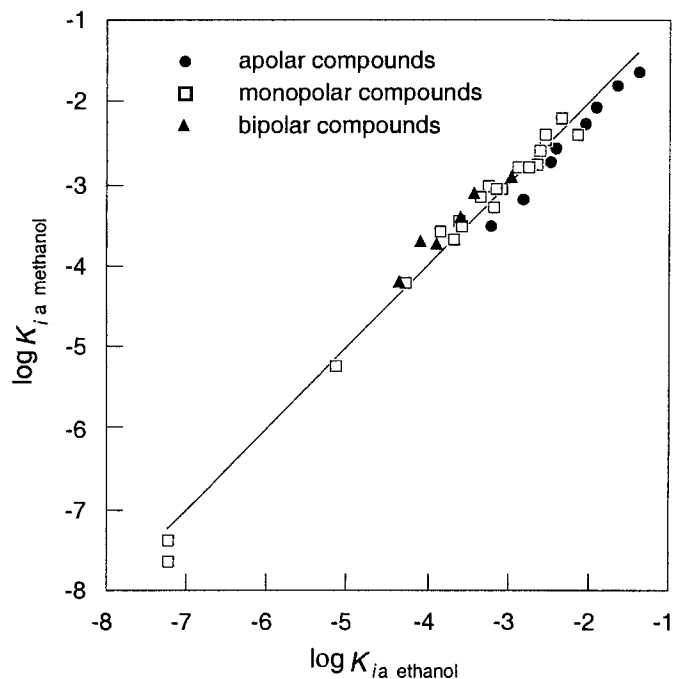
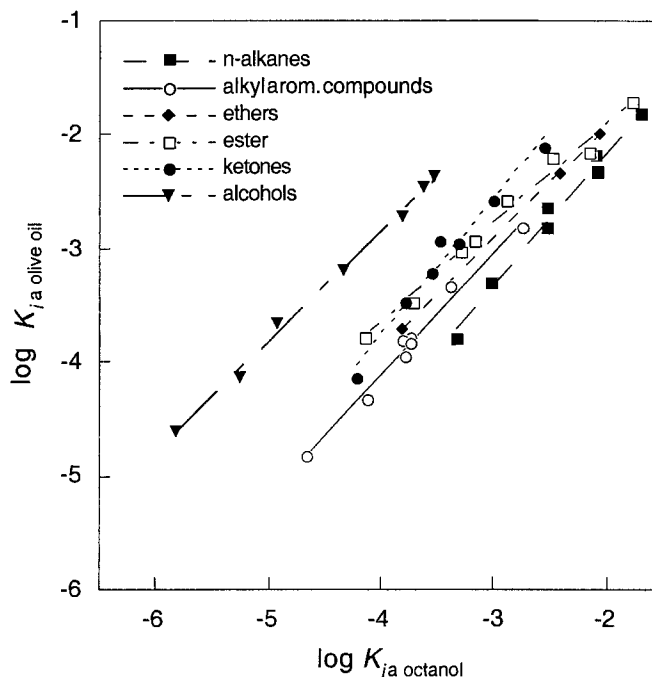
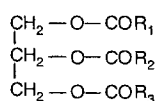


Figure 6.7 Plot of the decadic logarithms of the air–olive oil partition coefficients versus the air–octanol partition constants for various sets of structurally related apolar, monopolar, and bipolar compounds. Note that olive oil is a mixture of compounds that may vary in composition. Therefore, we refer to $K_{ia \text{ olive oil}}$ as the air–olive oil partition coefficient (and not constant, see Box 3.2). Adapted from Goss and Schwarzenbach (2001). The a and b values for the LFERs (Eq. 6-12) are: alkanes ($a = 1.15$, $b = 0.16$), alkyl aromatic compounds ($a = 1.08$, $b = 0.22$), ethers ($a = 0.97$, $b = 0.01$), esters ($a = 0.88$, $b = -0.14$), ketones ($a = 1.21$, $b = 1.06$), alcohols ($a = 0.98$, $b = 1.07$).



oil are monopolar carboxylic acid esters (see margin), while *n*-octanol is a bipolar solvent. As demonstrated in Fig. 6.7, good LFERs are found for sets of compounds involving homologues (i.e., compounds differing only by the number of $-\text{CH}_2-$ units) or families of compounds for which the polar properties change proportionally with size (e.g., PAHs; see also Section 5.3). Of course, we may be able to combine various sets of compounds that are not too different in polarity into one LFER (e.g., the ethers and esters in Fig. 6.7) with only limited loss in precision.



General structure of olive oil, R_1 , R_2 , $R_3 = \text{C}_{14}$, C_{16} , C_{18} saturated or unsaturated (for details see Hui, 1996).

Model for Description of Air–Solvent Partitioning

We previously used our insights regarding the solute:water and water:water intermolecular interactions to assemble a mathematical model for estimating a compound's aqueous activity coefficient (Section 5.3, Eqs. 5-19 to 5-22). Now we can easily modify this model for the prediction of air–organic solvent partitioning. First, since K_{ial} is proportional to the product, $\gamma_{il} \cdot p_{il}^*$ (Eq. 6-6), we can remove the $-\ln p_{il}^*$ term in Eq. 5-21 (which reflects the free energy of transfer from the pure liquid to the gas phase). Next, we do not need to include a specific volume term. This was previously included to account for the large entropy costs associated with inserting an organic solute into bulk water (i.e., forming the solute cavity). In organic solvents the free energy costs for creating a cavity are much smaller than in water, and they are not a dominating contribution to the overall $\Delta_{al}G_i$. Furthermore, the cavity term is proportional to the size of the molecule and, therefore, correlates with the dispersive energy term. Hence, for organic solvents, by analogy to Eq. 5-21, we may express $\log K_{ial}$ as:

$$\ln K_{ial} = s \left[V_{ix}^{2/3} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right] + p(\pi_i) + a(\alpha_i) + b(\beta_i) + \text{constant} \quad (6-13)$$

Note that V_{ix} is in $\text{cm}^3 \text{mol}^{-1}$.

As is illustrated in Fig. 6.8 for the air–olive oil system, this multiparameter LFER Eq. 6-13 is able to fit the experimental K_{ial} data quite satisfactorily.

The set of coefficients ($s, p, a, b, \text{constant}$) obtained from fitting experimental K_{ial} values for olive oil, as well as for some other organic solvents, are summarized in Table 6.2. These constants clearly quantify the importance of the individual intermolecular interactions for each solvent. For example, *n*-hexadecane has nonzero s and p coefficients, representing this solvent's ability to interact via dispersive and polarizability mechanisms. But the a and b coefficients are zero, consistent with our expectation from hexadecane's structure that hydrogen bonding is impossible for this hydrocarbon. At the other extreme in "polarity," methanol has nonzero coefficients for all of the terms, demonstrating this solvent's capability to interact via all mechanisms.

