

## Chapter 5

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## 5.1 Introduction

Whether an organic compound “likes” or “dislikes” being surrounded by liquid water, or alternatively whether water “likes” or “dislikes” to accommodate a given organic solute, is of utmost importance to the environmental behavior and impact of that compound. Due to its small size and hydrogen-bonding characteristics, water is a rather exceptional solvent. Indeed, environmentally relevant compounds have aqueous solubilities ranging over more than ten orders of magnitude — from completely soluble compounds (i.e., miscible) to levels of saturation that are so low that the concentration can be measured only with very sophisticated methods (Appendix C). In this chapter, we will discuss and try to visualize the molecular factors that cause this immense range of results associated with transferring an organic compound from a nonaqueous phase to an aqueous solution (or vice versa).

We will start our discussion by considering a special case, that is, the situation in which the molecules of a pure compound (gas, liquid, or solid) are partitioned so that its concentration reflects equilibrium between the pure material and aqueous solution. In this case, we refer to the equilibrium concentration (or the *saturation* concentration) in the aqueous phase as the *water solubility* or the *aqueous solubility* of the compound. This concentration will be denoted as  $C_{iw}^{\text{sat}}$ . This compound property, which has been determined experimentally for many compounds, tells us the maximum concentration of a given chemical that can be dissolved in pure water at a given temperature. In Section 5.2, we will discuss how the aqueous activity coefficient *at saturation*,  $\gamma_{iw}^{\text{sat}}$ , is related to aqueous solubility. We will also examine when we can use  $\gamma_{iw}^{\text{sat}}$  as the activity coefficient of a compound in *diluted* aqueous solution,  $\gamma_{iw}^{\infty}$  (which represents a more relevant situation in the environment).

In the next step in Section 5.3, we will explore how chemical structures of the solutes govern their aqueous activity coefficients. This will be done by inspecting how the chemical structures of the solutes correspond to different enthalpic and entropic contributions to the excess free energy of putting those substances in aqueous solution. Using these insights we will extend the molecular interaction model that we introduced and applied in Chapter 4 to quantitatively describe activity coefficients in pure water. In Section 5.4, we will then deal with the effects of temperature and of certain dissolved water constituents that may be present in the environment (i.e., inorganic ions, organic cosolutes and cosolvents) on the solubilities and the aqueous activity coefficients of organic compounds. Finally, in Section 5.5 we will comment on experimental methods and on predictive tools used to estimate aqueous solubilities and aqueous activity coefficients of organic compounds.

## 5.2 Thermodynamic Considerations

### Solubilities and Aqueous Activity Coefficients of Organic Liquids

Let us first imagine an experiment in which we bring a pure, water-immiscible organic *liquid* into contact with pure water at a given temperature and ask what will happen. Intuitively, we know that some organic molecules will leave the organic phase and

dissolve into water, while some water molecules will enter the organic liquid. After some time, so many organic molecules will have entered the water that some will begin to return to the organic phase. When the fluxes of molecules into and out of the organic phase are balanced, the system has reached a state of equilibrium. At this point, the amount of organic molecules in the water is the water solubility of that liquid organic compound. Similarly, the amount of water molecules in the organic phase reflects the solubility of water in that organic liquid.

To describe this process thermodynamically, at any instant in time during our experiment, we can express the chemical potentials of the organic compound  $i$  in each of the two phases (Chapter 3). For the compound in the *organic liquid phase*, we have:

$$\mu_{iL} = \mu_{iL}^* + RT \ln \gamma_{iL} \cdot x_{iL} \quad (5-1)$$

where we use the subscript L to indicate the pure liquid organic phase, although it contains some water molecules. For the compound in the aqueous phase, the corresponding expression of its chemical potential is:

$$\mu_{iw} = \mu_{iL}^* + RT \ln \gamma_{iw} \cdot x_{iw} \quad (5-2)$$

where we use the subscript  $w$  to refer to parameters of the compound  $i$  in the *water*. Note that both expressions relate chemical potential to the same reference potential,  $\mu_{iL}^*$ . Hence at any given time, the difference in chemical potentials of the “product” (solutes in aqueous solution) minus the “reactant” ( $i$  in its pure liquid) molecules is given by:

$$\mu_{iw} - \mu_{iL} = RT \ln \gamma_{iw} \cdot x_{iw} - RT \ln \gamma_{iL} \cdot x_{iL} \quad (5-3)$$

In the beginning of our experiment,  $\mu_{iL}$  is much larger than  $\mu_{iw}$  ( $x_{iw}$  is near zero). Therefore, a net flux of organic molecules from the organic phase (higher chemical potential) to the aqueous phase (lower chemical potential) occurs. This process continues and  $x_{iw}$  increases until the chemical potentials (or the fugacities) become equal in both phases. At this point, equilibrium is reached and we may say:  $\gamma_{iw} x_{iw} = \gamma_{iL} x_{iL}$  and  $\mathcal{F}_{iw} = \mathcal{F}_{iL}$ ! Once at equilibrium, we obtain:

$$\ln \frac{x_{iw}^{\text{sat}}}{x_{iL}} = \frac{RT \ln \gamma_{iL} - RT \ln \gamma_{iw}^{\text{sat}}}{RT} \quad (5-4)$$

where now we use the superscript “sat” to indicate that we are dealing with a saturated aqueous solution of the compound. In Eq. 5-4 we also retain the product of the gas constant and system temperature,  $RT$ , to indicate that the ratio of concentrations in the two phases is related to a difference in free energies (i.e., each term,  $RT \ln \gamma$ , is a free energy term for one mole of molecules in a particular state).

For the majority of the compounds of interest to us, we can now make two important simplifying assumptions. First, in the organic liquid, the mole fraction of water is small compared with the mole fraction of the compound itself; that is,  $x_{iL}$  remains nearly 1 (see Table 5.1). Also, we may assume that the compound shows ideal behavior in its water-saturated liquid phase; that is, we set  $\gamma_{iL} = 1$ . With these assumptions, after some rearrangement, Eq. 5-4 simplifies to:

**Table 5.1** Mole Fraction of Some Common Organic Liquids Saturated with Water <sup>a</sup>

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

<sup>a</sup> Data from a compilation presented by Demond and Lindner (1993).

$$\ln x_{iw}^{\text{sat}} = -\frac{RT \ln \gamma_{iw}^{\text{sat}}}{RT} = -\frac{G_{iw}^{\text{E,sat}}}{RT} \quad (5-5)$$

where  $G_{iw}^{\text{E,sat}}$  is the *excess free energy* of the compound in *saturated* aqueous solution (see Chapter 3).

Now we can see a key result. The aqueous mole fraction solubility of an organic liquid is simply given by the inverse aqueous activity coefficient:

$$x_{iw}^{\text{sat}} = \frac{1}{\gamma_{iw}^{\text{sat}}} \quad \text{for liquids}$$

or in the more usual molar units (Eq. 3-43): (5-6)

$$C_{iw}^{\text{sat}} = \frac{1}{\bar{V}_w \cdot \gamma_{iw}^{\text{sat}}} \quad \text{for liquids}$$

where  $\bar{V}_w$  is the molar volume of water (0.018 L/mol).

Obviously, we can also say that for a liquid compound, the aqueous activity coefficient at saturation is given by the inverse of its mole fraction solubility:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}} \quad (5-7)$$

or:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\bar{V}_w \cdot C_{iw}^{\text{sat}}}$$

### Solubilities and Aqueous Activity Coefficients of Organic Solids

When considering the solubility of a solid organic compound in water, conceptually we can imagine first converting it to the liquid state and then proceeding as above for a liquid compound. The free energy cost involved in the solid-to-liquid conversion is referred to as the free energy of fusion,  $\Delta_{\text{fus}}G_i$  (Chapter 4). This entity can be derived from experimental vapor pressure data (Eq. 4-14):

$$\Delta_{\text{fus}}G_i = RT \ln \frac{p_{iL}^*}{p_{is}^*} \quad (5-8)$$

It can also be estimated from the melting point of the compound (Eq. 4-41).

Now, we can express the difference in chemical potential as:

$$\begin{aligned} \mu_{iw} - \mu_{is} &= \mu_{iw} - (\mu_{iL} - \Delta_{\text{fus}}G_i) \\ &= RT \ln \gamma_{iw} \cdot x_{iw} - (RT \ln \gamma_{iL} \cdot x_{iL} - \Delta_{\text{fus}}G_i) \end{aligned} \quad (5-9)$$

By setting  $x_{iL}$  and  $\gamma_{iL}$  equal to 1, and by proceeding as above for liquids, we then obtain at equilibrium ( $\mu_{iw} - \mu_{is} = 0$ ):

$$x_{iw}^{\text{sat}}(s) = \frac{1}{\gamma_{iw}^{\text{sat}}} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \quad \text{for solids} \quad (5-10)$$

or in molar units:

$$C_{iw}^{\text{sat}}(s) = \frac{1}{\bar{V}_w \cdot \gamma_{iw}^{\text{sat}}} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \quad \text{for solids}$$

Now it is clear that the solubilities of organic solids in water are dependent on both the incompatibility of the chemicals with the water *and* the ease with which the solids are converted to liquids.

One may also see how the aqueous activity coefficient is related to solubility for organic substances that are solids:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{x_{iw}^{\text{sat}}(s)} \cdot e^{-\Delta_{\text{fus}}G_i/RT} \quad (5-11)$$

or:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\bar{V}_w \cdot C_{iw}^{\text{sat}}(s)} \cdot e^{-\Delta_{\text{fus}}G_i/RT}$$

Recalling the concept of a *subcooled* liquid compound as one that has cooled below its freezing temperature without becoming solid (Chapter 4.2), we may evaluate the solubility of such a hypothetical liquid,  $C_{iw}^{\text{sat}}(L)$ , from Eq. 5-11 as:

$$\gamma_{iw}^{\text{sat}} = \frac{1}{\bar{V}_w \cdot C_{iw}^{\text{sat}}(L)} \quad (5-12)$$

where the liquid compound solubility is related to the actual experimental solubility of the solid compound by:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{\text{sat}}(\text{s}) \cdot e^{+\Delta_{\text{fus}}G_i/RT} \quad (5-13)$$

### Solubilities and Aqueous Activity Coefficients of Organic Gases

The aqueous solubility of a gaseous compound is commonly reported for 1 bar (or 1 atm = 1.013 bar) partial pressure of the pure compound. One of the few exceptions is the solubility of O<sub>2</sub> which is generally given for equilibrium with the gas at 0.21 bar, since this value is appropriate for the earth's atmosphere at sea level. As discussed in Chapter 3, the partial pressure of a compound in the gas phase (ideal gas) at equilibrium above a liquid solution is identical to the fugacity of the compound in the solution (see Fig. 3.9d). Therefore equating fugacity expressions for a compound in both the gas phase and an equilibrated aqueous solution phase, we have:

$$p_i = \gamma_{iw} \cdot x_{iw} \cdot p_{iL}^* \quad (5-14)$$

Now we can see how to express the mole fraction solubility of a gaseous organic substance as a function of the partial pressure  $p_i$ :

$$x_{iw}^{p_i} = \frac{1}{\gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad \text{for gases} \quad (5-15)$$

or in molar units:

$$C_{iw}^{p_i} = \frac{1}{\bar{V}_w \cdot \gamma_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad \text{for gases}$$

It thus follows that the aqueous activity coefficient of a gaseous pure compound is related to the solubility by:

$$\gamma_{iw}^{p_i} = \frac{1}{x_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*} \quad (5-16)$$

or:

$$\gamma_{iw}^{p_i} = \frac{1}{\bar{V}_w \cdot C_{iw}^{p_i}} \cdot \frac{p_i}{p_{iL}^*}$$

Note that  $\gamma_{iw}^{p_i}$  is not necessarily constant with varying  $p_i$ . In fact, evaluation of the air–water equilibrium distribution ratio as a function of  $p_i$  is one of the methods that can be used to assess the concentration dependence of  $\gamma_{iw}$  of an organic compound, regardless whether the compound is a gas, liquid, or solid at the temperature considered (see below).

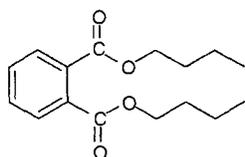
If, for sparingly soluble gases, we assume that  $\gamma_{iw}^{p_i}$  is independent of concentration (even at saturation, i.e., at  $p_i = p_{iL}^*$ , where the compound is also present as a liquid), then we can calculate the solubility of the *superheated liquid compound*,  $C_{iw}^{\text{sat}}(\text{L})$ , from the actual solubility determined at  $p_i$  (e.g., at 1 bar) by:

$$C_{iw}^{\text{sat}}(\text{L}) = C_{iw}^{p_i} \cdot \frac{p_{iL}^*}{p_i} \quad (5-17)$$

Some example calculations demonstrating how to derive  $\gamma_{iw}$  and  $G_{iw}^E$  values from experimental solubility data are given in Illustrative Example 5.1.

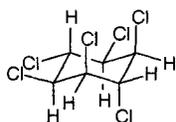
**Illustrative Example 5.1****Deriving Liquid Aqueous Solubilities, Aqueous Activity Coefficients, and Excess Free Energies in Aqueous Solution from Experimental Solubility Data****Problem**

Calculate the  $C_{iw}^{\text{sat}}$  (L),  $\gamma_{iw}^{\text{sat}}$  and  $G_{iw}^E$  of (a) di-*n*-butyl phthalate, (b)  $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane ( $\gamma$ -HCH, lindane), and (c) chloroethene (vinyl chloride) at 25°C using the data provided in Appendix C.

di-*n*-butyl phthalate

$$C_{iw}^{\text{sat}}(25^\circ\text{C}) = 3.4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$T_m < 25^\circ\text{C}$$

1,2,3,4,5,6-hexachlorocyclohexane  
( $\gamma$ -HCH)

$$C_{iw}^{\text{sat}}(25^\circ\text{C}) = 2.5 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$T_m = 113^\circ\text{C}$$



Chloroethene (vinyl chloride)

$$C_{iw}^{\text{bar}}(25^\circ\text{C}) = 4.4 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

$$p_L^*(25^\circ\text{C}) = 3.55 \text{ bar}$$

**Answer (a)**

Di-*n*-butylphthalate is a liquid at 25°C. Hence,  $C_{iw}^{\text{sat}} = C_{iw}^{\text{sat}}(\text{L}) = 3.4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ , and (Eq. 5-7):

$$\gamma_{iw}^{\text{sat}} \cong \frac{1}{(0.018 \text{ L} \cdot \text{mol}^{-1})(3.4 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1})} = 1.6 \times 10^6$$

which yields an excess free energy of:

$$G_{iw}^{\text{E,sat}} = RT \ln \gamma_{iw}^{\text{sat}} = (8.314 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1})(298.1 \text{ K})(14.3) = 35.4 \text{ kJ} \cdot \text{mol}^{-1}$$

**Answer (b)**

$\gamma$ -HCH is a solid at 25°C. To calculate the solubility of liquid  $\gamma$ -HCH, estimate first the free energy of fusion from the normal melting point temperature (Eq. 4-41, see also Problem 4.7):

$$\Delta_{\text{fus}} G_i \cong (56.5) [386 - 298] \cong 5.0 \text{ kJ} \cdot \text{mol}^{-1}$$

Insert the values for  $C_{iw}^{\text{sat}}$  and  $\Delta_{\text{fus}} G_i$  into Eq. 5-13 to get  $C_{iw}^{\text{sat}}(\text{L})$ :

$$C_{iw}^{\text{sat}}(\text{L}) = (2.5 \times 10^{-5}) \cdot e^{+(5.0/2.48)} = 1.9 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

Insertion of  $C_{iw}^{\text{sat}}(\text{L})$  into Eq. 5-12 yields:

$$\gamma_{iw}^{\text{sat}} \cong 2.9 \times 10^5, \text{ and } G_{iw}^E = 31.2 \text{ kJ} \cdot \text{mol}^{-1}$$

**Answer (c)**

Chloroethene (Vinylchloride) is a gas at 25°C. Calculate first the solubility of superheated liquid vinylchloride (Eq. 5-17):

$$C_{iw}^{\text{sat}}(\text{L}) = (4.4 \times 10^{-2}) \left( \frac{3.55}{1} \right) = 1.6 \times 10^{-1} \text{ mol} \cdot \text{L}^{-1}$$

This yields

$$\gamma_{iw}^{\text{sat}} \cong 3.5 \times 10^2, \text{ and } G_{iw}^E = 14.5 \text{ kJ} \cdot \text{mol}^{-1}$$

**Table 5.2** Comparison of Activity Coefficients and Corresponding Excess Free Energies of a Series of Organic Compounds in Dilute and Saturated Aqueous Solution at 25°C (recall that  $G_{iw}^E = RT \ln \gamma_{iw}$ )

Compound	$\gamma_{iw}^{\text{sat}}$	$G_{iw}^{\text{E,sat}}$ <sup>a</sup> (kJ·mol <sup>-1</sup> )	$\gamma_{iw}^{\infty}$	$G_{iw}^{\text{E},\infty}$ <sup>b</sup> (kJ·mol <sup>-1</sup> )
Methanol	miscible	miscible	1.6	1.2
Ethanol	miscible	miscible	3.7	3.2
Acetone	miscible	miscible	7.0	4.8
1-Butanol	$7.0 \times 10^1$	10.5	$5.0 \times 10^1$	9.7
Phenol	$6.3 \times 10^1$	10.3	$5.7 \times 10^1$	10.0
Aniline	$1.4 \times 10^2$	12.3	$1.3 \times 10^2$	12.1
3-Methylphenol	$2.5 \times 10^2$	13.7	$2.3 \times 10^1$	13.5
1-Hexanol	$9.0 \times 10^2$	16.9	$8.0 \times 10^2$	16.5
Trichloromethane	$7.9 \times 10^2$	16.5	$8.2 \times 10^2$	16.6
Benzene	$2.5 \times 10^3$	19.4	$2.5 \times 10^3$	19.4
Chlorobenzene	$1.4 \times 10^4$	23.7	$1.3 \times 10^4$	23.5
Tetrachloroethene	$7.5 \times 10^4$	27.8	$5.0 \times 10^4$	26.8
Naphthalene	$6.7 \times 10^4$	27.5	$6.9 \times 10^4$	27.6
1,2-Dichlorobenzene	$6.2 \times 10^4$	27.3	$6.8 \times 10^4$	27.6
1,3,5-Trimethylbenzene	$1.3 \times 10^5$	29.2	$1.2 \times 10^5$	29.0
Phenanthrene	$2.0 \times 10^6$	35.9	$1.7 \times 10^6$	35.5
Anthracene	$2.5 \times 10^6$	36.5	$2.7 \times 10^6$	36.7
Hexachlorobenzene	$4.3 \times 10^7$	43.6	$3.5 \times 10^7$	43.0
2,4,4'-Trichlorobiphenyl	$5.6 \times 10^7$	44.2	$4.7 \times 10^7$	43.8
2,2',5,5'-Tetrachlorobiphenyl	$7.0 \times 10^8$	46.5	$7.5 \times 10^7$	44.9
Benzo(a)pyrene	$3.2 \times 10^8$	48.5	$2.7 \times 10^8$	48.1

<sup>a</sup> Data from Appendix C using enthalpy and entropy of fusion values given by Hinckley et al. (1990), and Lide (1995). <sup>b</sup> Data from Sherman et al. (1996), Staudinger and Roberts (1996), Mitchell and Jurs (1998).

### Concentration Dependence of the Aqueous Activity Coefficient

From an environmental point of view, it is often of most interest to know the activity coefficient of an organic compound in *dilute* aqueous solution. This activity coefficient is commonly denoted as  $\gamma_{iw}^{\infty}$ , and is referred to as *limiting* activity coefficient or *infinite dilution* activity coefficient.

As we have shown above, activity coefficients can be deduced from the aqueous solubilities (together with vapor pressure or melting data, as necessary). In this case, the activity coefficient reflects the compatibility of the organic solute with water solutions that may have been significantly modified by the presence of the solute itself. It is important to know when such values of  $\gamma_{iw}^{\text{sat}}$  will be the same as the corresponding  $\gamma_{iw}^{\infty}$  values. Table 5.2 shows a comparison of  $\gamma_{iw}^{\text{sat}}$  values obtained from solubility measurements (Eqs. 5-6 and 5-10) with  $\gamma_{iw}^{\infty}$  values determined by various methods (that will be addressed in Section 5.5) for a series of compounds covering a very large range in activity coefficients. As is evident, even for compounds exhibiting

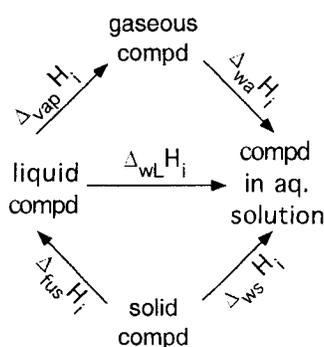
a substantial aqueous solubility (e.g., 1-butanol, phenol), the differences between the activity coefficients in dilute solution and in saturated solution are not larger than about 30%. In fact, particularly for the more sparingly soluble compounds, the differences are well within the range of error of the experimental data. Hence, for compounds exhibiting activity coefficients larger than about 100 (which represents the majority of the chemicals of interest to us), we will assume that  $\gamma_{iw}$  is independent of the concentration of the compound (and, therefore, we will typically omit any superscript). By making this assumption, we imply that the organic solutes do not “feel” each other in the aqueous solution even under saturation conditions. Or to put it more scientifically, we assume that the solvation of a given organic molecule by water molecules is not influenced by the other organic molecules present. But, as we will see in the following, this assumption is not always true!

## 5.3

### Molecular Interpretation of the Excess Free Energy of Organic Compounds in Aqueous Solutions

#### Enthalpic and Entropic Contributions to the Excess Free Energy

Water is a very unique solvent that has two outstanding characteristics: (1) the small size of its molecules, and (2) the strong hydrogen bonding between these molecules. Hence, when we consider the molecular factors that govern the free energy of the transfer of an organic compound from its pure liquid into a pure aqueous phase, we have to be aware that it takes quite a number of water molecules to surround each organic molecule. Also, the water molecules adjacent to the organic solute are in a special situation with respect to forming hydrogen bonds as compared to the other bulk water molecules.



**Figure 5.1** Enthalpies of the various phase transfers that can be used to derive the excess enthalpy,  $H_{iw}^E$ , of an organic compound in saturated and in dilute aqueous solution.

Before we deal with these molecular aspects in detail, it is instructive to inspect the enthalpic ( $H_{iw}^E$ ) and entropic ( $-T \cdot S_{iw}^E$ ) contributions to the excess free energies of various organic compounds in aqueous solution (Table 5.3). Values representative of *saturated* aqueous solutions of the compounds have been derived from measurements of the enthalpies of dissolution of the liquids (i.e.,  $H_{iw}^E = \Delta_{wL}H_i$ , Fig. 5.1) or solids ( $H_{iw}^E = \Delta_{ws}H_i - \Delta_{fus}H_i$ , Fig. 5.1). Data suited to *dilute* conditions have been obtained from enthalpies of air–water partitioning (i.e.,  $H_{iw}^E = \Delta_{vap}H_i + \Delta_{wa}H_i$ , Fig. 5.1). Since in both the saturated and dilute solution, the excess free energies are indistinguishable [data in Table 5.2 gives  $G_{iw}^E$  (dilute) = 0.989  $G_{iw}^{E,sat}$  (saturated) – 0.038,  $R^2 = 0.99$ ], the entropy contributions have been calculated using one (average)  $G_{iw}^E$  value. Note that the experimental data reported in the literature show considerable scatter, particularly when comparing  $H_{iw}^E$  values determined for saturated conditions with those determined for dilute solutions. Therefore, the numbers given in Table 5.3 should be treated with some caution. Nevertheless, these data allow us to draw some important general conclusions.

The first and most important feature that can be seen from the data (Table 5.3) is that the excess enthalpies of the smaller-sized compounds are close to zero (i.e., between  $-10$  and  $+10$  kJ  $\cdot$  mol $^{-1}$ ). This is even true for apolar compounds such as tetrachloroethene or hexane. Hence in these cases, the intermolecular interactions that must be disrupted to remove a small organic molecule from its pure liquid (i.e., the enthalpy

**Table 5.3** Enthalpic ( $H_{iw}^E$ ) and Entropic ( $S_{iw}^E$ ) Contributions to the Excess Free Energy of a Series of Organic Compounds in Saturated (“Sat”) and Dilute (“Dil”) Aqueous Solution at 20 to 25°C. The Compounds are Ordered by Increasing Size Expressed by Their Molar Volume

Compound	Molar Volume <sup>a</sup> (cm <sup>3</sup> ·mol <sup>-1</sup> )	$G_{iw}^E$ (kJ·mol <sup>-1</sup> )	$H_{iw}^E$ (kJ·mol <sup>-1</sup> ) Sat <sup>b</sup> /Dil <sup>c,d</sup>	$T \cdot S_{iw}^E$ (kJ·mol <sup>-1</sup> ) Sat/Dil
Trichloromethane	81	17	-2/3	-19/-20
Benzene	89	19	2/4	-21/-23
2-Butanone	90	8	-7/-5	-15/-13
Trichloroethene	90	22	-4/2	-26/-20
Phenol	90	10	1/8	-9/-2
Aniline	91	12	2	-10
Tetrachloromethane	97	23	-4/-2	-27/-25
Tetrachloroethene	102	27	-5/3	-32/-24
Benzaldehyde	102	19	4/10	-15/-9
4-Methylphenol	103	13	2/11	-11/-2
Diethylether	104	18	-20/-14	-31/-25
Benzylalcohol	104	12	-7	-19
Methylbenzene	106	23	2/6	-21/-17
2-Pentanone	106	11	-7	-19
Diethylsulfide	108	18	-1/-1	-19/-19
1-Pentanol	109	13	-8	-21
n-Pentane	116	29	-2	-31
1,4-Dimethylbenzene	123	26	3/9	-23/-16
Naphthalene	130	28	9/12	-19/-16
n-Hexane	132	32	-0	-32
1,3,5-Trimethylbenzene	139	29	8	-21
n-Propylbenzene	139	29	2	-27
1-Octanol	158	23	-3	-26
n-Octane	164	40	6	-34
Hexachlorobenzene	167	43	11/27	-32/-16
Phenanthrene	171	36	17/46	-19/+10!
Anthracene	171	37	20/43	-17/+6!
Benzo(a)pyrene	223	48	25/61	-23/+13!

<sup>a</sup> Calculated from density and molar mass. <sup>b</sup> Data from Whitehouse (1984), Abraham et al. (1990), and Shiu et al. (1997). <sup>c</sup> Data from Dewulf et al. (1995), Dohnal and Fenclová (1995), Staudinger and Roberts (1996), and Alaei et al. (1996). <sup>d</sup> Enthalpies of vaporization from Hinckley et al. (1990), and Lide (1995).

of vaporization) are more or less replaced by intermolecular interactions of equal strength in the water.

Only for larger apolar and weakly monopolar compounds (e.g., PAHs, PCBs) are significantly more positive  $H_{iw}^E$  values found. Indeed, if we examine the  $H_{iw}^E$  values within single compound classes, we can see that this parameter becomes more positive as the sizes of the structures increase (e.g., benzene, naphthalene, anthracene, benzo(a)pyrene).

Thus, for small organic compounds (molar volumes  $< 150 \text{ cm}^3 \text{ mol}^{-1}$ ), it is the unfavorable entropy term that dominates the excess free energy of solution. Since these chemicals were historically studied first, this is probably the origin of the “sense” that entropic effects determine the “hydrophobicity” of organic compounds. However, since larger organic compounds have increasingly disfavorable enthalpic contributions, when we are interested in these substances both enthalpy and entropy must be considered. At this point it should be noted that for these compounds (e.g., hexachlorobenzene, phenanthrene, anthracene) the  $H_{iw}^E$  values derived for saturated and dilute conditions show considerable differences (Table 5.3). In all these cases the  $H_{iw}^E$  values are significantly larger for dilute conditions. This difference in excess enthalpy is obviously compensated by an increase in excess entropy, since  $G_{iw}^E$  is more or less independent of concentration (see above). To date, however, there are not enough experimental data available to assess whether this is a real phenomenon, or whether these findings are due to experimental artifacts.

### Molecular Picture of the Dissolution Process

Let us now try to visualize the various molecular changes that determine the enthalpies and entropies of transferring an organic molecule from its pure liquid into water. As already pointed out, one of the key concerns in this process is how the water molecules surrounding the organic compound arrange themselves to optimize their own interactions from an energetic point of view. Since water is an “associated” liquid, meaning that its molecules are hydrogen-bonded so extensively that they act as “packets” of several  $\text{H}_2\text{O}$  molecules tied together, one must also consider the organic solute’s influence on water molecules that are not in direct contact with the organic solute.

In the classical model view, it is thought that the water molecules form an ice-like structure around the organic molecule (Frank and Evans, 1945; Shinoda, 1977). This results from the need of water molecules to maximize their hydrogen bonding. Since the apolar portions of organic solutes cannot participate in this type of intermolecular interaction, the water molecules lining the “solute cavity” were believed to orient so as to maximize their hydrogen bonding to the waters away from the solute. Such orientation would limit the directions these cavity-lining water molecules could face, thereby having the effect of “freezing” them in space. This freezing effect would give rise to an enthalpy gain and an entropy loss, which would be in accordance with the experimental solubility data.

However, the results from numerous, more recent experimental and theoretical studies support an alternative picture (Blokzijl and Engberts, 1993; Meng and Kollman, 1996). In this scenario, the water surrounding a nonpolar solute maintains, but does not enhance, its H-bonding network. One can imagine that, at ambient temperatures, the packets of water molecules adjacent to an apolar organic molecule lose only a very small proportion of their total hydrogen bonds (i.e., the packet:packet interactions). By doing so, they are able to host an apolar solute of limited size without losing a significant number of their H-bonds (Blokzijl and Engberts, 1993). Hence, the introduction of a relatively small apolar or weakly polar organic solute that undergoes primarily vdW interactions should not provoke a significant loss in enthalpy due to the breaking of H-bonds among the water molecules. For such solutes it is, therefore, not surprising that the enthalpy that has to be spent to isolate the com-

pounds from their pure liquid (i.e., the enthalpy of vaporization) is about equal to the enthalpy gained from the vdW interactions of the organic molecules with the water molecules in the aqueous solution. Examples of such compounds include benzene, tetrachloromethane, tetrachloroethene, methylbenzene (toluene), *n*-pentane, 1,4-dimethylbenzene, and *n*-hexane (Table 5.3).