Indeed, we can use the coefficient values to directly see how chemical structures enable specific kinds of intermolecular interactions. For example, focusing on the a values in Table 6.2, we can contrast the relative importance of H-bonding accepting for these different liquids. We are probably not surprised to see that the two alcohols, octanol and methanol, are the most effective (as indicated by a values between -8 and -9) at donating their oxygen atom's nonbonded electrons to an H-donor partner. We may also expect that olive oil (contains $-\text{C}(=\text{O})\text{O}-$ as part of structure) and acetonitrile (CH_3CN) may be able to donate nonbonded electrons from their oxygen and nitrogen atoms, respectively, to hydrogen-bonding partners. Hence, we anticipate these liquids will have nonzero a coefficients, and the "best-fit" values show this is true but that they hydrogen-bond less effectively than the two alcohols. Note that benzene and trichloromethane have nonzero a coefficients. Although the a values are small compared to those of the alcohols, their significant

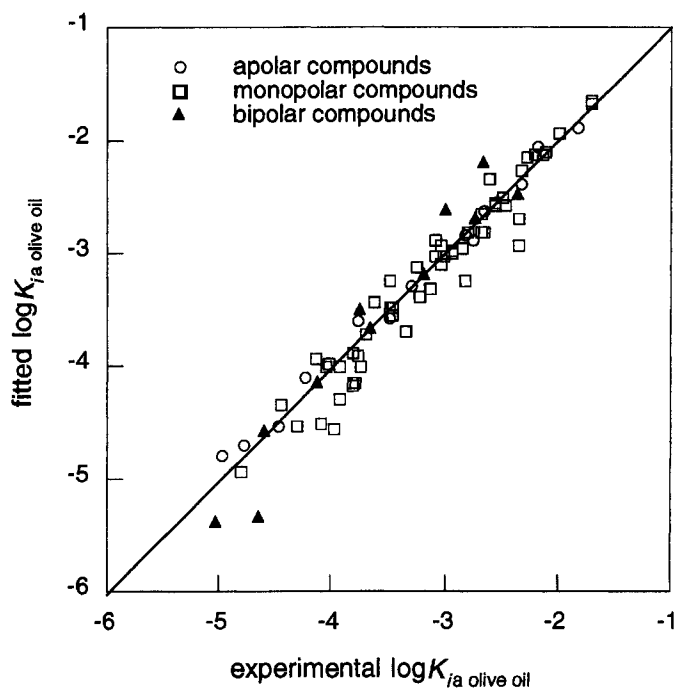


Figure 6.8 Fitted (Eq. 6-13) versus experimental air–olive oil partition coefficients for a series of compounds including those in Fig. 6.7. Note that some of the relatively large scatter in the data may be due to the fact that olive oils from different origins may differ in composition.

difference from zero in the fitting of K_{ial} values means that the π -electrons of the benzene ring can be donated somewhat to a hydrogen donor compound (or other electron-deficient positions of substances). Likewise, the nonbonded electrons of trichloromethane's chlorine atoms must be somewhat available to share with electron-deficient moieties, although, when inspecting the b coefficient, this compound is a much stronger electron acceptor (H-donor). Similar "structure-activity" interpretations can be made for all the other LFER parameters in Table 6.2.

In summary, multiparameter LFERs such as the ones given for some organic solvents in Table 6.2 are very useful in many respects. First, they allow one to get an estimate of the K_{ial} value of a given compound for a given solvent, provided that the compound's π_i , α_i , and β_i values are known. Second, such LFERs characterize a given solvent with respect to its ability to host different apolar, monopolar, and/or bipolar solutes (see above). This may help us anticipate where organic chemicals will accumulate. Next, we can use such multiparameter LFER information to rationalize when a simple one-parameter LFER (Eq. 6-12) should be appropriate. For example, we can see now that an LFER between air–olive oil partition coefficients and air–*n*-octanol partition constants can be expected to hold only for confined sets of compounds, and not for the universe of chemicals (Fig. 6.7). Another result that we could have anticipated from such data sets is the existence of single LFERs for the solvent system methanol/ethanol (Fig. 6.6). Finally, comparison of the a and b values permits us to attach quantitative reasoning to our (sometimes incorrect) intuitive reasoning regarding the interactions of chemicals with one another. For example, by comparing the relevant a and b coefficients of the alcohols and water, we now know that water is a much stronger H-acceptor, but that all these solvents are similar in their ability to act as H-donors toward organic solutes.

Table 6.2 Air–Organic Solvent Partitioning: Multiparameter LFERs (Eq. 6-13) for Some Organic Solvents at 25°C^a

Solvent	vdW <i>s</i>	Coefficient for Parameter					ln K_{air} range ^b	R^2	<i>n</i> ^c
		(π_i) <i>p</i>	(α_i) <i>a</i>	(β_i) <i>b</i>	constant				
<i>n</i> -Hexadecane (apolar)	-1.67	-1.49	0	0	2.01	1.8 to 12.6	0.98	302	
Benzene (monopolar)	-1.38	-3.47	-1.45	0	0.26	4.4 to 13.6	0.96	36	
Olive oil (monopolar)	-1.74	-2.83	-4.47	0	2.86	-3.9 to 11.6	0.94	79	
Trichloromethane (bipolar) ^d	-1.47	-3.41	-0.96	-4.21	1.27	-3.5 to 18.8	0.95	108	
Acetonitrile (bipolar)	-0.49	-2.14	-2.30	-0.82	0.46	-1.3 to 5.7	0.98	42	
<i>n</i> -Octanol (bipolar)	-1.47	-2.60	-8.32	-3.71	2.42	2.6 to 19.6	0.97	254	
Methanol (bipolar)	-1.26	-3.41	-8.92	-3.90	1.57	1.7 to 14.4	0.97	65	

^a Data from Maher and Smith (1979), Ocampo and Klinger (1983), Srivastava et al. (1986), Tiegs et al. (1986), Abraham et al. (1987), Abraham et al. (1994a and b), Abraham et al. (1998), Abraham et al. (1999). ^b Range of experimental K_{air} values that were used to establish the LFER. ^c Number of compounds. ^d Primarily H-donor (electron acceptor).

Temperature Dependence of Air–Organic Solvent Partition Constants

As indicated by Eqs. 6-8 to 6-10, the temperature dependence of $K_{ia\ell}$ is determined by the corresponding $\Delta_{a\ell}H_i$. This enthalpy is given by the difference between the enthalpy of vaporization ($\Delta_{\text{vap}}H_i$) and the excess enthalpy of the compound in the organic phase ($H_{i\ell}^E$). For most organic solvents and compounds, we may assume that $H_{i\ell}^E$ is much smaller than $\Delta_{\text{vap}}H_i$. For example, $H_{i\ell}^E$ is less than a tenth of $\Delta_{\text{vap}}H_i$ in the case of hexadecane (Abraham et al., 1990) and *n*-octanol as solvents (Harner and Mackay, 1995; Harner and Bidleman, 1996; Gruber et al., 1997). Hence, as a first approximation, we may use $\Delta_{\text{vap}}H_i$ to assess the effect of temperature on $K_{ia\ell}$ (i.e., $\Delta_{a\ell}H_i \cong \Delta_{\text{vap}}H_i$). This means that, like vapor pressure (Chapter 4), $K_{ia\ell}$ values are strongly temperature dependent. Finally, we should recall from Section 4.4 (Eq. 4-29) that we may estimate $\Delta_{\text{vap}}H_i$ from the liquid–vapor pressure of the compound.

Applications

We conclude this section with a few comments on the practical importance of considering air (or gas)–organic solvent partitioning. First, knowledge of the respective $K_{ia\ell}$ value(s) is, of course, required to assess how much a given organic liquid (e.g., olive oil) will tend to become “contaminated” by organic chemicals present in the air around it. This problem might be of interest in our private and/or professional lives (see Illustrative Example 6.1). Second, when analyzing organic compounds by gas chromatography, it is of great importance to know how specific compounds partition between the gaseous mobile phase (i.e., H_2 , He, N_2) and the stationary phase. This latter phase is commonly a liquid organic coating at the inner surface of a glass or silica capillary column. In fact, for choosing the appropriate stationary phase (e.g., polar versus nonpolar) for the separation of a given group of compounds, it is necessary to understand the molecular factors that determine the activity coefficients of the compounds in various stationary phases. This information can be gained from analyzing $K_{ia\ell}$ values of the compounds for different solvents.

Furthermore, air–organic solvent partition constants, in particular the air–octanol partition constant, are widely used to evaluate and/or predict the partitioning of organic compounds between air and natural organic phases. Such organic phases are present, for example, in aerosols or soils (Chapters 9 and 11) or as part of biological systems (Chapter 10).

Finally, the relationships between the air–organic solvent, the air–water, and the organic solvent–water partition constants of a given compound (Eq. 6-11) will make it very easy to understand organic solvent–water partitioning, which we will treat in Chapter 7.