The factors that determine the large unfavorable entropy terms for these compounds are somewhat more difficult to rationalize. First, there is a diminishing effect of the favorable entropy of dissolving (or mixing) a (large) organic compound in a solvent consisting of very small molecules, which is, of course, particularly true for water. This excess entropy term can be as big as  $-8 \text{ kJ} \cdot \text{mol}^{-1}$ , depending on the size of the organic compound. Note that a difference of about  $6 \text{ kJ} \cdot \text{mol}^{-1}$  (i.e.,  $RT \ln 10$ ) means a factor of 10 difference in the activity coefficient. However, as can be seen from Table 5.3, the actual negative entropy contributions found for the apolar compounds mentioned above are much larger (i.e.,  $20 - 30 \text{ kJ} \cdot \text{mol}^{-1}$ ). Hence, there must be other factors that contribute significantly to this large negative entropy. It is conceivable that the water molecules forming the hydration shell lose some of their freedom of motion as compared to the bulk water molecules when accommodating an (apolar) organic compound. Alternatively, the organic compound itself could experience such a loss of freedom when being transferred from its pure liquid into an environment that is more "rigid," because it is now surrounded by many solvent molecules that are interconnected by hydrogen bonds. Moving from a liquid to a more solid-like environment (thus losing translational, rotational, and flexing freedom) could explain the quite substantial differences in excess entropy found between rigid aromatic (e.g., benzene, methylbenzene, naphthalene) and aliphatic compounds (e.g., pentane, hexane) of similar size (Table 5.3). Indeed, we have already noticed these differences when discussing entropies of fusion in Section 4.4 (Table 4.5) and the involved magnitudes are similar.

Let us now examine what happens to the enthalpy and entropy of solution in water if we introduce a polar group on a small nonpolar organic structure. Generally, the presence of a monopolar or bipolar group leads to a decrease in the enthalpy term and an increase in the entropy term. For example, we can see such changes if we contrast data for 2-pentanone with that for pentane (Table 5.3). Both of these thermodynamic parameters imply that the polar moiety promotes the new compound's solubility over the unsubstituted structure. Note that in the case of bipolar compounds (e.g., alcohols), the effect might not seem as dramatic as may be expected (e.g., compare pentane, 2-pentanone, and 1-pentanol in Table 5.3). But one has to keep in mind that for bipolar compounds (in contrast to the monopolar compounds), polar attractions in the pure organic liquid have to be overcome as part of the total energy of transferring the compound to water.

To rationalize the effect of polar groups on  $H_{iw}^E$  and  $S_{iw}^E$ , we can imagine that polar interactions with the water molecules around the solute cavity replace some of the hydrogen bonds between the water molecules. As indicated by the experimental data, this loss of water:water interaction enthalpy seems to be compensated by the enthalpy gained from the organic solute:water polar interactions. At this point it should also be mentioned that additional polarization effects could enhance the interaction between the organic solute and the water molecules in the hydration shell

(Blokzijl and Engberts, 1993). To explain the entropy gain, we can imagine that a (partial) “loosening up” of the waters surrounding an organic solute will increase the freedom of motion of both the water molecules and the organic solute involved.

So far, we have considered rather small-sized organic molecules. Larger molecules such as the PAHs or the PCBs exhibit large positive excess enthalpies (Table 5.3). Apparently, with increasing apolar solute size, water is not able to maintain a maximum of hydrogen bonds among the water molecules involved. Hence, for these types of compounds the excess enthalpy term may become dominant (Table 5.3).

In summary, we can conclude that the excess free energy of an organic compound in aqueous solution, and thus its activity coefficient, depends especially on (1) the size and the shape of the molecule, and (2) its H-donor and/or H-acceptor properties.

### Model for Description of the Aqueous Activity Coefficient

Let us now extend our molecular descriptor model introduced in Chapter 4 (Eqs. 4-26 and 4-27) to the aqueous activity coefficient. We should point out it is not our principal goal to derive an optimized tool for prediction of  $\gamma_{iw}$ , but to develop further our understanding of how certain structural features determine a compound’s partitioning behavior between aqueous and nonaqueous phases. Therefore, we will try to keep our model as simple as possible. For a more comprehensive treatment of this topic [i.e., of so-called linear solvation energy relationships (LSERs)] we refer to the literature (e.g., Kamlet et al., 1983; Abraham et al., 1990; Abraham, 1993; Abraham et al., 1994a and b; Sherman et al., 1996).

First, we consider how a compound’s size may influence its activity coefficient, which is related to its liquid aqueous solubilities (Section 5.2). Generally, within any one compound class, we have already seen that the excess free energy of solution in water becomes more positive as we consider larger and larger members of each compound class. In each case, we are increasing the size of the molecules in the compound class by adding apolar portions to the overall structure (e.g.,  $-\text{CH}_2-$  groups). Consequently, the integral interactions with the solvent water molecules become increasingly unfavorable.

In light of such empirical trends, and as is illustrated by Fig. 5.2, we should not be surprised to see that relationships of the following forms can be found for individual compound classes:

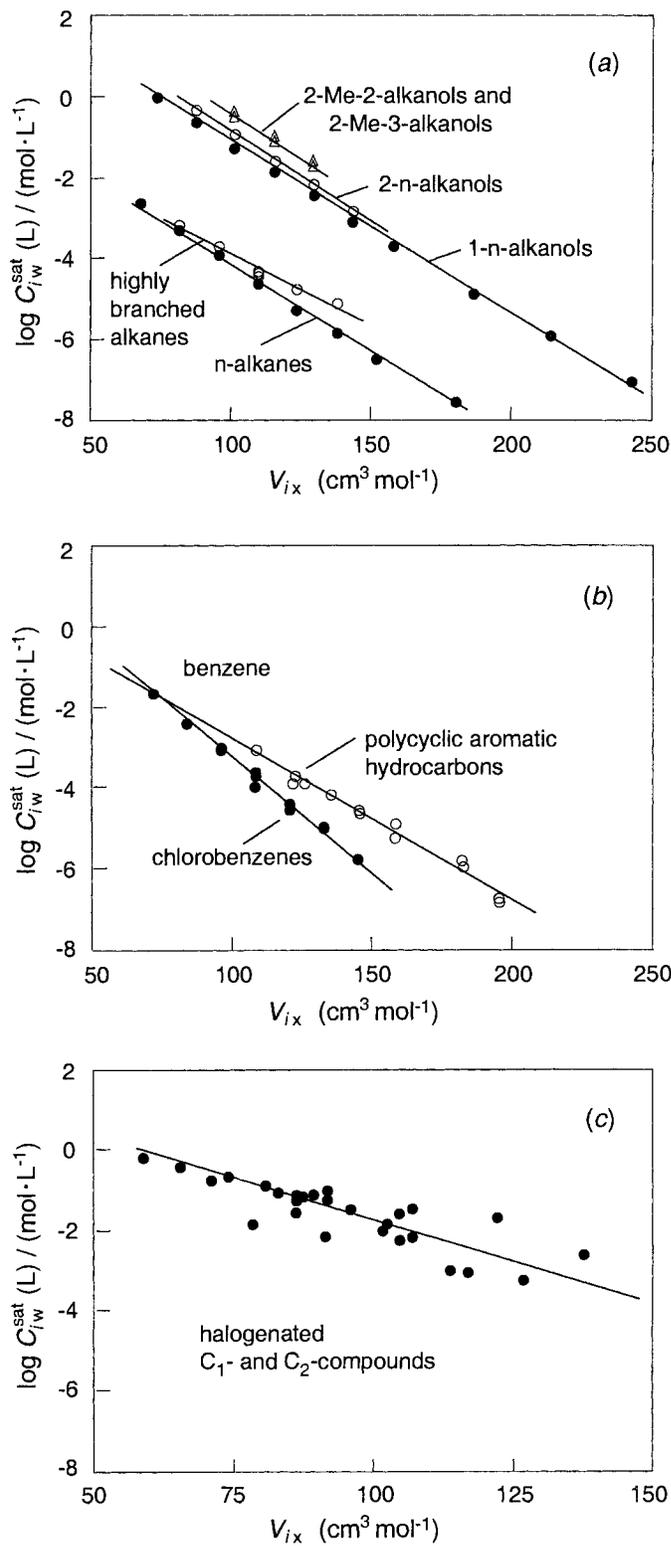
$$\ln \gamma_{iw} = a \cdot (\text{size}_i) + b \quad (5-18)$$

or:

$$\ln C_{iw}^{\text{sat}}(\text{L}) = -c \cdot (\text{size}_i) + d$$

The size parameter in such correlations can come from molecular weights, molar volumes, or other related parameters. One such parameter is the estimate of compound size based on the incremental contributions of the atoms involved. Such an approach is the basis for methods like those of McGowan (see Box 5.1 below).

Having means to estimate relative solute sizes, we recognize that we can now estimate a new compound’s aqueous activity coefficient and/or liquid solubility from



**Figure 5.2** Aqueous solubility of the (subcooled) liquid compound at 25°C as a function of the estimated molar volume ( $V_{i,x}$ , see Box 5.1) of the molecule for various compound classes. The linear regression equations and correlation coefficients ( $R^2$ ) for the various sets of compounds are given in Table 5.4. Note that for practical reasons, decadic instead of natural logarithms are used.

(a) *n*-alkanes ( $C_4$ – $C_{16}$ ), highly branched alkanes ( $C_5$ – $C_9$ ), 1-3-methyl-3-alkanols ( $C_6$ – $C_8$ ); (b) chlorobenzenes ( $Cl_1$ – $Cl_6$ ), polycyclic aromatic hydrocarbons (benzene–benzo(a)pyrene); (c) polyhalogenated methanes, ethanes, and ethenes. Data from Appendix C and from data compilations reported by Ruelle and Kesselring (1997a and b).

**Table 5.4** Linear Relationships Between  $\log C_{iw}^{\text{sat}}(\text{L})$  and  $V_{ix}^a$  for the Various Sets of Compounds Shown in Fig. 5.2 (all data for 25°C).

Set of Compounds	$n^c$	$\log C_{iw}^{\text{sat}}(\text{L}) / (\text{mol} \cdot \text{L}^{-1})$ $= -c \cdot V_{ix} + d^b$		$R^2$
		$c$	$d$	
<i>n</i> -Alkanes	8	0.0442	0.34	0.99
Branched alkanes	7	0.0349	-0.38	0.97
Primary alkanols	10	0.0416	3.01	0.99
Secondary alkanols	5	0.0435	3.52	0.99
Tertiary alkanols	6	0.0438	4.01	0.99
Chlorinated benzenes	13	0.0556	2.27	0.99
Polycyclic aromatic hydrocarbons	13	0.0399	1.90	0.99
Polyhalogenated C <sub>1</sub> - and C <sub>2</sub> -compounds	27	0.0404	1.85	0.86

<sup>a</sup> Molar volume in  $\text{cm}^3 \cdot \text{mol}^{-1}$  estimated by the method discussed in Box. 5.1. <sup>b</sup> Eq. 5-18; note that decadic instead of natural logarithms are used. <sup>c</sup> Number of compounds.

knowledge of the liquid solubilities of other chemicals in its compound class (see examples given in Table 5.4).

While the relations of chemical size and solubility are gratifying to recognize, we still notice that each compound class exhibits its own behavior (Fig. 5.2). Hence, we may wonder if there is any means to account for variations from compound class to compound class. Based on our visualizations of organic solute intermolecular interactions, it is not surprising to learn that parameters that quantify the importance of interactions like hydrogen bonding can be used to adjust for differences between compound classes.

Thinking in analogy to our discussions of the influence of molecular structure on vapor pressures (Eqs. 4-24 to 4-27), we can try to express  $\ln \gamma_{iw}$  by a series of terms describing the various molecular interactions and freedoms of motions when transferring a compound from its pure liquid to water. Unlike the cases discussed in Chapter 4, where one of the phases was the gas phase, now we need to account for both the molecular interactions between the compound and the water and the interactions in the pure liquid. This latter group of interactions, however, can simply be characterized by using the vapor pressure of the compound as a quantitative measure of the intermolecular interactions in the pure liquid. Our problem then reduces to describing the transfer of an organic compound from the gas phase to water:

$$\ln \gamma_{iw} = -\ln p_{iL}^* + \text{terms describing the gas-water transfer} \quad (5-19)$$

It is easy to see that for describing the solvation of an organic solute in water we need to account not only for the size of the molecule (or of the cavity that needs to be formed), but also for the vdW and hydrogen-bonding interactions of the solute with the water molecules. By assuming that the average vdW, H-donor, and H-acceptor properties of the water forming the hydration shell do not vary much with the type of organic solute that they surround, we can include these properties in a correlation equation with appropriate scaling coefficients:

$$\ln \gamma_{iw} = -\ln p_{iL}^* + s \left[ (V_i)^{2/3} \left( \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right] + a(\alpha_i) + b(\beta_i) + vV_i + \text{constant} \quad (5-20)$$

vdW (dispersive)    H-donor    H-acceptor    size

Note that our *multiparameter LFER* Eq. 5-20 includes two terms that contain a volume term (a quantitative measure of the volume of one mole molecules) as a size parameter (“vdW,” “size”-terms). This  $V_i$  value can be the molar volume,  $\bar{V}_i$ , of the compound (derived from the molar mass and the density of the compound, see Chapters 3 and 4), or it can be an estimated entity (see Box 5.1). Therefore, we denote this term as  $V_i$  and not  $\bar{V}_i$ . We will, however, use the term “molar volume” even if we refer to estimated  $V_i$  values.

A question that one might ask is whether it is necessary to include two volume terms in Eq. 5-20, because one could imagine that these two terms are strongly correlated

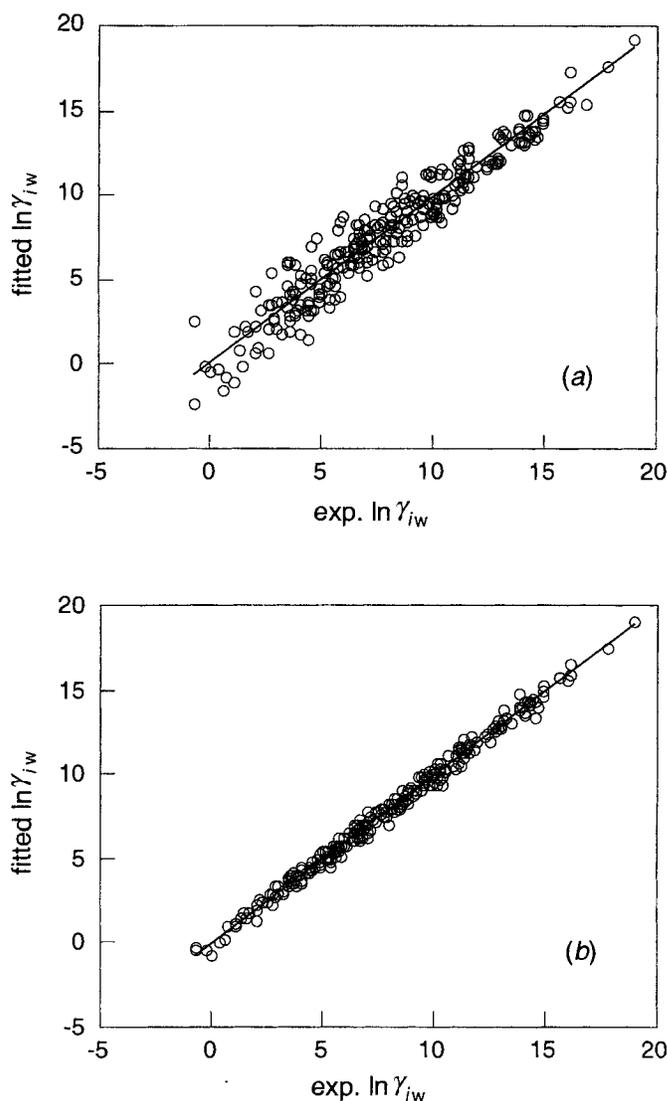
### Box 5.1 Estimating Molar Volumes from Structure

A very common way of expressing the bulk size of the molecules of a given compound (or more precisely of 1 mole of the compound) is to use the “molar volume,”  $V_i$ , of the compound. As we have already discussed in Chapters 3 and 4, we can derive  $V_i$  from the molar mass and from the liquid density (i.e.,  $V_i = \bar{V}_i = M_i / \rho_{iL}$  at a given temperature). This way of defining  $V_i$  has, however, certain disadvantages when we want to express the bulk size of a given compound molecule in equations such as Eq. 5-20. First, because  $\rho_{iL}$  is a bulk property, for polar compounds (e.g., alcohols) that have a network-like hydrogen-bond structure, the calculated  $V_i$  value represents a molar volume that 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 the compound have been developed (for an overview see Chapter 18 and 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). A simple method that seems to work almost as well as the more sophisticated approaches has been proposed by McGowan and coworkers (McGowan and Mellors, 1986; Abraham and McGowan, 1987). In this method, each element is assigned a characteristic atomic volume (see table below) and the total volume, which is denoted as  $V_{ix}$ , is calculated by just summing up all atomic volumes and by subtracting 6.56 cm<sup>3</sup> mol<sup>-1</sup> for each bond, no matter whether single, double, or triple. Thus,  $V_{ix}$  for benzene is calculated as  $V_{ix} = (6)(16.35) + (6)(8.71) - (12)(6.56) = 71.6$  cm<sup>3</sup> mol<sup>-1</sup>, an example that illustrates how trivial the calculation is. Of course, by this method, identical  $V_{ix}$  values will be obtained for structural isomers, which is, however, a reasonable first approximation for many applications. Note again that for each bond between two atoms, 6.56 cm<sup>3</sup> mol<sup>-1</sup> is to be subtracted. Some example calculations are included in some of the illustrative examples.

Characteristic Atomic Volumes in cm<sup>3</sup> mol<sup>-1</sup> (From Abraham and McGowan, 1987)

C	16.35	H	8.71	O	12.43	N	14.39	P	24.87	F	10.48	Cl	20.95
Br	26.21	I	34.53	S	22.91	Si	26.83						





**Figure 5.3** Plot of experimental versus fitted  $\ln \gamma_{iw}$  values for 266 compounds covering a wide variety of compound classes. (a) Fit without using the polarizability parameter  $\pi_i$  (Eq. 5-20). (b) Fit including  $\pi_i$  (Eq. 5-21). The fitting parameters for case (b) are given in Eq. 5-22.

compound (e.g., Platts et al., 2000), its activity coefficient and therefore also its liquid aqueous solubility (Eqs. 5-7 and 5-12) can be predicted from Eq. 5-22 within a factor of 2 to 3.

It should be noted that when replacing the London dispersive interactions term by other properties such as, for example, the air-hexadecane partition constant, by expressing the surface area in a more sophisticated way, and/or by including additional terms, the predictive capability could still be somewhat improved. From our earlier discussions, we should recall that we do not yet exactly understand all the molecular factors that govern the solvation of organic compounds in water, particularly with respect to the entropic contributions. It is important to realize that for many of the various molecular descriptors that are presently used in the literature to model  $\gamma_{iw}$  or related properties (see Section 5.5), it is not known exactly how they contribute to the excess free energy of the compound in aqueous solution. Therefore, when also considering that some of the descriptors used are correlated to each other (a fact that

**Table 5.5** Some Representative  $\pi_i$  Values

Compound or Group of Compounds	$\pi_i^a$	Compound or Group of Compounds	$\pi_i^a$
Alkanes	0.00	1,2,3-Trimethylbenzene	0.61
Cycloalkanes	0.10	1,3,5-Trimethylbenzene	0.52
1-Alkenes	0.08	Naphthalene	0.92
1-Alkynes	0.23	Acenaphthene	1.04
Aliphatic ethers (ROR')	0.25	Chlorobenzene	0.65
Aliphatic aldehydes (RCHO)	0.65	1,2-Dichlorobenzene	0.76
Aliphatic ketones (RCOR')	0.68	1,4-Dichlorobenzene	0.75
Aliphatic carboxylic acid esters (RCOOR')	0.55-0.60	1,2,3-Trichlorobenzene	0.86
Aliphatic amines (RNH <sub>2</sub> )	0.35	1,3,5-Trichlorobenzene	0.73
Primary aliphatic alcohols (R-CH <sub>2</sub> OH)	0.42	1,2,3,4-Tetrachlorobenzene	0.92
Secondary aliphatic alcohols (RR'CHOH)	0.36	1,2,4,5-Tetrachlorobenzene	0.86
Aliphatic carboxylic acids (RCOOH)	0.63	Benzaldehyde	1.00
Trichloromethane	0.49	Benzonitrile	1.11
Tetrachloromethane	0.38	Nitrobenzene	1.11
1,1,2,2-Tetrachloroethane	0.76	Phenol	0.89
Tetrachloroethene	0.42	Alkylphenol	0.80-0.90
Tribromomethane	0.68	2-Chlorophenol	0.88
Benzene	0.52	4-Chlorophenol	1.08
Toluene	0.52	2-Nitrophenol	1.05
1,2-Dimethylbenzene	0.56	4-Nitrophenol	1.72
1,4-Dimethylbenzene	0.52		

<sup>a</sup> Data from Abraham et al. (1994a).

is often not recognized in the literature!), our policy should be to use as few and as *clearly defined* parameters as possible. There is certainly still room for further improvements in this area of research. Nevertheless, as is demonstrated by the examples discussed in Illustrative Example 5.2, Eq. 5-22 is very useful to assess which molecular factors primarily determine the aqueous activity coefficient (or the excess free energy in water) of a given compound.

A very important conclusion that we can draw from our effort to use insights on intermolecular interactions to develop a means to estimate  $\gamma_{iw}$  is that this important compound property is very sensitive to changes in the structure of a compound. Hence, as we will also notice in the following chapters, in any simple structure–property or property–property relationship involving  $\gamma_{iw}$  (or  $C_{iw}^{\text{sat}}(L)$ ), we have to be careful to confine a given equation to a set of compounds for which structural differences either are not reflected, or are proportionally reflected in the type of molecular descriptors used in Eq. 5-22. Otherwise, we are in danger of mixing apples with oranges (and grapes!). For example, as already addressed above, it is common practice to try to correlate the aqueous activity coefficient (or the liquid aqueous solubility as in Fig. 5.2) with the size (molar volume, total surface area) of the organic molecule. As is illustrated by Fig. 5.2, good correlations can be expected only

for sets of compounds that fulfill the above-mentioned criteria. Fig. 5.2a shows, for example, that even sets of quite closely related compounds such as *n*-alkanes and highly branched alkanes, or primary, secondary, and tertiary aliphatic alcohols, exhibit different linear relationships between liquid aqueous solubility and molar volume. In the case of the apolar alkanes (i.e.,  $\pi_i = \alpha_i = \beta_i = 0$ ), the differences must be due to the different shapes of the *n*-alkanes as compared to the highly branched ones. In the case of the aliphatic alcohols, the differences between the three sets of compounds can be found primarily in the polar interaction terms of the alcohol moieties. Within each series, however, very good correlations are obtained. Two other examples where quite satisfying correlations are obtained, are shown in Fig. 5.2b. The rather good correlation found for the apolar, rigid chlorinated benzenes (i.e.,  $\alpha_i = \beta_i = 0$ ) does not come as a surprise, because these compounds exhibit also very similar  $\pi_i$  values (Table 5.5). In the case of the PAHs, however, the correlation does hold only because the polar parameters (i.e.,  $\pi_i$  and  $\beta_i$ ) increase both with increasing size. Finally, Fig. 5.2c shows a group of compounds, the polyhalogenated C<sub>1</sub>- and C<sub>2</sub>-compounds, for which, intuitively, we might have expected a much better result. A closer inspection of the polar parameters of the various compounds shows, however, that the rather large scatter could have been anticipated. For example, the  $\pi_i$ ,  $\alpha_i$  and  $\beta_i$  values of the similarly sized 1,1,2,2-tetrachloroethane and tetrachloroethene differ substantially (0.76, 0.16, 0.12 versus 0.42, 0.0, 0.0, respectively), which is reflected in the 20-times-higher liquid aqueous solubility of 1,1,2,2-tetrachloroethane as compared to tetrachloroethene. This example should remind us again that such simple one-parameter correlations work, in general, only for limited sets of “structurally closely related” compounds for which they may, however, be very powerful predictive tools. Obviously, as shown by the examples in Fig. 5.2, it may not always be clear whether two compounds are structurally closely related with respect to the factors that govern their aqueous activity coefficients. In such cases inspection of the type of parameters used in Eq. 5-22 may be very helpful for selecting appropriate reference compounds.

### Illustrative Example 5.2

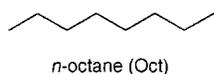
#### Evaluating the Factors that Govern the Aqueous Activity Coefficient of a Given Compound

##### Problem

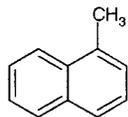
Calculate the activity coefficients as well as the excess free energies of *n*-octane (Oct), 1-methylnaphthalene (1-MeNa), and 4-*t*-butylphenol (4-BuPh) in aqueous solution at 25°C using Eq. 5-22. Compare and discuss the contributions of the various terms in Eq. 5-22.

##### Answer

Get the  $p_{iL}^*$  values from the data given in Appendix C. Note that 4-BuPh ( $T_m = 99^\circ\text{C}$ ) is a solid at 25°C (use Eq. 4-40 to estimate  $p_{iL}^*$  from  $p_{is}^*$ ). Calculate  $V_{ix}$  using the method described in Box 5.1. Get the  $n_{Di}$  values of the compounds from Lide (1995). Use the  $\alpha_i$ , and  $\beta_i$ , and  $\pi_i$  values given in Tables 4.3 and 5.5. The resulting data sets for the three compounds are given in the margin. Recall that  $G_{iw}^E = RT \ln \gamma_{iw}$ . Insertion of the respective values into Eq. 5-22 yields the following result:

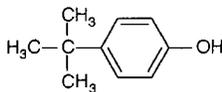


$$\begin{aligned}
 p_{iL}^* &= 1826 \text{ Pa} \\
 V_{ix} &= 123.6 \text{ cm}^3 \text{ mol}^{-1} \\
 n_{Di} &= 1.397 \\
 \pi_i &= \alpha_i = \beta_i = 0
 \end{aligned}$$



1-methyl-naphthalene (1-MeNa)

$$\begin{aligned}
 p_L^* &= 8.33 \text{ Pa} \\
 V_{ix} &= 122.6 \text{ cm}^3 \text{ mol}^{-1} \\
 n_{Di} &= 1.617 \\
 \pi_i &= 0.90 \\
 \alpha_i &= 0 \\
 \beta_i &= 0.20
 \end{aligned}$$



4-t-butyl-phenol

$$\begin{aligned}
 p_L^* &= 6.75 \text{ Pa} \\
 V_{ix} &= 133.9 \text{ cm}^3 \text{ mol}^{-1} \\
 n_{Di} &= 1.517 \\
 \pi_i &= 0.89 \\
 \alpha_i &= 0.56 \\
 \beta_i &= 0.39
 \end{aligned}$$

Term	Oct		1-MeNa		4-BuPh	
	$\Delta \ln \gamma_{iw}$ –	$(G_{iw}^E)$ (kJ · mol <sup>-1</sup> )	$\Delta \ln \gamma_{iw}$ –	$(G_{iw}^E)$ (kJ · mol <sup>-1</sup> )	$\Delta \ln \gamma_{iw}$ –	$(G_{iw}^E)$ (kJ · mol <sup>-1</sup> )
$-\ln p_{iL}^*$	+4.00	(+9.9)	+9.40	(+23.3)	+9.61	(+23.8)
$-\text{vdW}^a$	-3.42	(-8.5)	-4.94	(-12.2)	-4.53	(-11.2)
$-5.78 \pi_i$	0		-5.20	(-12.9)	-5.14	(-12.7)
$-8.77 \alpha_i$	0		0		-4.91	(-12.2)
$-11.12 \beta_i$	0		-2.22	(-5.5)	-4.33	(-10.7)
$+0.0472 V_{ix}$	+5.83	(+14.4)	+5.7	(+14.3)	+6.32	(+15.7)
+ constant	+9.49	(+23.5)	+9.49	(+23.5)	+9.49	(+23.5)
$\ln \gamma_{iw} (G_{iw}^E)$	15.9	(39.3)	12.2	(30.5)	6.51	(16.2)
exp. value	16.0		12.5		7.15	

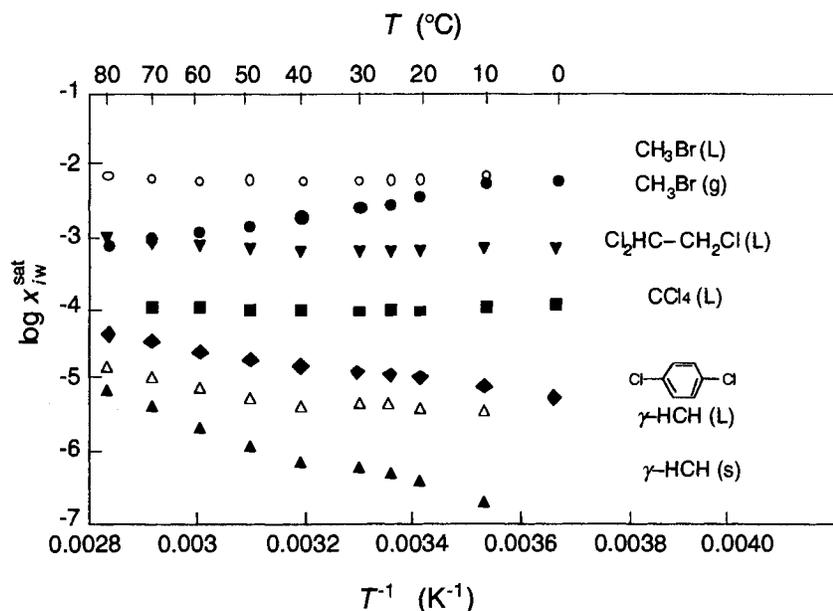
$$^a \text{ dispersive vdW} = 0.572 \left[ (V_{ix})^{2/3} \left( \frac{n_{Di}^2 - 1}{n_{Di}^2 + 2} \right) \right]$$

First, you note that, although the three compounds are of comparable size, there are significant differences in their  $\gamma_{iw}$  (i.e.,  $G_{iw}^E$ ) values.