Illustrative Example 6.1 Assessing the Contamination of Organic Liquids by Air Pollutants

Problem

You live in a town where air pollution caused primarily by traffic is quite substantial. From a recent article in the local newspaper you have learned that the benzene concentration in the air in your area 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, and that you have 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 25°C and a total pressure of 1 bar. Use the ideal gas law to convert ppbv to molar concentrations.



i = benzene

Answer

With 10 ppbv the partial pressure of benzene in the air is $p_i = 10 \times 10^{-9} \text{ bar} = 10^{-8} \text{ bar}$, which corresponds to a concentration of:

$$C_{ia} = \frac{p_i}{RT} = \frac{10^{-8}}{(0.0831)(298)} = 4.0 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1} = 0.03 \mu\text{g} \cdot \text{L}^{-1}$$

For estimating the air–olive oil partition coefficient, calculate first the air–octanol partition constant from the air–water (K_{iaw}) and octanol–water (K_{iow}) partition constants given in Appendix C (Eq. 6-11):

$$K_{iao} = \frac{K_{iaw}}{K_{iow}} = \frac{10^{-0.65}}{10^{+2.17}} = 10^{-2.82}$$

Use the LFER shown in Fig. 6-7 for alkyl aromatic compounds ($\log K_{ia \text{ olive oil}} = 1.08 \log K_{iao} + 0.22$) to estimate the air–olive oil partition coefficient:

$$\log K_{ia \text{ olive oil}} = (1.08) (-2.82) + 0.22 = -2.83$$

An alternative way of estimating the air–olive oil partition coefficient is to apply the LFER Eq. 6-13 using the constants given in Table 6.2 for the air–olive oil system:

$$\ln K_{ia \text{ olive oil}} = -1.74 \left[V_{ix}^{2/3} \left[\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right] \right] - 2.83(\pi_i) - 4.47(\alpha_i) + 2.86$$

The corresponding parameters for benzene are: $V_{ix} = 71.6 \text{ cm}^3 \text{ mol}^{-1}$ (Box 5.2), $n_{Di} = 1.50$ (Table 3.1), $\pi_i = 0.52$ (Table 5.4), $\alpha_i = 0$ (Table 4.3). Insertion of these values in the above equation yields:

$$\ln K_{ia \text{ olive oil}} = (-1.74) (5.07) - (2.83) (0.52) - (4.47) (0) + 2.86 = -7.44$$

or:

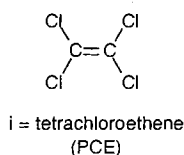
$$\log K_{ia \text{ olive oil}} = -3.23$$

Hence, both estimates yield a $K_{ia \text{ olive oil}}$ value for benzene of about 10^{-3} , and thus a maximum benzene concentration in the olive oil of $10^3 C_{ia} = 30 \mu\text{g} \cdot \text{L}^{-1}$. Considering

that the drinking water standard for benzene is $5 \mu\text{g} \cdot \text{L}^{-1}$ this concentration should, therefore, not create a serious problem for your health assuming that you do not consume tremendous amounts of olive oil each day.

Problem

In your laboratory refrigerator (5°C) you store pure cyclohexane that you use for extracting organic trace contaminants from water samples for subsequent analysis by gas chromatography. Among the compounds of interest is tetrachloroethene (also called perchloroethene or PCE). One day you realize that somebody is using tetrachloroethene in the laboratory. In fact, you can even smell the compound in the air (odor threshold values: $0.03 - 0.1 \text{ mg} \cdot \text{L}^{-1}$). You are worried that your cyclohexane is “contaminated,” particularly, because you have realized that the bottle was not well sealed in the refrigerator. Calculate the concentration of PCE in the air that, at 5°C , would be sufficient to “produce” an equilibrium PCE concentration in the cyclohexane of $1 \mu\text{g} \cdot \mu\text{L}^{-1}$, which you would consider to be a problem for your analysis.



Answer

Use the air–*n*-hexadecane partition constant of PCE ($K_{ia \text{ hexadecane}} = 2.5 \times 10^{-4}$ at 25°C ; Abraham et al., 1994a) as surrogate for the air–cyclohexane partition constant of PCE (Fig. 6.5). Furthermore, for determining the temperature dependence of $K_{ia \text{ hexadecane}}$ assume that $\Delta_a \text{ hexadecane } H + RT_{av} \cong \Delta_{vap} H_i + RT_{av}$ (Section 3.4). For PCE, this value is about $40 \text{ kJ} \cdot \text{mol}^{-1}$ (Lide, 1995). Hence, at 5°C , the $K_{ia \text{ hexadecane}}$ value is about 0.3 times the value at 25°C (Table 3.5); that is, $K_{ia \text{ hexadecane}} \cong 7.5 \times 10^{-5}$. This means that the PCE concentration in the air required to produce a concentration in the cyclohexane of $1 \mu\text{g} \cdot \text{mL}^{-1}$ or $1 \text{ mg} \cdot \text{L}^{-1}$ is:

$$C_{ia} = (7.5 \times 10^{-5}) (1) \text{ mg} \cdot \text{L}^{-1} = 0.000075 \text{ mg} \cdot \text{L}^{-1}$$

which is about 400 times lower than the odor threshold. Thus, your cyclohexane is in great danger of getting contaminated by the PCE in the air.

6.4 Air–Water Partitioning

“The” Henry’s Law Constant

For our discussion of air–water partitioning, we start by rewriting Eq. 6-5 for water as the solvent (Eq. 6-6):

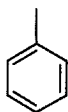
$$K_{iH} = \frac{P_i}{C_{iw}} = \gamma_{iw} \cdot P_{iL}^* \cdot \bar{V}_w \quad (6-14)$$

Recall that K_{iH} is commonly referred to in environmental literature as “the” Henry’s law constant. The “dimensionless” Henry constant is denoted K_{iaw} and is related to K_{iH} by (Eq. 6-6):

$$K_{iaw} = \frac{K_{iH}}{RT} \quad (6-15)$$

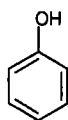
Inspection of Eq. 6-14 reveals that we do not need to learn anything new to understand air–water equilibrium partitioning of neutral organic compounds. All we have to do is to recall how chemical structures (controlling intermolecular interactions) and environmental factors (e.g., temperature, presence of salts or organic cosolvents in the aqueous phase) affect the vapor pressure and the aqueous activity coefficient of a given compound. Hence, our discussion of air–water partitioning can be quite brief.

First, consider how structural moieties affect the Henry's Law constant. We can see that within a class of apolar or weakly polar compounds (e.g., *n*-alkanes, chlorinated benzenes, alkylbenzenes, PCBs, PAHs), the K_{iaw} values vary by less than one order of magnitude (see data in Appendix C.) This is also true for sets of compounds that differ only by apolar moieties (e.g., polyalkyl- or polychlorophenols). This is in contrast to vapor pressure and aqueous solubility data for the same families of compounds. These latter properties vary by five or more orders of magnitude within any one group of those compounds. We can rationalize these findings by recalling that an increase in size of the compound leads to an increase in γ_{iw} (or a decrease in water solubility), as well as to a decrease in p_{iL}^* . Hence, the effect of molecular size is canceled out to a large degree when multiplying γ_{iw} with p_{iL}^* (Eq. 6-14).



toluene

$$K_{iaw}(25^\circ\text{C}) = 2.5 \times 10^{-1}$$



phenol

$$K_{iaw}(25^\circ\text{C}) = 2.5 \times 10^{-5}$$

However, as is illustrated by the two substituted benzenes, toluene and phenol (see margin), the presence of a polar group has a tremendous effect on K_{iaw} . Replacing an apolar moiety with a bipolar hydrogen-bonding one leads to a decrease in both γ_{iw} (it increases C_{iw}^{sat}) and p_{iL}^* . Thus, K_{iaw} values differ widely between apolar and bipolar derivatives.