As is evident, the lack of any polar interactions with the water molecules is the major cause for the large hydrophobicity of Oct, although this compound exhibits the highest vapor pressure (which facilitates the transfer of Oct from the pure liquid into another phase as compared to the other two compounds). Comparison of 1-MeNa with Oct reveals that the lower activity coefficients (i.e., the higher liquid water solubilities) of aromatic compounds as compared to aliphatic compounds of similar size are primarily due to the relatively large polarizability term ( $\pi_i$ ) of aromatic structures. Finally, from comparing 4-BuPh with 1-MeNa it can be seen that H-bond interactions ( $\alpha_i$ ,  $\beta_i$ -terms) may decrease  $\gamma_{iw}$  by several orders of magnitude (note that for these two compounds, all other terms contribute similarly to the overall  $\gamma_{iw}$ ).

## 5.4 Effect of Temperature and Solution Composition on Aqueous Solubility and Activity Coefficient

So far, we have focused on how differences in molecular structure affect the solubilities and activity coefficients of organic compounds in pure water at 25°C. The next step is to evaluate the influence of some important environmental factors on these properties. In the following we consider three such factors: temperature, ionic strength (i.e., dissolved salts), and organic cosolutes. The influence of pH of the aqueous solution, which is most important for acids and bases, will be discussed in Chapter 8.



**Figure 5.4** Effect of temperature on the mole fraction solubility in water of some halogenated hydrocarbons.  $\gamma$ -HCH is  $\gamma$ -1,2,3,4,5,6-hexachlorocyclohexane (lindane; for structure see Illustrative Example 5.1). Data from Horvath (1982).

### Temperature

Let us consider the temperature dependence of the mole fraction solubility of organic *liquids*. Since  $x_{iw}^{\text{sat}}/x_{iL} \equiv x_{iw}^{\text{sat}}$  ( $x_{iL} \equiv 1$ ) represents the partitioning constant between the aqueous phase and the pure liquid, for a narrow temperature range, its temperature dependence is given by (Section 3.4):

$$\ln x_{iw}^{\text{sat}}(\text{L}) = -\frac{H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad (5-23)$$

When expressing aqueous solubility in molar units we may write Eq. 5-23 as:

$$\ln C_{iw}^{\text{sat}}(\text{L}) = -\frac{H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant}' \quad (5-24)$$

Now  $\text{constant}' = \text{constant} - \log \bar{V}_w$  and we assume a temperature-independent molar volume ( $\bar{V}_w$ ) of the aqueous solution (see Section 3.4).

For the majority of the (subcooled) liquid compounds, the excess enthalpy,  $H_{iw}^{\text{E}}$ , is quite small and may even be negative at 25°C (Table 5.3). Thus, for a temperature range between 0 and 80°C, the change in the liquid solubility with increasing temperature is therefore rather small (Fig. 5.4). For some compounds like  $\text{CH}_3\text{Br}(\text{L})$ ,  $\text{CHCl}_2\text{-CH}_2\text{Cl}$ , and  $\text{CCl}_4$ , a solubility minimum is found at ambient temperatures. This occurs because, at low temperatures,  $H_{iw}^{\text{E}}$  is negative and, in general,  $H_{iw}^{\text{E}}$  becomes more positive with increasing temperature [in contrast to  $\Delta_{\text{vap}}H_i$ , which decreases with increasing temperature (see Chapter 4)]. This observation can be explained by the fact that at elevated temperatures, some of the hydrogen bonds among the water molecules forming the hydration shell are broken, which leads to a more positive excess enthalpy. Thus, when applying Eqs. 5-23 or 5-24, we know that  $H_{iw}^{\text{E}}$

is not constant over the whole ambient temperature range and we can see some curvature in the plots of  $\log x_{iw}^{\text{sat}}$  versus  $1/T$  (Fig. 5.4). This is, however, not too much of a problem since the temperature effect is small anyway. For most compounds  $x_{iw}^{\text{sat}}$  (L) (or  $C_{iw}^{\text{sat}}$  (L)) will vary less than a factor of 2 between 0 and 30°C. Only for the larger, rigid, apolar compounds such as PAHs, PCBs, and polychlorinated dibenzodioxines (PCDDs), is the effect of temperature on the liquid aqueous solubility significant [see Illustrative Example 5.3, case (b)].

When we are interested in the actual solubilities of *solids or gases*, however, the effect of temperature becomes much more important (e.g.,  $\text{CH}_3\text{Br}(\text{g})$  and  $\gamma\text{-HCH}(\text{s})$  in Fig. 5.4). Now we must consider the total enthalpy change when transferring a molecule from the solid or gas phase, respectively, to water. This total enthalpy change includes the sum of the enthalpy of the phase change (i.e., conversion of a solid into a subcooled liquid or a gas into a superheated liquid at the temperature of interest) and the excess enthalpy of solution. Hence, for solids the temperature dependence of solubility over a narrow temperature range is given by:

$$\ln C_{iw}^{\text{sat}}(\text{s}) = -\frac{\Delta_{\text{fus}}H_i + H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad (5-25)$$

and for gases:

$$\ln C_{iw}^{\text{1bar}}(\text{g}) = -\frac{-\Delta_{\text{vap}}H_i + H_{iw}^{\text{E}}}{R} \cdot \frac{1}{T} + \text{constant} \quad (5-26)$$

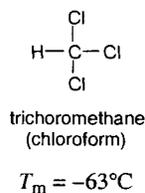
Note that, in general, the resulting enthalpy change will be positive in the case of solids (due to the large positive  $\Delta_{\text{fus}}H_i$ ) and negative (dominating positive  $\Delta_{\text{vap}}H_i$ ) in the case of gases. Consequently, the solubility of solids increases with increasing temperature, since the “cost” of melting decreases with increasing temperature (and becomes zero at the melting point). Conversely, the difficulty in condensing gaseous organic compounds increases with increasing temperature; thus, heating an aqueous solution tends to diminish solubilities of (organic) gases through this term. Some applications of Eqs. 5-23 to 5-26 are given in the Illustrative Example 5.3.

### Illustrative Example 5.3

### Evaluating the Effect of Temperature on Aqueous Solubilities and Aqueous Activity Coefficients

#### Problem

Estimate the solubilities,  $C_{iw}^{\text{sat}}$ , the activity coefficients,  $\gamma_{iw}^{\text{sat}}$ , and the excess enthalpies,  $H_{iw}^{\text{E}}$ , in water of (a) trichloromethane at 5°C, (b) dibenzofuran at 10°C, and (c) chloroethene (vinyl chloride) at 40°C.



#### Answer (a)

Since trichloromethane is a liquid at ambient temperatures, the magnitude of change in its solubility with solution temperature is dictated by its excess enthalpy,  $H_{iw}^{\text{E}}$  (Eq. 5-23). Generally, for low-molecular-weight compounds, you can expect that  $H_{iw}^{\text{E}}$  will not be too different from zero ( $\pm 10 \text{ kJ} \cdot \text{mol}^{-1}$ ; see Table 5.3). Hence, at 5°C both

$T / (^{\circ}\text{C})$	$x_{iw}^{\text{sat } a}$
0	0.001514
10	0.001366
20	0.001249
25	0.001203
30	0.001168

<sup>a</sup> Data from Horvath (1982).

$C_{iw}^{\text{sat}}$  and  $\gamma_{iw}^{\text{sat}}$  should not differ too much from the corresponding values at 25°C. In fact, inspection of the experimental data reported by Horvath (1982) shows that between 0 and 30°C the mole fraction solubility of trichloromethane *decreases*, but only about 20% (see margin). Since  $H_{iw}^E$  increases with increasing temperature, use only the two  $x_{iw}^{\text{sat}}$  values given at 0 and 10°C to estimate  $x_{iw}^{\text{sat}}$  at 5°C (Eq. 5-23):

$$\ln x_{iw}^{\text{sat}} = \frac{799}{T} - 9.418 \quad (1)$$

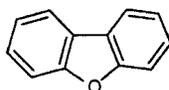
Note again that the excess enthalpy of solution of trichloromethane between 0 and 10°C is slightly negative, i.e.,  $H_{iw}^E = -(799 \text{ K}) (8.31) = -6.6 \text{ kJ} \cdot \text{mol}^{-1}$ .

Insertion of  $T = 278.2 \text{ K}$  into Eq. 1 yields  $x_{iw}^{\text{sat}}(5^{\circ}\text{C}) = 0.001436$  or, in molar concentrations (Eq. 3-43):

$$C_{iw}^{\text{sat}}(5^{\circ}\text{C}) = x_{iw}^{\text{sat}} / \bar{V}_w = (0.001436) / (0.018) = 8.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$$

The aqueous activity coefficient is given by  $1 / x_{iw}^{\text{sat}}$  (trichloromethane is a liquid; see Eq. 5.6):

$$\gamma_{iw}^{\text{sat}}(5^{\circ}\text{C}) = 1 / (0.001436) = 7.0 \times 10^2$$



dibenzofuran

$$M_i = 168.2 \text{ g} \cdot \text{mol}^{-1}$$

$$T_m = 87^{\circ}\text{C}$$

### Answer (b)

Dibenzofuran is a solid at ambient temperatures. Hence, the enthalpy of solution ( $\Delta_{ws}H_i$ ) is given by the sum of the enthalpy of fusion ( $\Delta_{fus}H_i$ ) and the excess enthalpy in aqueous solution ( $H_{iw}^E$ ) (Fig. 5.1 and Eq. 5-25). In a paper by Shiu et al. (1997) you find aqueous solubility data expressed in  $\text{g} \cdot \text{m}^{-3}$  for dibenzofuran at various temperatures (see margin). For simplicity, assume that  $\bar{V}_w$  is temperature independent.

$T / (^{\circ}\text{C})$	$C_{iw}^{\text{sat } a} / (\text{g} \cdot \text{m}^{-3})$
5	1.92
15	3.04
25	4.75
35	7.56
45	11.7

<sup>a</sup> Data from Shiu et al. (1997).

Calculate  $1/T$  in  $\text{K}^{-1}$  and  $\log C_{iw}^{\text{sat}}$ :

$1 / T (\text{K}^{-1})$	0.003597	0.003472	0.003356	0.003247	0.003145
$\log C_{iw}^{\text{sat}} / (\text{g} \cdot \text{m}^{-3})$	0.282	0.483	0.677	0.879	1.069

and perform a least square fit of  $\log C_{iw}^{\text{sat}}$  versus  $1 / T$ :

$$\log C_{iw}^{\text{sat}} / (\text{g} \cdot \text{m}^{-3}) = -\frac{1742}{T} + 6.536 \quad (2)$$

From the slope one obtains an average  $\Delta_{ws}H_i [= (1742) (2.303) (8.31)]$  value of  $33.4 \text{ kJ} \cdot \text{mol}^{-1}$ . Note that because we use decadic logarithms, the slope in Eq. 2 is equal to  $\Delta_{ws}H_i / (2.303) R$ . Hence, the aqueous solubility increases by about a factor of 1.6 per 10 degrees increase in temperature (Table 3.5). Insertion of  $T = 283.2 \text{ K}$  into Eq. 2 yields:

$$\log C_{iw}^{\text{sat}} (10^{\circ}\text{C}) = 0.385 \text{ or } C_{iw}^{\text{sat}} (10^{\circ}\text{C}) = 2.43 \text{ g} \cdot \text{m}^{-3}$$

or, in molar concentrations:

$$C_{iw}^{\text{sat}}(10^\circ\text{C}) = \frac{(2.43 \times 10^{-3})}{(168.2)} = 1.44 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

To get the activity coefficient, estimate first the aqueous solubility of subcooled liquid dibenzofuran at 283 K (Eq. 5-12). To the end, estimate  $\Delta_{\text{fus}}G_i$  at  $10^\circ\text{C}$  from  $T_m$  using Eq. 4-41:

$$\Delta_{\text{fus}}G_i(10^\circ\text{C}) = (56.5 + 0 - 19.2 \log 2) (77) = 3.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Insertion into Eq. 5-13 yields

$$C_{iw}^{\text{sat}}(\text{L}, 10^\circ\text{C}) = (1.44 \times 10^{-5}) (5.3) = 7.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

and thus (Eq. 5-12)

$$\gamma_{iw}^{\text{sat}}(10^\circ\text{C}) = 1 / (7.6 \times 10^{-5}) (0.018) = 7.3 \times 10^5$$

To estimate  $H_{iw}^E$ , assume a constant  $\Delta_{\text{fus}}H_i$  below the melting point:

$$\Delta_{\text{fus}}H_i \cong \Delta_{\text{fus}}H_i(T_m) = T_m \cdot \Delta_{\text{fus}}S_i(T_m)$$

Use Eq. 4-39 to estimate  $\Delta_{\text{fus}}S_i(T_m)$ :

$$\Delta_{\text{fus}}S_i(T_m) = (56.5 + 0 - 19.2 \log 2) = 50.8 \text{ J} \cdot \text{mol}^{-1} \text{ K}^{-1}$$

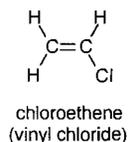
This yields

$$\Delta_{\text{fus}}H_i = (50.8) (360) = 18.3 \text{ kJ} \cdot \text{mol}^{-1}$$

and

$$H_{iw}^E = \Delta_{\text{ws}}H_i - \Delta_{\text{fus}}H_i = 33.4 - 18.3 = 15.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Note that this  $H_{iw}^E$  value represents an average value for the ambient temperature range.



$$T_b = -13.4^\circ\text{C}$$

### Answer (c)

Chloroethene (vinyl chloride) is a gas at the temperature considered. Hence, the enthalpy of solution ( $\Delta_{\text{wa}}H_i$ ) is given by the sum of the enthalpy of condensation ( $\Delta_{\text{cond}}H_i$ , which is equal to the negative enthalpy of vaporization) and the excess enthalpy in aqueous solution ( $H_{iw}^E$ ) (Fig. 5.1 and Eq. 5-26). Horvath et al. (1982) gives the solubilities of chloroethene at  $0^\circ\text{C}$ ,  $25^\circ\text{C}$ , and  $50^\circ\text{C}$  and 1 bar partial pressure. Also given are the vapor pressures of the superheated liquid at these three temperatures.

$T / (^\circ\text{C})$	$x_{iw}^{\text{sat}^a}$	$p_L^* / \text{bar}^a$
0	0.00158	1.70
25	0.000798	3.86
50	0.000410	7.69

<sup>a</sup> Data from Horvath (1982).

After conversion of  $^\circ\text{C}$  to K, perform a least square fit of  $\ln x_{iw}^{1\text{bar}}$  versus  $1/T$ :

$$\ln x_{iw}^{1\text{bar}} = + \frac{2375}{T} - 15.134 \quad (3)$$

From the slope you obtain a  $\Delta_{wa}H_i$  [= - (2375) (8.31)] value of  $-19.7 \text{ kJ}\cdot\text{mol}^{-1}$ , meaning that the solubility of chloroethene decreases by about a factor of 1.3 per 10 degrees increase in temperature (Table 3.5). Insertion of  $T = 313.2 \text{ K}$  into Eq. 3 yields  $x_{iw}^{\text{1bar}}$  ( $40^\circ\text{C}$ ) = 0.000526 or in molar concentration (Eq. 3-43):

$$C_{iw}^{\text{1bar}} (40^\circ\text{C}) = 2.9 \times 10^{-2} \text{ mol}\cdot\text{L}^{-1}$$

To get the activity coefficient of chloroethene (Eq. 5-15) calculate its vapor pressure at  $40^\circ\text{C}$  using the least square fit of  $\ln p_{iL}^*$  versus  $1/T$ :

$$\ln p_{iL}^* / \text{bar} = - \frac{2662}{T} + 10.283 \quad (4)$$

Insertion of  $T = 313.2 \text{ K}$  into Eq. 4 yields a  $p_{iL}^*$  value of 5.95 bar, which yields a  $\gamma_{iw}^{\text{sat}}$  value of (Eq. 5-16):

$$\gamma_{iw}^{\text{1bar}} (40^\circ\text{C}) = \frac{1}{(0.000526)} \cdot \frac{1 \text{ bar}}{5.95 \text{ bar}} = 3.2 \times 10^2$$

From the slope in Eq. 4 you can obtain  $\Delta_{\text{vap}}H_i$  [= (2662) (8.31)] =  $22.1 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus, one obtains an average  $H_{iw}^E$  value of:

$$H_{iw}^E = \Delta_{wa}H_i + \Delta_{\text{vap}}H_i = -19.7 + 22.1 = + 2.4 \text{ kJ}\cdot\text{mol}^{-1}$$

which means that the activity coefficient of chloroethene is more or less constant over the ambient temperature range.

### Dissolved Inorganic Salts

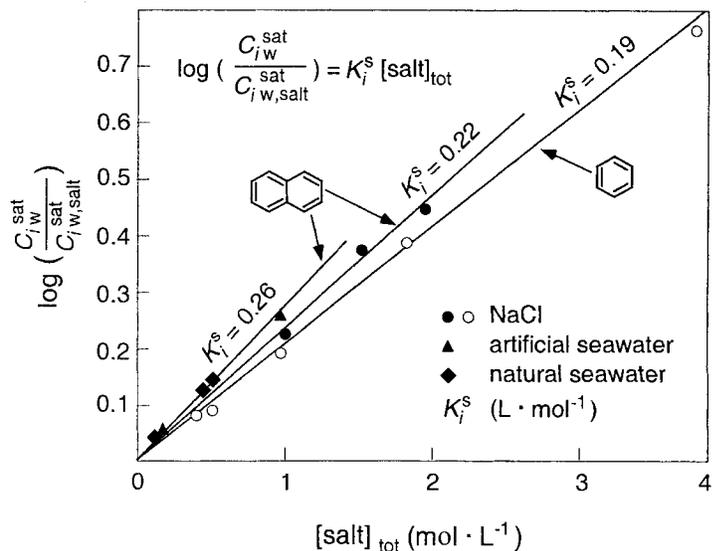
When considering saline environments (e.g., seawater, salt lakes, subsurface brines), we have to consider the effects of dissolved inorganic salt(s) on aqueous solubilities and on activity coefficients of organic compounds. Although the number of studies that have been devoted to this topic is rather limited, a few important conclusions can be drawn. Qualitatively, it has been observed that the presence of the predominant inorganic ionic species found in natural waters (i.e.,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) generally decrease the aqueous solubility (or increase the aqueous activity coefficient) of nonpolar or weakly polar organic compounds. Furthermore, it has been found that the magnitude of this effect, which is commonly referred to as *salting-out*, depends on the compound and on the type of ions present.

Long ago, Setschenow (1889) established an *empirical* formula relating organic compound solubilities in saline aqueous solutions ( $C_{iw,\text{salt}}^{\text{sat}}$ ) to those in pure water ( $C_{iw}^{\text{sat}}$ ):

$$\log \left( \frac{C_{iw}^{\text{sat}}}{C_{iw,\text{salt}}^{\text{sat}}} \right) = K_i^s [\text{salt}]_{\text{tot}} \quad (5-27)$$

or:

$$C_{iw,\text{salt}}^{\text{sat}} = C_{iw}^{\text{sat}} \cdot 10^{-K_i^s [\text{salt}]_{\text{tot}}}$$



**Figure 5.5** Effect of salt concentrations on the aqueous solubility of benzene (McDevit and Long, 1952), and naphthalene (Gordon and Thorne, 1967a).

where  $[\text{salt}]_{\text{tot}}$  is the total *molar* salt concentration and  $K_i^s$  is the *Setschenow* or *salting constant* (unit  $\text{M}^{-1}$ ). This salting constant relates the effectiveness of a particular salt or combination of salts to the change in solubility of a given compound  $i$ . For a particular salt (e.g., NaCl) or salt mixture (e.g., seawater; for composition see Table 5.6), Eq. 5-27 is valid over a wide range of salt concentrations (Fig. 5.5). Note that the “salting-out” effect increases exponentially with increasing salt concentration.  $K_i^s$ -values for a given organic solute and salt composition can be determined experimentally by linear regression of experimental solubilities measured at various salt concentrations (i.e., plots of  $\log C_{i,w}^{\text{sat}}$  versus  $[\text{salt}]_{\text{tot}}$ ). We should point out that at very high salt concentrations, the effect of the dissolved salts on the molar volume of the solution has to be taken into account. However, as a first approximation, in many cases (e.g., seawater) we may neglect the effect. Written in terms of activity coefficients, Eq. 5-27 is:

$$\gamma_{i,w,\text{salt}} = \gamma_{i,w} \cdot 10^{+K_i^s [\text{salt}]_{\text{tot}}} \quad (5-28)$$

Hence  $\gamma_{i,w,\text{salt}}$  increases exponentially with increasing salt concentration.

Note that if  $K_i^s$  has been determined from solubility measurements,  $\gamma_{i,w,\text{salt}}$  is strictly valid only for saturated conditions. For dilute solutions  $\gamma_{i,w,\text{salt}}$  can be determined from measurements of air–water or organic solvent–water partition constants at different salt concentrations. From the few compounds for which  $\gamma_{i,w,\text{salt}}$  has been determined by both solubility and air–water or solvent–water partitioning experiments, because of the large scatter in the data, it is not clear whether  $K_i^s$  varies with organic solute concentration. It can, however, be concluded that, if there is an effect, it is not very large.

Before we inspect  $K_i^s$  values of a variety of organic compounds for seawater (the most important natural saline environment), we first take a look at the salting-out efficiencies of various ion combinations. Since it is very difficult to quantify the contribution of individual ions, salting constants are available only for combined salts. Nevertheless, the data in Table 5.6 illustrate that smaller ions that form

**Table 5.6** Salt Composition of Seawater and Salting Constants for Benzene, Naphthalene, and 1-Naphthol at 25°C for Some Important Salts

Salt	Weight (g · mol <sup>-1</sup> )	Mole fraction in seawater <sup>b</sup> $x_{\text{salt}}$	Salting constant <sup>a</sup>		
			$K_i^s$ (benzene) (L · mol <sup>-1</sup> )	$K_i^s$ (naphthalene) (L · mol <sup>-1</sup> )	$K_i^s$ (1-naphthol) (L · mol <sup>-1</sup> )
NaCl	58.5	0.799	0.19	0.22	0.21
MgCl <sub>2</sub>	95.3	0.104		0.30	0.33
Na <sub>2</sub> SO <sub>4</sub>	142.0	0.055	0.53	0.72	
CaCl <sub>2</sub>	110.0	0.020		0.32	0.35
KCl	74.5	0.017	0.16	0.19	0.18
NaHCO <sub>3</sub>	84.0	0.005		0.32	
KBr				0.13	0.13
CsBr				0.01	
(CH <sub>3</sub> ) <sub>4</sub> NCl					-0.36
(CH <sub>3</sub> ) <sub>4</sub> NBr			-0.15		

<sup>a</sup> Data from McDevit and Long (1952), Gordon and Thorne (1967a,b), Almeida et al. (1983), and Sanemasa et al. (1984). <sup>b</sup> Gordon and Thorne (1967a,b).

hydration shells with more water molecules (e.g., Na<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>) have a bigger effect than larger ions that tend to bind water molecules only very weakly (e.g., Cs<sup>+</sup>, N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>, Br<sup>-</sup>). In fact, larger organic ions such as tetramethyl-ammonium (N(CH<sub>3</sub>)<sub>4</sub><sup>+</sup>) can even have an opposite effect; that is, they promote solubility (or decrease the activity coefficient). Note that such *salting-in* effects can also be observed for very polar compounds that may strongly interact with certain ions (Almeida et al., 1984). In a simple way, we can rationalize the salting-out of nonpolar and weakly polar compounds by imagining that the dissolved ions compete (successfully) with the organic compound for solvent molecules. Many of the environmentally relevant ions bind water molecules quite tightly in aqueous solution, which can be seen even macroscopically in that the volume of the aqueous solution is reduced. As a consequence, the freedom of some water molecules to solvate an organic molecule is disrupted, and depending on the type of salt and/or compound present, may lead to a loss or gain in solubility (Leberman and Soper, 1995). Furthermore, the solvation of an organic compound, particularly when it is large and nonpolar, requires a large number of water molecules. Hence, we may intuitively anticipate that larger nonpolar organic compounds will exhibit higher  $K_i^s$  values as compared to smaller and/or more polar compounds.

Let us now inspect the  $K_i^s$  values of some organic compounds in seawater. Using the data given in Table 5.6 we can make our own artificial seawater (at least with respect to the major ion composition) by dissolving an appropriate amount of the corresponding salts in water. The weight of 1 mole of "seawater salt" is given by (0.799) (58.5) + (0.104) (95.3) + (0.055) (142) + (0.02) (110) + (0.017) (74.5) + (0.005) (84) = 68.35 g. Hence, if we dissolve 34.17 g of seawater-salt in 1 L, we obtain a seawater with a

salinity of 34.2‰, which corresponds to a total molar salt concentration ( $[\text{salt}]_{\text{tot}}$  in Eq. 5-27) of 0.5 M. As has been demonstrated by various studies, the differences between  $K_i^s$  values determined in artificial and real seawater are usually only marginal. Furthermore, since seawater is dominated by one salt, that is, NaCl (Table 5.6), as a first approximation  $K_i^s$  values determined for sodium chloride can be used as a surrogate. Let us illustrate this by calculating  $K_{i,\text{seawater}}^s$  for naphthalene using the data given in Table 5.6. If we assume that naphthalene does not specifically interact with any of the inorganic ions present, we may estimate  $K_{i,\text{seawater}}^s$  by summing up the contributions of the various salts present (Gordon and Thorne, 1967a,b):

$$K_{i,\text{seawater}}^s \cong \sum_k K_{i,\text{salt } k}^s \cdot x_k \quad (5-29)$$

where  $x_k$  is the mole fraction and  $K_{i,\text{salt } k}^s$  is the salting constant of salt  $k$  in the mixture. For naphthalene we then obtain (Table 5.6):

$$K_{i,\text{seawater}}^s = (0.799) (0.22 \text{ M}^{-1}) + (0.104) (0.30 \text{ M}^{-1}) + (0.055) (0.72 \text{ M}^{-1}) + (0.02) (0.32 \text{ M}^{-1}) + (0.01) (0.19 \text{ M}^{-1}) + (0.005) (0.32 \text{ M}^{-1}) = 0.26 \text{ M}^{-1}$$

which compares very favorably with the experimental value for seawater (average value  $0.27 \text{ M}^{-1}$ ). The  $K_i^s$  value of naphthalene for NaCl is  $0.22 \text{ M}^{-1}$ . Hence, the contribution of the other salts is only 0.04. With insertion of the two  $K_i^s$  values into Eq. 5-28 and assuming a  $[\text{salt}]_{\text{tot}} = 0.5 \text{ M}$  (typical seawater), we obtain  $\gamma_{i\text{w,salt}} / \gamma_{i\text{w}}$  ratios of 1.66 for  $K_i^s = 0.22$  and 1.84 for  $K_i^s = 0.265$ , respectively. In general, the error introduced when using  $K_{i,\text{NaCl}}^s$  instead of  $K_{i,\text{seawater}}^s$  is only in the order of 10%, which is often well within the experimental error of  $K_i^s$  measurements. Therefore, in the data set given in Table 5.7, some  $K_i^s$  values determined for NaCl have been included. Some more data can be found in the review by Xie et al. (1997).

A few general comments on the data given in Table 5.7 are necessary. First, where available, average  $K_i^s$  values taken from different studies are reported. The ranges indicated for these values show that in general, one has to expect rather large uncertainties (i.e., up to  $\pm 20\%$ ) in the reported  $K_i^s$  values. Furthermore, it should also be noted that Table 5.7 contains values determined from solubility as well as from partitioning (i.e., air–water, organic solvent–water) experiments. Finally, the results of the few studies in which the effect of temperature on salting-out has been investigated (Whitehouse, 1984; Zhou and Mopper, 1990; Dewulf et al., 1995; Alaei et al., 1996) suggest that  $K_i^s$  increases somewhat with decreasing temperature. Unfortunately, due to the relatively large scatter in the data, no quantitative relationship can be derived. As a first approximation, the data given in Table 5.7 should, however, also be applicable at temperatures other than  $25^\circ\text{C}$ .