We may also recall that for most compounds of interest, we can assume that γ_{iw} is more or less independent of concentration (Section 5.2). Hence, in Eq. 6-14, we may substitute γ_{iw} by γ_{iw}^{sat} . This activity coefficient, in turn, can be expressed by the liquid aqueous solubility of the compound (i.e., $\gamma_{iw}^{\text{sat}} = 1/(C_{iw}^{\text{sat}}(\text{L}) \cdot \bar{V}_w)$; Eq. 5-12). Using this relation, we then obtain:

$$K_{iH} \cong \gamma_{iw}^{\text{sat}} \cdot p_{iL}^* \cdot \bar{V}_w \cong \frac{p_{iL}^*}{C_{iw}^{\text{sat}}(\text{L})} \quad (6-16)$$

For solid compounds we may also write:

$$K_{iH} \cong \frac{p_{is}^*}{C_{iw}^{\text{sat}}(\text{s})} \quad (6-17)$$

because the free energy term relating the liquid and solid vapor pressure and the liquid and solid aqueous solubility, respectively (Eqs. 4-15 and 5-13), cancels when dividing the two entities. From a practical point of view, Eqs. 6-16 and 6-17 are very interesting, because they tell us that we may estimate the Henry's law constant of a compound directly from its vapor pressure and its aqueous solubility. In fact, many of the K_{iH} or K_{iaw} values listed in data compilations (including the data given in Appendix C) have been derived in this way. Comparison of calculated with experimental K_{iaw} values (compare values given in parentheses in Appendix C, or

see article by Brennan et al., 1998) shows that, in most cases, Eqs. 6-16 and 6-17 yield very satisfactory estimates (less than a factor of 2 deviation).

Effect of Temperature on Air–Water Partitioning

As indicated by Eq. 6-9, the standard enthalpy of transfer of a compound i from water to air is given by:

$$\Delta_{aw}H_i = \Delta_{vap}H_i - H_{iw}^E \quad (6-18)$$

Typically, for many smaller organic molecules, H_{iw}^E is rather small (i.e., $|H_{iw}^E| < 10 \text{ kJ} \cdot \text{mol}^{-1}$; Table 5.3). As a result, for such small compounds, similar to the situation encountered in air–organic solvent partitioning, $\Delta_{aw}H_i$ will not be very different from the enthalpy of vaporization of the compound (Table 6.3), and therefore, the effect of temperature on air–water partitioning, will, in general, be significant (see Illustrative Example 6.2).

There are, however, also many cases in which $\Delta_{aw}H_i$ differs quite substantially from $\Delta_{vap}H_i$. Due to their relatively high positive H_{iw}^E values (see Table 5.3), large, apolar compounds exhibit a significantly smaller $\Delta_{aw}H_i$ as compared to $\Delta_{vap}H_i$ (see examples given in Table 6.3). Nevertheless, even in these cases, $\Delta_{aw}H_i$ is still quite large, so that the effect of temperature on K_{iaw} cannot be neglected.

For monopolar compounds (e.g., ethers, ketones, aldehydes), $\Delta_{aw}H_i$ may even be larger than $\Delta_{vap}H_i$. This happens because of the additional polar interactions in the aqueous phase, leading to negative H_{iw}^E values (Table 5.3).

At this point we should note that it is not a trivial task to measure accurately $\Delta_{aw}H_i$ values. This is particularly true for very hydrophobic compounds. Therefore, it is also not too surprising that experimentally determined $\Delta_{aw}H_i$ values reported by different authors may differ substantially (see examples given in Table 6.3). Furthermore, particularly for many very hydrophobic compounds, there seems to be a discrepancy between $\Delta_{aw}H_i$ values derived from measurements of K_{iaw} at different temperatures (Eq. 6-10) under *dilute* conditions, and $\Delta_{aw}H_i$ values calculated from the enthalpy of vaporization and the enthalpy of solution ($\Delta_{wL}H_i = H_{iw}^E$; see Fig. 5.1; note that $\Delta_{wa}H_i = -\Delta_{aw}H_i$). Note that this latter approach reflects *saturated* conditions. Nevertheless, before using an experimentally determined $\Delta_{aw}H_i$ value, it is advisable to check this value for consistency with that calculated from $\Delta_{aw}H_i$ and H_{iw}^E .

Effect of Solution Composition on Air–Water Partitioning

To evaluate the effects of salts or organic cosolvents on air–water (or more correctly, air–aqueous phase or air–organic solvent/water mixture) partitioning, we may simply apply the approaches discussed in Section 5.4 (Eqs. 5-27 and 5-29). Thus, knowing how salt affects a compound's aqueous solubility, while having no effect on its saturation vapor pressure, we deduce that the impact of salt on K_{iaw} may be expressed by:

$$K_{iaw, \text{saltwater}} = K_{iaw} \cdot 10^{+K_i^s [\text{salt}]_{\text{tot}}} \quad (6-19)$$

Table 6.3 Experimental Standard Enthalpies of Vaporization ($\Delta_{\text{vap}}H_i$) and Standard Enthalpies of Transfer from Water to Air ($\Delta_{\text{aw}}H_i$) of Selected Organic Compounds at 25°C^a

Compound Name	$\Delta_{\text{vap}}H_i$ (kJ·mol ⁻¹)	$\Delta_{\text{aw}}H_i$ (kJ·mol ⁻¹)	Compound Name	$\Delta_{\text{vap}}H_i$ (kJ·mol ⁻¹)	$\Delta_{\text{aw}}H_i$ (kJ·mol ⁻¹)
<i>n</i> -Hexane	32	32	2,5-Dichlorobiphenyl	74	47
<i>n</i> -Heptane	37	34	2,4,4'-Trichlorobiphenyl	78	50
<i>n</i> -Octane	41	36	2,2',5,5'-Tetrachlorobiphenyl	81	52
Cyclohexane	33	33	γ -Hexachlorocyclohexane (γ -HCH)	70	46
Benzene	34	30	Diethylether	27	42, 47
Methylbenzene	38	32	Methyl- <i>t</i> -butylether (MTBE)	30	61
Ethylbenzene	42	39	Methanol	37	45
1,2-Dimethylbenzene	43	33	1-Hexanol	62	68
1,4-Dimethylbenzene	42	33	Cyclohexanol	62	70
Naphthalene	56	45, 47	1-Octanol	71	74
Anthracene	70	27, 47, 48	Phenol	58	48, 57
Phenanthrene	74	30, 47, 60	2-Methylphenol	62	46, 59
Pyrene	87	43, 56	4-Methylphenol	62	49, 60
Dichlorodifluoromethane	21	27	Aminobenzene (Aniline)	52	54
Trichlorofluoromethane	27	23	Butanone	35	42
Dichloromethane	29	30	2-Hexanone	43	49
Trichloromethane	31	35	Hexanol	53	62
Trichloroethene	35	33, 38, 39	Benzaldehyde	49	45, 56
Tetrachloroethene	40	37	Butylacetate	44	52
Chlorobenzene	41	30, 43	Dimethylsulfide	28	30
Hexachlorobenzene	76	49	Diethylsulfide	36	37

^a Data from Abraham et al. (1990), Zhou and Mopper (1990), Kucklick et al. (1991), Ten Hulscher et al. (1992), Dewulf et al. (1995), Dohnal and Fenclová (1995), Lide (1995), Alaei et al. (1996), Staudinger and Robert (1996), Allen et al. (1998), Goss and Schwarzenbach (1999a).

Illustrative Example 6.2 Evaluating the Direction of Air–Water Gas Exchange at Different Temperatures

Problem

What is the direction (into water? or out of water?) of the air–water exchange of benzene for a well-mixed shallow pond located in the center of a big city in each of the following seasons: (a) a typical summer situation ($T = 25^\circ\text{C}$), and (b) a typical winter situation ($T = 5^\circ\text{C}$)? In both cases, the concentrations detected in air and water are $C_{ia} = 0.05 \text{ mg}\cdot\text{m}^{-3}$ and $C_{iw} = 0.4 \text{ mg}\cdot\text{m}^{-3}$. Assume that the temperature of the water and of the air is the same.