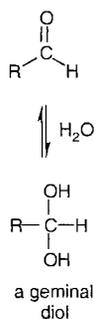
Inspection of Table 5.7 shows that our conclusion drawn above from our simple picture of the salting effect, which is that smaller and/or polar compounds should exhibit smaller  $K_i^s$  values as compared to larger, nonpolar compounds, is more or less confirmed by the experimental data. When considering the rather limited experimental data set, and the relatively large uncertainty in the data, it is, however, presently not feasible to derive any reliable quantitative relationship using molecular descriptors that would allow prediction of  $K_i^s$  values of other compounds. One

**Table 5.7** Salting Constants for Some Organic Compounds for Seawater

Compound	$K_i^s$ (L · mol <sup>-1</sup> )	Compound	$K_i^s$ (L · mol <sup>-1</sup> )
<i>Halogenated C<sub>1</sub>- and C<sub>2</sub>-Compounds</i> <sup>a,b,c,d</sup>		<i>Substituted Benzenes and Phenols</i> <sup>b,d,e,f,h</sup>	
Trichloromethane	0.2	Benzene	0.20 (±0.02)
Tetrachloromethane	0.2	Toluene	0.24 (±0.03)
Methylbromide	0.15	Ethylbenzene	0.29 (±0.02)
Dichlorodifluoromethane	0.29	1,2-Dimethylbenzene	0.30
Trichlorofluoromethane	0.30	1,3-Dimethylbenzene	0.29
1,1-Dichloroethane	0.2	1,4-Dimethylbenzene	0.30
1,2-Dichloroethane	0.2	<i>n</i> -Propylbenzene (NaCl)	0.28
1,1,1-Trichloroethane	0.25	Chlorobenzene (NaCl)	0.23
Trichloroethene	0.21 (±0.01)	1,4-Dichlorobenzene (NaCl)	0.27
Tetrachloroethene	0.24 (±0.02)	Benzaldehyde	0.20 (±0.04)
		Phenol	0.13 (±0.02)
		2-Nitrophenol	0.13 (±0.01)
		3-Nitrophenol	0.15
		4-Nitrophenol	0.17
		4-Nitrotoluene	0.16
		4-Aminotoluene	0.17
<i>Miscellaneous Aliphatic Compounds</i> <sup>e,f</sup>		<i>Polycyclic Aromatic Compounds</i> <sup>e,h,i,j,k,l</sup>	
Pentane (NaCl)	0.22	Naphthalene	0.28 (±0.04)
Hexane (NaCl)	0.28	Fluorene (NaCl)	0.27
1-Butanal	0.3	Phenanthrene	0.30 (±0.03)
1-Pentanal	0.3	Anthracene	0.30 (±0.02)
1-Hexanal	0.4	Fluoranthene (NaCl)	0.34
1-Heptanal	0.5	Pyrene	0.30 (±0.02)
1-Octanal	0.6	Chrysene (NaCl)	0.34
1-Nonanal	~ 1.0	Benzo[a]pyrene	0.34
1-Decanal	~ 1.0	Benzo[a]anthracene (NaCl)	0.35
Dimethylsulfide	0.17	1-Naphthol (NaCl)	0.23
2-Butanone	0.20		
<i>PCBs</i> <sup>e,g</sup>			
Biphenyl	0.32 (±0.05)		
Various PCBs (dichloro to hexachloro)	0.3–0.4		

<sup>a</sup> Warner and Weiss (1995). <sup>b</sup> Dewulf et al. (1995). <sup>c</sup> DeBruyn and Saltzman (1997). <sup>d</sup> Peng and Wang (1998). <sup>e</sup> Sanemasa et al. (1984). <sup>f</sup> Zhou and Mopper (1990). <sup>g</sup> Brownawell (1986). <sup>h</sup> Hashimoto et al. (1984). <sup>i</sup> Eganhouse and Calder (1975).

<sup>j</sup> Whitehouse (1984). <sup>k</sup> Gordon and Thorne (1967b). <sup>l</sup> Almeida et al. (1983).



class of compounds that does not quite fit the qualitative picture is the *n*-alkanals (Table 5.7). One possible cause for the unexpectedly high salting constants of these compounds is their tendency to form diols in aqueous solution (Bell and McDougall, 1960). For example, acetaldehyde (R = CH<sub>3</sub>, see margin) forms about 50% diol in pure water. If, in saltwater, the aldehyde/diol ratio is changed in favor of the aldehyde, one would expect a stronger salting-out effect, because it can be assumed that the diol form is more easily accommodated in water as compared to the aldehyde form. An additional reason for the large  $K_i^s$  values of the larger-chain aldehydes could be the fact that the effect of salt on the activity coefficients of flexible molecules is larger than the effect on the more rigid compounds. However, there are presently no reliable data available to verify this hypothesis.

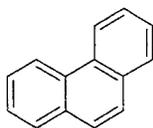
In summary, we can conclude that at moderate salt concentrations typical for seawater ( $\sim 0.5$  M), salinity will affect aqueous solubility (or the aqueous activity coefficient) by a factor of between less than 1.5 (small and/or polar compounds) and about 3 (large, nonpolar compounds, *n*-alkanes). Hence, in marine environments for many compounds, salting-out will not be a major factor in determining their partitioning behavior. Note, however, that in environments exhibiting much higher salt concentrations [e.g., in the Dead Sea (5 M) or in subsurface brines near oil fields], because of the exponential relationship (Eq. 5-28), salting-out will be substantial (see also Illustrative Example 5.4).

### Illustrative Example 5.4

### Quantifying the Effect of Inorganic Salts on Aqueous Solubility and Aqueous Activity Coefficients

#### Problem

Estimate the solubility and the activity coefficient of phenanthrene in (a) seawater at 25°C and 30‰ salinity, and (b) a salt solution containing 117 g NaCl per liter water.



*i* = phenanthrene

$$C_{iw}^{\text{sat}} (25^\circ\text{C}) = 6.3 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

$$T_m = 101^\circ\text{C}$$

$$\gamma_{iw}^{\text{sat}} (25^\circ\text{C}) = 2.0 \times 10^6$$

(see Table 5.2)

#### Answer (a)

At 25°C phenanthrene is a solid. Because the free energy contributions of phase change (i.e., melting, or condensation in the case of a gas) to the overall free energy of solution are not affected by salts in the solution, it is the aqueous activity coefficient that is increased as salt concentration increases (Eq. 5-28). Hence, the actual solubility  $C_{iw}^{\text{sat}}$  decreases by the same factor (Eq. 5-27). The  $K_i^s$  value of phenanthrene is  $0.30 \text{ M}^{-1}$  (Table 5.7). Since 34.2‰ salinity corresponds to a total salt concentration of 0.5 M (see text),  $[\text{salt}]_{\text{tot}}$  for 30‰ is equal to 0.44 M. Insertion of these values into Eq. 5-28 yields:

$$\gamma_{iw}^{\text{sat}} \cdot 10^{+(0.30)(0.44)} = (1.34) \gamma_{iw}^{\text{sat}} = 2.7 \times 10^6$$

The aqueous solubility in 30‰ seawater is then given by:

$$C_{iw,\text{salt}}^{\text{sat}} = C_{iw}^{\text{sat}} / (1.34) = 4.7 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

Hence, in 30‰ seawater  $\gamma_{iw}^{\text{sat}}$  increases ( $C_{iw}^{\text{sat}}$  decreases) by about 30% as compared to pure water.

#### Answer (b)

Use the  $K_i^s$  value given for seawater as a surrogate for the NaCl solution. 117 g NaCl per liter correspond to a molar concentration of 2 M. Thus:

$$\gamma_{iw,\text{NaCl}}^{\text{sat}} = \gamma_{iw}^{\text{sat}} \cdot 10^{+(0.30)(2.0)} = (4.0) \gamma_{iw}^{\text{sat}} = 8.0 \times 10^6$$

and

$$C_{iw,\text{salt}}^{\text{sat}} = 1.6 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$$

**Problem**

At oil exploitation facilities it is common practice to add salt to the wastewater in order to decrease the solubility of the oil components, although in the wastewater treatment one then has to cope with a salt problem. Calculate how much NaCl you have to add to 1 m<sup>3</sup> of water in order to increase the activity coefficient of *n*-hexane by a factor of ten. How much Na<sub>2</sub>SO<sub>4</sub> would be required to do the same job?



*i* = *n* - hexane

**Answer**

In order to increase the activity coefficient of a given compound by a factor of ten, the exponent in Eq. 5-28 has to be equal to 1:

$$K_i^s [\text{salt}]_{\text{tot}} = 1$$

The  $K_i^s$  value for hexane for NaCl is 0.28 M<sup>-1</sup> (Table 5.7). Then a total salt concentration  $[\text{salt}]_{\text{tot}} = 1 / 0.28 \text{ M}^{-1} = 3.57 \text{ M}$  is needed, which corresponds to an amount of 208.8 kg · m<sup>-3</sup>.

For estimating the amount of Na<sub>2</sub>SO<sub>4</sub> required, assume a similar relative  $K_i^s$  value (relative to NaCl) as determined for benzene (i.e., 0.53 M<sup>-1</sup> for Na<sub>2</sub>SO<sub>4</sub> versus 0.19 M<sup>-1</sup> for NaCl, see Table 5.6):

$$K_i^s (\text{hexane, Na}_2\text{SO}_4) = (0.28) (0.53) / (0.19) = 0.78 \text{ M}^{-1}$$

Thus in the case of Na<sub>2</sub>SO<sub>4</sub>, the required  $[\text{salt}]_{\text{tot}}$  is  $1 / 0.78 \text{ M}^{-1} = 1.28 \text{ M}$  or 181.8 kg · m<sup>-3</sup>, which is about the same amount as the NaCl needed although, on a molar base, Na<sub>2</sub>SO<sub>4</sub> is much more potent as a salting-out agent.

**Advanced Topic****Organic Cosolvents**

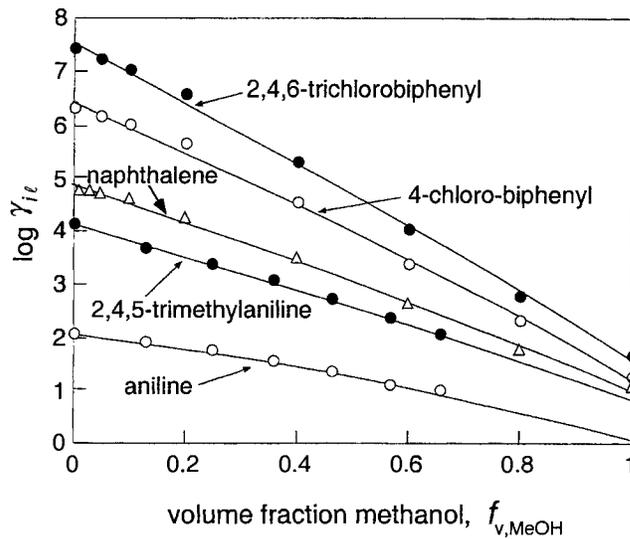
So far we have considered only situations in which a given organic compound was present as the sole *organic* solute in an aqueous solution. Of course, in reality, in any environmentally relevant aquatic system there will be numerous other natural and/or anthropogenic organic chemicals present that may or may not affect the solubility or, even more important, the activity coefficient of the compound of interest to us. We will treat this issue of organic cosolutes in Chapter 7 when discussing the organic phase–water partitioning of organic compounds present in complex mixtures (e.g., gasoline, oil, PCBs). In this section we will focus on the effect of highly water-soluble organic compounds (i.e., *organic cosolvents*) that may completely change the solvation properties of an “aqueous” phase. We may encounter such situations in industrial waste waters or at waste disposal sites where, because of careless dumping procedures, leachates may contain a high portion of organic solvent(s). Furthermore, one of the remediation techniques for contaminated soils is to “wash” the soil with mixtures of water and water-miscible cosolvents (Li et al., 1996). Finally, from an analytical point of view, knowledge of how cosolvents influence the activity coefficient of a given organic compound in organic solvent–water mixtures is pivotal for choosing appropriate mobile phases in reversed-phase liquid chromatography.

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

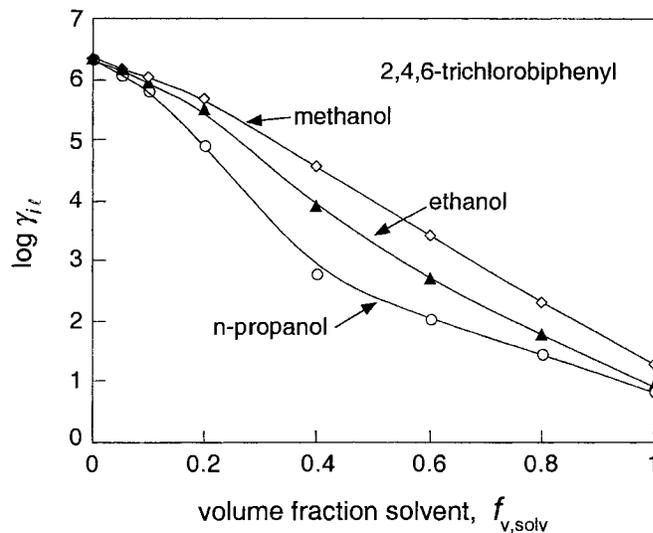
Let us first look at some qualitative aspects of how CMOSs affect the activity coefficient, and thus the solubility and partitioning behavior, of a given organic compound when present in a water/CMOS mixture. The following general conclusions are illustrated by the examples given in Figs. 5.6 to 5.8 and in Table 5.8.

First, we point out that, in general, the activity coefficient of an organic solute,  $\gamma_{i\ell}$ , decreases (i.e., solubility increases) in an *exponential way* with increasing volume fraction of CMOS. (Note that we use the subscript  $\ell$  to denote that we are dealing with a liquid solution, and, in the following, we do not distinguish between  $\gamma_{i\ell}$  values at saturated and dilute solutions.) Second, a significant effect (i.e.,  $> \text{factor } 2$ ) is observed only at cosolvent volume fractions greater than 5 to 10% (depending on the solvent). Below 1%, the effect can more or less be neglected (see below). Hence, when conducting experiments, we do not have to worry about significant changes in the activities of organic solutes in an aqueous phase when adding a small amount of a CMOS, as is, for example, common practice when spiking an aqueous solution with a sparingly soluble organic compound dissolved in an organic solvent. Third, the magnitude of the cosolvent effect, as well as its dependence on the amount of cosolvent present, is a function of both the type of cosolvent (Fig. 5.7, Table 5.8) and the type of organic solute (Figs. 5.6 and 5.8) considered. For example, the activity coefficient (or the mole fraction solubility) of naphthalene decreases (increases) by a factor of about 15 when going from pure water to a 40% methanol/60% water mixture, while the effect is about 3 times smaller or 20 times larger when glycerol or acetone, respectively, are the cosolvents (Table 5.8). Furthermore, as can be seen from Fig. 5.8, in 20% methanol/80% water (volume

**Figure 5.6** Illustration of the effect of a completely water-miscible solvent (CMOS, i.e., methanol) on the activity coefficient of organic compounds in water-organic solvent mixtures: decadic logarithm of the activity coefficient as a function of the volume fraction of methanol. Note that the data for naphthalene (Dickhut et al., 1989; Fan and Jafvert, 1997) and for the two PCBs (Li and Andren, 1994) have been derived from solubility measurements; whereas for the anilins (Jayasinghe et al., 1992), air-water partition constants determined under dilute conditions have been used to calculate  $\gamma_{it}$ .



**Figure 5.7** Effect of three different CMOSs (i.e., methanol, ethanol, propanol) on the activity coefficient of 2,4,6-trichlorobiphenyl. Data from Li and Andren (1994).



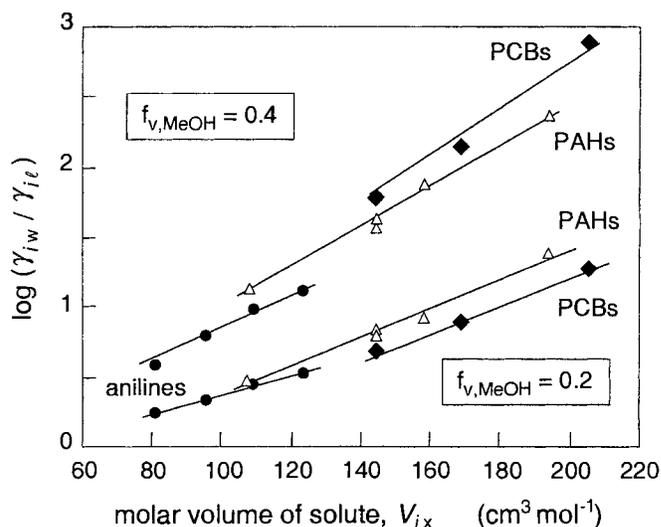
**Figure 5.8** Ratio of the activity coefficient in water ( $\gamma_{iw}$ ) and in methanol/water [20% (v : v) and 40% (v : v) methanol] as a function of the molar volume ( $V_{ix}$ , see Box 5.1) of the solute:  $\log(\gamma_{iw}^{sat} / \gamma_{it}^{sat}) = a \cdot V_{ix} + b$ . The three compound classes include the following compounds:

Anilines: aniline, 4-methyl-aniline, 3,4-dimethyl-aniline, 2,4,5-trimethyl-aniline;  $f_{v,MeOH} = 0.2$ :  $a = 0.00700$ ,  $b = -0.309$ ;  $f_{v,MeOH} = 0.4$ :  $a = 0.0128$ ,  $b = -0.432$ .