$i = \text{benzene}$

Answer (a)

The air–water partition constant, K_{iaw} , of benzene is 0.22 at 25°C (Appendix C). The quotient of the concentrations of benzene in the air and in water is:

$$\frac{C_{ia}}{C_{iw}} = \frac{0.05}{0.4} = 0.125$$

Hence, at 25°C , $C_{ia}/C_{iw} < K_{iaw}$, and therefore, there is a net flux from the water to the air (the system wants to move toward equilibrium).

Answer (b)

The $\Delta_{aw}H_i$ the value of benzene is $30 \text{ kJ}\cdot\text{mol}$ (Table 6.3). With $\Delta_{aw}H_i + RT_{av}$ ($T_{av} = 288 \text{ K}$) $= 30 + 2.4 = 32.4 \text{ kJ}\cdot\text{mol}^{-1}$, you get a K_{iaw} value at 5°C of (Table 3.5):

$$K_{iaw}(5^\circ\text{C}) = 0.4 K_{iaw}(25^\circ\text{C}) = 0.05$$

Thus, at 5°C the ratio $C_{ia}/C_{iw} > K_{iaw}$; therefore, this time there is a net flux from the air to the water.

This example shows that the direction of gas exchange may be strongly influenced by temperature.

Note that in Eq. 6-19 we neglect the effect of the dissolved salt on the molar volume of the aqueous phase. This is a reasonable first approximation if we deal with salt solutions that are not too concentrated (e.g., seawater; see Illustrative Example 6.3).

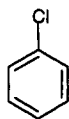
For assessing $K_{ia\ell}$ values for organic solvent/water mixtures, we can estimate the activity coefficient of the compound of interest in the liquid phase using Eq. 5-30. Inserting this value, together with p_{iL}^* , and the appropriate molar volume of the solvent mixture into Eq. 6-6 (see Illustrative Example 6.3), then yields the corresponding $K_{ia\ell}$.

Illustrative Example 6.3

Assessing the Effect of Solution Composition on Air–Aqueous/Phase Partitioning

Problem

Recall Problem 3.1. You are the boss of an analytical laboratory and, this time, you check the numbers from the analysis of chlorobenzene in water samples of very different origins, namely (a) moderately contaminated groundwater, (b) seawater ($[\text{salt}]_{\text{tot}} \approx 0.5 \text{ M}$), (c) water from a brine ($[\text{salt}]_{\text{tot}} \approx 5.0 \text{ M}$), and (d) leachate of a hazardous-waste site containing 40% (v : v) methanol. For all samples, your laboratory reports the same chlorobenzene concentration of $10 \mu\text{g} \cdot \text{L}^{-1}$. Again the sample flasks were unfortunately not completely filled. This time, the 1 L flasks were filled with 400 mL liquid, and stored at 25°C before analysis. What were the original concentrations (in $\mu\text{g} \cdot \text{L}^{-1}$) of chlorobenzene in the four samples?

 $i = \text{chlorobenzene}$

$$p_i^{\text{L}}(25^\circ\text{C}) = 0.016 \text{ bar}$$

$$\gamma_{iw}^{\text{sat}} = 14000 \text{ (Table 5.2)}$$

$$K_{iaw}(25^\circ\text{C}) = 0.16$$

$$K_i^{\text{L}} = 0.23 \text{ M}^{-1} \text{ (Table 5.7)}$$

Answer

For calculating the original concentration of a compound i in a two-phase system that contains an air volume V_a and a liquid volume V_ℓ , divide the total mass of i present by the volume of the liquid phase:

$$C_{i\ell}^{\text{orig}} = \frac{C_{i\ell} \cdot V_\ell + C_{ia} \cdot V_a}{V_\ell} \quad (1)$$

Substitute C_{ia} by $K_{ial} \cdot C_i$ into Eq. (1) and rearrange the equation to get

$$C_{i\ell}^{\text{orig}} = C_i \left(1 + K_{ial} \frac{V_a}{V_\ell} \right) \quad (2)$$

Case (a) ($\ell = \text{water}$)

Insert $C_{i\ell} = 10 \text{ mg} \cdot \text{L}^{-1}$, $K_{iaw} = 0.16$, and $V_a / V_\ell = 1.5$ into Eq. (2) to get an original concentration of $12.4 \text{ mg} \cdot \text{L}^{-1}$.

Case (b) ($\ell = \text{seawater}$) and (c) ($\ell = \text{brine}$)

In this case use Eq. 6-19 to calculate K_{ial} :

$$K_{ial} = K_{iaw} \cdot 10^{+K_i^{\text{L}}[\text{salt}]_{\text{tot}}} \quad (6-19)$$

Insertion of K_{iaw} , K_i^{L} and $[\text{salt}]_{\text{tot}}$ into Eq. 6-19 yields for case (b):

$$K_{ial} = (0.16) (1.30) = 0.21 \text{ and, therefore, } C_{i\ell}^{\text{orig}} = 13.2 \text{ mg} \cdot \text{L}^{-1}$$

for case (c):

$$K_{ial} = (0.16) (14.1) = 2.26 \text{ and, therefore, } C_{i\ell}^{\text{orig}} = 43.9 \text{ mg} \cdot \text{L}^{-1}$$

Case (d) ($\ell = 40\% \text{ methanol} / 60\% \text{ water}$)

Use the linear relationship between $\log(\gamma_{iw}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}})$ and the molar volume, V_{ix} (in

$\text{cm}^3 \text{mol}^{-1}$) shown in Fig. 5.8 for PCBs and $f_{v,\text{MeOH}} = 0.4$ to estimate γ_{il}^{sat} for chlorobenzene:

$$\log(\gamma_{iw}^{\text{sat}}/\gamma_{il}^{\text{sat}}) = (0.0180) V_{ix} - 0.850$$

Insertion of γ_{iw}^{sat} and V_{ix} ($83.8 \text{ cm}^3 \text{mol}^{-1}$) of chlorobenzene yields a γ_{il}^{sat} value of 3070. The molar volume of methanol is $40 \text{ cm}^3 \text{mol}^{-1}$. Hence, when assuming that, as a first approximation, Amagat's law (Eq. 3-44) is valid (which is not exactly true in this case), the molar volume of the 40% methanol / 60% water mixture is (Eq. 5-34): $\cong (0.23)(40) + (0.77)(18) = 23.3 \text{ cm}^3 \text{mol}^{-1} = 0.0231 \text{ L}\cdot\text{mol}^{-1}$. Inserting this value together with γ_{il}^{sat} and p_{iL}^* into Eq. 6-6 yields:

$$K_{i\text{a}l} = (3070)(0.0231)(0.016)/(0.0831)(298) = 0.046$$

and therefore $C_{il}^{\text{orig}} = 10.07 \text{ mg}\cdot\text{L}^{-1}$.

Availability of Experimental Data

The experimental determination of air–water partition constants is not an easy task to perform, particularly when dealing with compounds exhibiting very small $K_{i\text{a}w}$ values. Although the available values of experimental $K_{i\text{a}w}$ are steadily growing in number, compared to vapor pressures, aqueous solubilities, or *n*-octanol–water partition constants, the data are still quite limited. Compilations of experimental air–water partition constants can be found in handbooks such as the one published by Mackay et al. (1992–1997), or in review articles including those by Staudinger and Roberts (1996), or Brennan et al. (1998). Note that in some cases, considerable differences (i.e., up to an order of magnitude) may exist between experimental $K_{i\text{a}w}$ values reported by different authors. Therefore, it is advisable to “check” such values by comparison with estimated ones. For example, one may see if experimental results appear reasonable by using the ratio of vapor pressure and aqueous solubility (Eqs. 6-16 and 6-17) or an LFER such as the one given below (Eq. 6-22).

There are two general experimental approaches commonly used for determining air–water partition constants, the *static* and the *dynamic* equilibration approach. A detailed description of the different existing variations of the two methods can be found in the review by Staudinger and Roberts (1996) and in the literature cited therein. Here we will confine ourselves to a few remarks on the general concepts of these experimental approaches.

The *static* equilibrium approach is, in principle, straightforward. In this method, the air–water partition constant is directly determined by measuring concentrations of a compound at a given temperature in the air and/or water in closed systems (e.g., in a gas-tight syringe, or in sealed bottles). If chemical concentrations are measured only in one phase, the concentration in the other is assessed as difference to the total amount of *i* in the system. In this approach, the error in determining $K_{i\text{a}w}$ can be reduced either by equilibrating a given volume of an aqueous solution of a com-

pound subsequently with several given volumes of solute-free air (e.g., in a syringe; see Problem 6.5), or by using multiple containers having different headspace-to-liquid volume ratios. The main experimental challenges of the static methods are to ensure that equilibrium is reached and also maintained during sampling, and to minimize sampling errors. Since with the static approach, it is possible to use neither very large nor very small air-to-water volume ratios, these methods are primarily suited for compounds with no extreme preference for one of the phases. In more extreme cases, dynamic methods may provide much better results.

The most widely applied *dynamic* method is the batch air or gas stripping technique. By using a stripping apparatus, bubbles of air or another inert gas are produced near the bottom of a vessel and then rise to the surface of the solution, the exit gas achieving equilibrium with the water. Hence, this experimental design requires that the velocity of the rising bubbles is sufficiently small and the height of the well-mixed water column is sufficiently great to establish air–water equilibrium. Furthermore, the bubbles need to be large enough so that *adsorption* at the air–water interface can be neglected (this interface may be important for very hydrophobic compounds; see Section 11.2). If all this is achieved, the air–water partition constant can be determined by measuring the decrease in water concentration, C_{iw} , as a function of time (Mackay et al., 1979):

$$C_{iw}(t) = C_{iw}(0) \cdot e^{-\frac{K_{iaw} \cdot G}{V_w} \cdot t} \quad (6-20)$$

where G is the gas volume flow per unit time and V_w is the volume of the aqueous solution. Hence, if G and V_w are known, K_{iaw} can be deduced from the slope of the linear regression of $\ln C_{iw}(t)$ versus t :

$$\ln C_{iw}(t) = -\text{slope} \cdot t + \text{constant} \quad (6-21)$$

where $K_{iaw} = (\text{slope}) (V_w/G)$. Note that, conversely, if K_{iaw} is known, Eq. 6-20 allows one to estimate the time required to purge a given compound from a water sample (e.g., the time required to lower its concentration to 1% of the initial concentration) for a given gas flow rate. This issue may be important when dealing with the behavior of organic pollutants in water treatment plants. It also pertains to problems in analytical chemistry, where the purge-and-trap method is widely used to enrich volatile compounds from water samples (Standard Methods for Examination of Water and Wastewater, 1995; see Problem 6.6).

An alternative dynamic approach to gas stripping is the concurrent flow technique, which is based on the use of a wetted wall column apparatus. Compound-laden water is introduced continuously at the top of a wetted wall column where it comes into contact with a compound-free gas stream flowing concurrently down the column. As with gas stripping, the major challenge is to allow sufficient contact time to ensure phase equilibrium is reached by the time the two streams reach the bottom of the column. The two streams are separated at the bottom of the column, and either solvent extracted or trapped on solid-phase sorbents for subsequent analysis. To determine the K_{iaw} value of a given compound, the system is run for a set amount of time. Given knowledge of the flow rates employed along with the compound masses

present in the separated phase streams, K_{iaw} can be calculated. With this method, a rigorous mass balance can be conducted.

Estimation of Air–Water Partition Constants

As already discussed, the K_{iaw} value of a given compound may also be approximated by the ratio of its vapor pressure and its aqueous solubility (Eqs. 6-16 and 6-17). When using this approximation one has to be aware that, particularly for compounds exhibiting very small p_{iL}^* and/or C_{iw}^{sat} values, rather large errors may be introduced due to the uncertainties in the experimental vapor pressure and solubility data (see Sections 4.4 and 5.5).

Another possibility to predict K_{iaw} is to use our multiparameter LFER approach. As we introduced in Chapter 5, we may consider the intermolecular interactions between solute molecules and a solvent like water to estimate values of γ_{iw} (Eq. 5-22). Based on such a predictor of γ_{iw} , we may expect a similar equation can be found to estimate K_{iaw} values, similar to that we have already applied to air–organic solvent partitioning in Section 6.3 (Table 6.2). Considering a database of over 300 compounds, a best-fit equation for K_{iaw} values which reflects the influence of various intermolecular interactions on air–water partitioning is:

$$\ln K_{iaw} = -0.540 \left[(V_{ix})^{2/3} \left(\frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right] - 5.71(\pi_i) - 8.74(\alpha_i) - 11.2(\beta_i) \quad (6-22)$$

$$+ 0.0459 V_{ix} + 2.25 \quad (R^2 = 0.99)$$

Note that the values of the coefficients s , p , a , b and v in Eq. 6-22 are slightly different from those in Eq. 5-22, because a larger set of compounds has been used for their derivation. Nevertheless, Eq. 6-22 is, of course, identical to the part in Eq. 5-22 that describes the transfer of a compound from the gas phase to the aqueous phase. Hence, we do not need to repeat our discussion of the various terms describing this process. Furthermore, our comments made on the various other methods developed for estimating aqueous activity coefficients, including QSPRs or group contribution methods such as UNIFAC or AQUAFAC (see Section 5.5), also apply directly for the methods suggested to predict K_{iH} values (Staudinger and Roberts, 1996; Brennan et al., 1998). In all cases, the key problem is the same; we need a quantitative description of the solubilization of an organic compound in the complex solvent water.

We conclude this section by addressing a simple LFER approach to estimate K_{iaw} values based solely on chemical structure. The underlying idea of this LFER of the type Eq. 3-57 (Section 3.4) was introduced by Hine and Mookerjee (1975) and expanded by Meyland and Howard (1991). In this method, each bond type (e.g., a C–H bond) is taken to have a substantially constant effect on $\Delta_{aw}G_i$, regardless of the substance in which it occurs. This assumption is reasonably valid for simple molecules in which no significant interactions between functional groups take place. Hence, the method is interesting primarily from a didactic point of view, in that we can see how certain substructural units affect air–water partitioning.

Table 6.4 Bond Contributions for Estimation of $\log K_{iaw}$ at 25°C ^a

Bond ^b	Contribution	Bond ^b	Contribution
C – H	+0.1197	C _{ar} – OH	–0.5967 ^c
C – C	–0.1163	C _{ar} – O	–0.3473 ^c
C – C _{ar}	–0.1619	C _{ar} – N _{ar}	–1.6282
C – C _d	–0.0635	C _{ar} – S _{ar}	–0.3739
C – C _t	–0.5375	C _{ar} – O _{ar}	–0.2419
C – CO	–1.7057	C _{ar} – S	–0.6345
C – N	–1.3001	C _{ar} – N	–0.7304
C – O	–1.0855	C _{ar} – I	–0.4806
C – S	–1.1056	C _{ar} – F	+0.2214
C – Cl	–0.3335	C _{ar} – C _d	–0.4391
C – Br	–0.8187	C _{ar} – CN	–1.8606
C – F	+0.4184	C _{ar} – CO	–1.2387
C – I	–1.0074	C _{ar} – Br	–0.2454
C – NO ₂	–3.1231	C _{ar} – NO ₂	–2.2496
C – CN	–3.2624	CO – H	–1.2102
C – P	–0.7786	CO – O	–0.0714
C = S	+0.0460	CO – N	–2.4261
C _d – H	+0.1005	CO – CO	–2.4000
C _d = C _d	–0.0000 ^d	O – H	–3.2318
C _d – C _d	–0.0997	O – P	–0.3930
C _d – CO	–1.9260	O – O	+0.4036
C _d – Cl	–0.0426	O = P	–1.6334
C _d – CN	–2.5514	N – H	–1.2835
C _d – O	–0.2051	N – N	–1.0956 ^e
C _d – F	+0.3824	N = O	–1.0956 ^e
C _t – H	–0.0040	N = N	–0.1374
C _t ≡ C _t	–0.0000 ^d	S – H	–0.2247
C _{ar} – H	+0.1543	S – S	+0.1891
C _{ar} – C _{ar}	–0.2638 ^f	S – P	–0.6334
C _{ar} – C _{ar}	–0.1490 ^g	S = P	+1.0317
C _{ar} – Cl	+0.0241		

^a Data from Meylan and Howard (1991). ^b C: single-bonded aliphatic carbon; C_d: olefinic carbon; C_t: triple-bonded carbon; C_{ar}: aromatic carbon; N_{ar}: aromatic nitrogen; S_{ar}: aromatic sulfur; O_{ar}: aromatic oxygen; CO: carbonyl (C = O); CN: cyano (C ≡ N). *Note*: The carbonyl, cyano, and nitrofunctions are treated as single atoms. ^c Two separate types of aromatic carbon-to-oxygen bonds have been derived: (a) the oxygen is part of an –OH function, and (b) the oxygen is not connected to hydrogen. ^d The C = C and C ≡ C bonds are assigned a value of zero by definition (Hine and Mookerjee, 1975). ^e Value is specific for nitrosamines. ^f Intraring aromatic carbon to aromatic carbon. ^g External aromatic carbon to aromatic carbon (e.g., biphenyl).

Table 6.4 summarizes bond contribution values derived by Meyland and Howard (1991) from a large data set for a temperature of 25°C. These values can be used to calculate $\log K_{iaw}$ by simple addition of these bond contributions:

$$\log K_{iaw}(25^\circ\text{C}) = \sum_k (\text{number of bonds type } k) (\text{contribution of bond type } k) \quad (6-23)$$

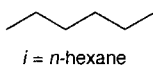
Most of the symbols in Table 6.4 are self-explanatory. For example, C–H is a singly bonded carbon–hydrogen subunit; C_{ar}–Cl is a chlorine bound to an aromatic carbon; and C–C_d is a carbon bound to an doubly bonded (olefinic) carbon. Some groups, such as the carbonyl group (C=O), are treated as a single “atom.” Just looking at the signs and values of the bond contribution, we readily see that units such as C–H bonds tend to encourage molecules to partition into the air, while other units like O–H groups strongly induce molecules to remain associated with the water. These tendencies correspond to expected behaviors deduced qualitatively from our earlier considerations of intermolecular interactions of organic molecules with water (Chapter 5). Some sample calculations are performed in Illustrative Example 6.4. This simple bond contribution approach is usually accurate to within a factor of 2 or 3. One major drawback, however, is that it does not account for special intermolecular or intramolecular interactions that may be unique to the molecule in which a particular bond type occurs. Therefore, additional correction factors may have to be applied (Meylan and Howard, 1991). Furthermore, the limited applicability of this simple approach for prediction of K_{iaw} values of more complex molecules has to be stressed.

Illustrative Example 6.4

Estimating Air–Water Partition Constants by the Bond Contribution Method

Problem

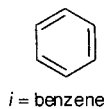
Estimate the K_{iaw} values at 25°C of (a) *n*-hexane, (b) benzene, (c) diethylether, and (d) ethanol using the bond contribution values given in Table 6.4. Compare these values with the experimental air–water partition constants given in Table 3.4. Note that for a linear or branched alkane (i.e., hexane) a correction factor of +0.75 log units has to be added (Meylan and Howard, 1991).



Answer (a)

$$\log K_{iaw} (\textit{n}\text{-hexane}) = 14 (\text{C-H}) + 5 (\text{C-C}) + 0.75 = 1.84.$$

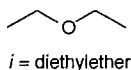
(The experimental value is 1.81)



Answer (b)

$$\log K_{iaw} (\text{benzene}) = 6 (\text{C}_{\text{ar}}\text{-H}) + 6 (\text{C}_{\text{ar}}\text{-C}_{\text{ar}}) = -0.66.$$

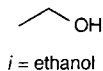
(The experimental value is -0.68)



Answer (c)

$$\log K_{iaw} (\text{diethylether}) = 10 (\text{C-H}) + 2 (\text{C-C}) + 2 (\text{C-O}) = -1.21.$$

(The experimental value is -1.18)



Answer (d)

$$\log K_{iaw}(\text{ethanol}) = 5(\text{C-H}) + 1(\text{C-C}) + 1(\text{C-O}) + 1(\text{O-H}) = -3.84.$$

(The experimental value is -3.70)

6.5 Questions and Problems

Questions

Q 6.1

Give examples of situations in which you need to know the equilibrium partition constant of an organic pollutant between (a) air and an organic liquid phase, and (b) air and water.

Q 6.2

How is the Henry's law constant defined? For which conditions is it valid?

Q 6.3

How do organic chemicals generally partition between a gas phase (i.e., air) and an *organic* liquid phase? Which molecular factors determine the magnitude of K_{ial} ?

Q 6.4

Why was *n*-octanol chosen as a surrogate for natural organic phases? Why not another solvent such as *n*-hexane, methylbenzene, trichloromethane, or diethyl-ether? Why is the use of any organic solvent as general surrogate of a natural organic phase somewhat questionable?

Q 6.5

Table 6.1 shows that *n*-octane partitions much more favorably from air into *n*-octanol than into ethyleneglycol. In contrast, for dioxane (see structure in Fig. 6.3), the corresponding K_{ial} values are more or less identical. Try to rationalize these findings.

Q 6.6

Has temperature a significant effect on the partitioning of organic compounds between air and a bulk liquid phase? How does K_{ial} change with increasing temperature?

Q 6.7

Describe in general terms in which cases you would expect that the enthalpy of transfer of an organic compound from a bulk liquid phase (including water) to air ($\Delta_{al}H_i$) is (a) larger, (b) about equal, and (c) smaller than the enthalpy of

vaporization ($\Delta_{\text{vap}}H_i$) of the compound. Give some specific examples for each of these cases.

Q 6.8

Within a given class of apolar or weakly polar compounds (e.g., alkanes, chlorobenzenes, alkylbenzenes, PCBs), the variation in the air–octanol partition constants (K_{iao}) is much larger than the variation in the air–water partition constants (K_{iaw}). For example, the K_{iao} values of the chlorinated benzenes vary between $10^{-3.5}$ (chlorobenzene) and 10^{-7} (hexachlorobenzene, see Harner and Mackay, 1995), whereas their K_{iaw} values are all within the same order of magnitude (Appendix C). Try to explain these findings.

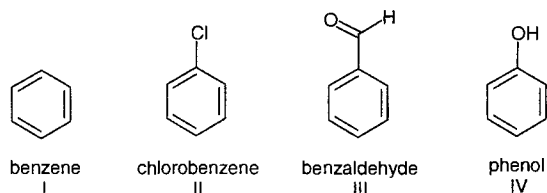
Q 6.9

What is the effect of dissolved salt on air–water partitioning? How is this effect related to the total salt concentration?

Problems

P 6.1 *A Small Ranking Exercise*

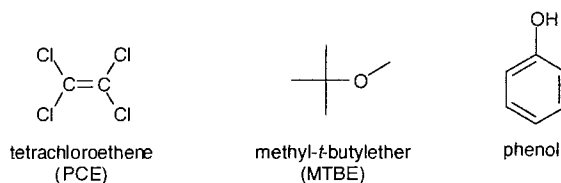
Rank the four compounds (I–IV) indicated below in the order of increasing tendency to distribute from (a) air into hexadecane (mimicking an apolar environment), (b) air to olive oil, and (c) air to water. Use the α_i , β_i , and V_{ix} values given in Table 4.3 and calculated by the method given in Box 5.1. Assume, that the four compounds have about the same n_{Di} value. Do not perform unnecessary calculations. Comment on your choices. Finally, check your result (c) by applying the bond contributions given in Table 6.4.



P 6.2 *Raining Out*

Because of the increasing contamination of the atmosphere by organic pollutants, there is also a growing concern about the quality of rainwater. In this context, it is interesting to know how well a given compound is scavenged from the atmosphere by rainfall. Although for a quantitative description of this process, more sophisticated models are required, some simple equilibrium calculations are quite helpful.

Assume that PCE, MTBE, and phenol (see below) are present in the atmosphere at low concentrations. Consider now a drop of water (volume ~ 0.1 mL, pH = 6.0) in a volume of 100 L of air [corresponds about to the air–water ratio of a cloud (Seinfeld, 1986)]. Calculate the fraction of the total amount of each compound present in the water drop at 25°C and at 5°C assuming equilibrium between the two phases. Use the data given in Appendix C and in Table 6.3, and comment on any assumption that you make.



P 6.3 Evaluating the Direction of Air–Water Gas Exchange in the Arctic Sea

C_1 - and C_2 -halocarbons of natural and anthropogenic origin are omnipresent in the atmosphere and in seawater. For example, for 1,1,1-trichloroethane (also called methyl chloroform, MCF), typical concentrations in the northern hemisphere air and in Arctic surface waters are $C_{ia} = 0.9 \text{ mg} \cdot \text{m}^{-3}$ air and $C_{iw} = 2.5 \text{ mg} \cdot \text{m}^{-3}$ seawater (Fogelqvist, 1985). Using these concentrations, evaluate whether there is a net flux of MCF between the air and the surface waters of the Arctic Ocean assuming a temperature of (a) 0°C , and (b) 10°C . If there is a net flux, indicate its direction (i.e., sea to air or air to sea). Assume that the salinity of the seawater is 35‰. You can find all the necessary data in Appendix C, and in Tables 5.7 and 6.3.

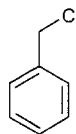


$i = 1,1,1$ -trichloroethane
(methyl chloroform, MCF)

P 6.4 Getting the “Right” Air–Water Partition Constant for Benzyl Chloride

In Chapter 24 the rate of elimination by gas exchange of benzyl chloride (BC) in a river will be calculated. To this end the K_{iaw} value of BC must be known. In the literature (Mackay and Shiu, 1981), you can find only vapor pressure and water solubility data for BC (see below). Because BC hydrolyzes in water with a half-life of 15 hours at 25°C (see Chapter 13), you wonder whether you can trust the aqueous solubility data. Approximate the K_{iaw} -value of BC by vapor pressure and aqueous solubility, and compare it to the value obtained by applying the bond contributions given in Table 6.4. (Use the K_{iaw} -value of toluene that you can find in the Appendix C as a starting value.) Which value do you trust more?

Hint: Use also other compound properties that are available or that can be estimated to perform simple plausibility tests on the experimental vapor pressure and aqueous solubility data of BC at 25°C .



$i =$ benzyl chloride (BC)

$$T_m = -39^\circ\text{C}$$

$$T_b = 179.3^\circ\text{C}$$

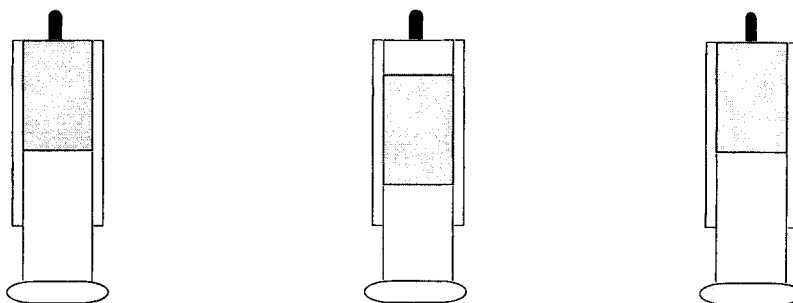
$$p_{iL}^*(25^\circ\text{C}) = 1.7 \times 10^{-3} \text{ bar}$$

$$C_{iw}^{\text{sat}}(25^\circ\text{C}) = 3.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

P 6.5 *Experimental Determination of the Air–Water Partition Constant of CF₃I (From Roberts, 1995)*

Not all stratospheric ozone destruction is caused by freons: up to 25% of the Antarctic “ozone hole” has been attributed to halons, compounds frequently used as fire extinguishers. A halon is a bromofluorocarbon; examples include CF₃Br, CF₂BrCl, and BrF₂C–CF₂Br. Because of their potential for damage to the environment, *production* of halons was banned as of Jan. 1, 1994 as part of an international agreement, although *use* of fire extinguishers containing halons is still allowed. Nevertheless, the chemical industry is still anxiously searching for alternatives to halons. One such promising alternative that has emerged is CF₃I, a gas with a boiling point of –22.5°C.

You are trying to measure the air–water partition constant of CF₃I. The method you are using is one of multiple equilibration. Essentially, a glass syringe containing 17 mL of water (but no headspace) is initially saturated with CF₃I. A very small sample (1 μL) of the aqueous phase is removed and is injected into a gas chromatograph, and the peak area is recorded (“initial peak area”). Next, 2 mL of air is drawn up into the syringe, which is closed off and shaken for 15 minutes to equilibrate the air and water phases. The air phase is dispelled from the syringe, 1 μL of the aqueous phase is injected into the GC, and the new peak area is recorded (“first equilibration”). The process of adding 2 mL of air, shaking the syringe, dispelling the gas phase, and reanalyzing the aqueous phase is repeated several times:



1. Fill with saturated CF₃I solution; analyze
2. Add 2 mL air to 17 mL water; equilibrate
3. Dispel air and reanalyze

4. Repeat steps 2 and 3 as required.

Shown below are data for CF₃I that you have obtained using the technique just described. Derive a mathematical relationship between peak area and the number of equilibration steps, and use this relationship to determine the K_{iaw} value for this compound from the appropriate regression of the experimental data provided. Assume that the peak area is linearly proportional to the concentration of CF₃I in the aqueous phase.

Experimental data (note all equilibrations conducted at room temperature):

Equilibration		Equilibration	
Number	Peak Area (mV · s)	Number	Peak Area (mV · s)
0	583.850	6	21.370
0	532.089	7	13.726
1	287.789	7	11.134
1	291.891	7	10.581
2	152.832	8	7.285
2	158.352	8	5.282
3	95.606	9	4.435
3	105.630	9	3.173
4	61.371	10	1.726
4	56.450	10	2.606
5	41.332	11	1.440
5	36.071	11	1.754

Hint: Make yourself clear that the peak area remaining after the headspace is dispelled after an equilibration (i.e., the n th one) is related to the peak area determined in the previous measurement (i.e., the $(n-1)$ th equilibrium) by:

$$(\text{Area})_{\text{measured at equil. } n} = f_w \cdot (\text{Area})_{\text{measured at equil. } n-1}$$

where f_w is the fraction of the total mass present in the water at equilibrium. Note that f_w is constant because the air-to-water volume ratio is always the same, and because it can be assumed that K_{iaw} is independent of concentration.

P 6.6 Purge and Trap: How Long Do You Need to Purge to Get 90% of a Given Compound Out of the Water?

The purge-and-trap method (see Section 6.4) is a common method to enrich volatile organic compounds from water samples. In your apparatus, you purge a 1 L water sample with a gas (air) volume flow of 1.5 L gas per minute at a temperature of 25°C. The compounds that you are interested in include tetrachloroethene, chlorobenzene and methyl-*t*-butylether (MTBE). Calculate the time required to purge 90% of each compound from the water. Any comments? How much time would you save if you would increase the temperature from 25°C to 35°C? What could be a problem when raising the temperature too much? You can find all necessary data in Appendix C and in Table 6.3.