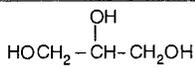
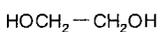
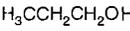
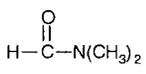
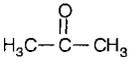
PAHs: naphthalene, anthracene, phenanthrene, pyrene, perylene;  $f_{v,MeOH} = 0.2$ :  $a = 0.0104$ ,  $b = -0.668$ ;  $f_{v,MeOH} = 0.4$ :  $a = 0.0147$ ,  $b = -0.469$ .

PCBs: 4-chlorobiphenyl, 2,4,6-trichlorobiphenyl, 2,2',4,4',6,6'-hexachlorobiphenyl;  $f_{v,MeOH} = 0.2$ :  $a = 0.0955$ ,  $b = -0.704$ ;  $f_{v,MeOH} = 0.4$ :  $a = 0.0180$ ,  $b = -0.848$ .

Data from Morris et al. (1988), Jayasinghe et al. (1992), Li and Andren (1994), Fan and Jafvert (1997).



**Table 5.8** Effect of Various CMOSs on the Activity Coefficient or Mole Fraction Solubility, Respectively, of Naphthalene at Two Different Solvent/Water Ratios ( $f_{v,\text{solvent}} = 0.2$  and 0.4)

Cosolvent	Structure	Solubility <sup>b</sup> Parameter (M Pa) <sup>1/2</sup>	Naphthalene <sup>a</sup> $\gamma_{iw}^{\text{sat}} / \gamma_{it}^{\text{sat}} = x_{it}^{\text{sat}} / x_{iw}^{\text{sat}}$	
			$f_{v,\text{solvent}} = 0.2$ ( $\sigma_i^c$ ) <sup>c</sup>	$f_{v,\text{solvent}} = 0.4$
Glycerol		36.2	2.5 (2.0)	5.5
Ethylene glycol		34.9	3 (2.4)	9
Methanol		29.7	3.5 (2.7)	14
Dimethylsulfoxide (DMSO)		26.7	5.5 (3.7)	3.6
Ethanol		26.1	7 (4.2)	48
Propanol		24.9	17 (6.2)	180
Acetonitrile		24.8	14 (5.7)	140
Dimethylformamide		24.8	15 (5.9)	130
1,4-Dioxane		20.7	14 (5.7)	180
Acetone		19.7	20 (6.5)	270

<sup>a</sup> Data from Dickhut et al. (1989), Li et al. (1996), and Fan and Jafvert (1997). <sup>b</sup> Hildebrand solubility parameter taken from Barton (1991). The parameter is defined as the square root of the ratio of the enthalpy of vaporization and the molar volume of the liquid.

<sup>c</sup> Cosolvency power for the range  $0 < f_{v,\text{solvent}} < 0.2$ ; see Eq. 5-30.

fractional methanol,  $f_{v,\text{MeOH}} = 0.2$ ) the activity coefficients of aniline ( $V_{ix} = 82 \text{ cm}^3 \text{ mol}^{-1}$ ) and 2,2',4,4',6,6'-hexachlorobiphenyl ( $V_{ix} = 206 \text{ cm}^3 \text{ mol}^{-1}$ ) are smaller by a factor of about 2 and 20, respectively, as compared to pure water, while at 40% methanol/60% water ( $f_{v,\text{MeOH}} = 0.4$ ) the corresponding factors are 4 and 750, respectively. In general, we may assume that for a given cosolvent–water system, the effect of the cosolvent on  $\gamma_{it}$  will be larger for large, nonpolar solutes that are only sparingly soluble in water (e.g., PCBs, PAHs) as compared to more polar, small molecules (e.g., aniline) exhibiting higher water solubilities. Finally, with respect to the “cosolvency-power” of CMOSs, we can see from Table 5.8 that, qualitatively, the more “water-like” solvents such as glycerol, ethylene glycol, or methanol, have a much smaller impact on the activity coefficient of an organic solute as compared to organic solvents for which hydrogen

bonding is important, but not the overall dominating factor. Note that the (Hildebrand) solubility parameter given in Table 5.8 (see footnote for explanation) is a measure of the cohesive forces among the molecules in the pure solvent. As can be seen, qualitatively, there is a trend that solvents exhibiting higher cohesive forces in their pure liquid tend to have a smaller cosolvent effect when mixed with water.

Before we address cosolvency in a more quantitative way, it is useful to try to picture how a cosolvent affects the solvation of an organic solute on a molecular level. From the examples given in Table 5.8 we can see that CMOSs are relatively small molecules with strong H-acceptor and/or H-donor properties. When mixed with water, they are, therefore, able to break up some of the hydrogen bonds between the water molecules and thus form a new H-bonded “mixed solvent” that will change its property in a rather complex way as a function of the nature and of the relative amount of the cosolvent. As we have seen in Section 5.3, for smaller and/or more polar organic compounds, the excess free energy in pure aqueous solution is dominated by the entropic contribution. Only for larger, particularly for nonpolar solutes, is the enthalpy term also significant (Table 5.3). Hence, it is reasonable to assume and is supported by experimental data (e.g., Bustamante et al., 1998) that in water-rich mixtures (i.e.,  $f_{v, \text{solv}} < 0.5$ ), the observed decrease in excess free energy (increase in solubility) of organic compounds with increasing CMOS/water ratio is primarily due to a substantial increase in the excess entropy, which may even compensate possible increases in excess enthalpy. Since these changes in excess enthalpy and entropy with changing cosolvent–water composition are, in general, not linearly correlated with each other, a nonlinear relationship between excess free energy (or  $\log \gamma_{i\ell}$ ) and  $f_{v, \text{solv}}$  can be expected and, as illustrated by Fig. 5.7, is actually found for many organic solute/CMOS/water systems.

Considering the rather complex factors that determine the excess free energy of an organic solute in a CMOS/water mixture, it is not too surprising that any quantitative models developed for describing cosolvent effects have only rather limited predictive capabilities. The models are, however, quite well suited for fitting experimental data, and for estimating activity coefficients of structurally closely related compounds in a given CMOS/water system for which experimental data are available.

For a discussion of the various approaches taken to quantify cosolvent effects we refer to the literature (e.g., Li and Andren, 1995; Li et al., 1996; Fan and Jafvert, 1997). For our purpose here, we adopt the most simple empirical approach where we assume a *log-linear* relationship between activity coefficient (or mole fraction solubility) of a given compound and volume fraction of the CMOS over a narrow  $f_{v, \text{solv}}$ -range (i.e.,  $\Delta f_{v, \text{solv}} = 0.2$ ) confined by  $f_{v, \text{solv}}^1$  and  $f_{v, \text{solv}}^2$ . Hence, for a given organic solute  $i$  and a given CMOS/water system, we get (note that we omit the subscript “solv” to indicate the CMOS):

$$\log \gamma_{i\ell}(f_v) = \log \gamma_{i\ell}(f_v^1) - \sigma_i^c \cdot (f_v - f_v^1) \quad (5-30)$$

or:

$$\log x_{i\ell}^{\text{sat}}(f_v) = \log x_{i\ell}^{\text{sat}}(f_v^1) + \sigma_i^c \cdot (f_v - f_v^1) \quad (5-31)$$

where the slope  $\sigma_i^c$ , which is dependent on both the solute and the cosolvent, is given by  $[\log \gamma_{i\ell}(f_v^1) - \log \gamma_{i\ell}(f_v^2)] / (f_v^2 - f_v^1)$ , and  $f_v^1 \leq f_v \leq f_v^2$ .  $\sigma_i^c$  is commonly

referred to as the cosolvency power of the solvent for the solute  $i$ . Note, however, that  $\sigma_i^c$  is not a constant, but changes with increasing  $f_v$ . If  $f_v^1 = 0$ , that is, if we consider only the range between pure water and a given cosolvent fraction  $f_v^2$  (e.g., 0.2), Eq. 5-30 simplifies to:

$$\log \gamma_{i\ell}(f_v) = \log \gamma_{i\ell} - \sigma_i^c \cdot f_v \quad (5-32)$$

with  $\sigma_i^c = [\log \gamma_{i\ell} - \log \gamma_{i\ell}(f_v^2)] / f_v^2$ . Eq. 5-32 can also be written as:

$$\gamma_{i\ell}(f_v) = \gamma_{i\ell} \cdot 10^{-\sigma_i^c \cdot f_v} \quad (5-33)$$

Hence, this approach is very similar to the one used for describing the effect of salt on aqueous solubility and aqueous activity coefficient (Eqs. 5-27 and 5-28). Some example calculations using Eq. 5-30 or 5-31, respectively, are given in Illustrative Example 5.5. Finally, we should note that the mole fractions of two solvents in a binary mixture are related to the volume fractions by:

$$x_1 = \frac{1}{1 + \frac{(1-f_{v1}) \cdot \bar{V}_1}{f_{v1} \cdot \bar{V}_2}} \quad \text{and} \quad x_2 = 1 - x_1 \quad (5-34)$$

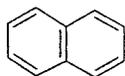
We conclude this section with some brief comments on the cosolvent effects of partially miscible organic solvents (PMOSs). These solvents include very polar liquids such as *n*-butanol, *n*-butanone, *n*-pentanol, or *o*-cresol, but also nonpolar organic compounds such as benzene, toluene, or halogenated methanes, ethanes, and ethenes. For the polar PMOS, a similar effect as for the CMOS can be observed; that is, these solvents decrease the activity coefficient of an organic solute when added to pure water or to a CMOS/water mixture (Pinal et al., 1990; Pinal et al., 1991; Li and Andren, 1994). For the less polar PMOS there is not enough data available to draw any general conclusions.

### Illustrative Example 5.5

### Estimating the Solubilities and the Activity Coefficients of Organic Pollutants in Organic Solvent–Water Mixtures

#### Problem

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



$i$  = naphthalene

$$C_{i\ell}^{\text{sat}}(25^\circ\text{C}) = 2.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$T_m = 80.2^\circ\text{C}$$

$$\gamma_{i\ell}^{\text{sat}}(25^\circ\text{C}) = 6.7 \times 10^4$$

(see Table 5.2)

#### Answer (a)

As in the case of inorganic salts (Illustrative Example 5.4) the free energy contributions of phase change to the overall free energy of solution are not affected by CMOS (with some exceptions in which the solvent changes the crystal structure of a solid, see text). Hence, you need only estimate the effect of the CMOS on the activity coefficient. Use the  $\gamma_{i\ell}^{\text{sat}} / \gamma_{i\ell}^{\text{sat}}$  ratios given for naphthalene in Table 5.8 for  $f_{v,\text{MeOH}} = 0.2$  and  $f_{v,\text{MeOH}} = 0.4$  to estimate  $\gamma_{i\ell}^{\text{sat}}$  for  $f_{v,\text{MeOH}} = 0.3$  by interpolation, using the log-linear relationship Eq. 5-30. Calculate first the  $\log \gamma_{i\ell}^{\text{sat}}$  values for  $f_{v,\text{MeOH}} = 0.2$  and 0.4, respectively:

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.2) = \log (\gamma_{iw}^{\text{sat}}) / 3.5 = 4.28$$

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.4) = \log (\gamma_{iw}^{\text{sat}}) / 14 = 3.68$$

The slope  $\sigma_i^c$  in Eq. 5-30 is then obtained by:

$$\sigma_i^c = (4.28 - 3.68) / (0.2) = 3.0$$

which yields (Eq. 5-30):

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.3) = 4.28 - (3.0) (0.1) = 3.98$$

or:

$$\gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.3) = 9.5 \times 10^3$$

which is about a factor of 7 smaller than  $\gamma_{iw}^{\text{sat}}$ . This also means that the mol fraction solubility of naphthalene will be about a factor of 7 larger (Eq. 5-31), that is:

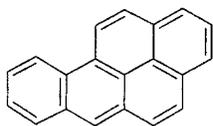
$$x_{il}^{\text{sat}} = (7) (2.5 \times 10^{-4}) (0.018) = 3.2 \times 10^{-5}$$

The mole fraction of methanol in a 30% methanol/70% water mixture is 0.16 (Eq. 5-34). The molar volume of methanol is  $0.0406 \text{ L} \cdot \text{mol}^{-1}$ . Hence, the molar volume of the mixture can be calculated as (Eq. 3-43, note that we assume additivity):

$$V_{il} = (0.16) (0.0406) + (0.84) (0.018) = 0.022 \text{ L} \cdot \text{mol}^{-1}$$

Hence, the molar solubility of naphthalene in the mixture is:

$$C_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.3) = (3.2 \times 10^{-5}) / (0.022) = 1.45 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$



*i* = benzo(a)pyrene

$$C_{iw}^{\text{sat}} (25^\circ\text{C}) = 7.2 \times 10^{-9} \text{ mol} \cdot \text{L}^{-1}$$

$$T_m = 176.5^\circ\text{C}$$

$$\gamma_{iw}^{\text{sat}} (25^\circ\text{C}) = 3.2 \times 10^8$$

(see Table 5.2)

### Answer (b)

For benzo(a)pyrene there are no experimental data available. Estimate  $\gamma_{iw}^{\text{sat}} / \gamma_{il}^{\text{sat}}$  for  $f_{v,\text{MeOH}} = 0.2$  and  $0.4$ , respectively using the data given for other PAHs in Fig. 5.8. From the original data sets reported in the literature, derive the corresponding linear relationships between  $\log \gamma_{iw}^{\text{sat}} / \gamma_{il}^{\text{sat}}$  and the molar volume,  $V_{ix}$  (in  $\text{cm}^3 \text{mol}^{-1}$ ), calculated by the method described in Box 5.1 (see caption Fig. 5.8):

$$f_{v,\text{MeOH}} = 0.2: \quad \log (\gamma_{iw}^{\text{sat}} / \gamma_{il}^{\text{sat}}) = (0.0104) V_{ix} - 0.668 \quad (1)$$

$$f_{v,\text{MeOH}} = 0.4: \quad \log (\gamma_{iw}^{\text{sat}} / \gamma_{il}^{\text{sat}}) = (0.0147) V_{ix} - 0.469 \quad (2)$$

Insertion of  $\log \gamma_{iw}^{\text{sat}}$  and  $V_{ix}$  ( $195.0 \text{ cm}^3 \text{mol}^{-1}$ ) of benzo(a)pyrene into Eqs. 1 and 2 yields:

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.2) = 7.15$$

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.4) = 6.10$$

which yields a slope  $\sigma_i^c = (7.15 - 6.10) / (0.2) = 5.25$  demonstrating that the effect of the cosolvent methanol is more pronounced for the more hydrophobic benzo(a)pyrene as compared to the less hydrophobic naphthalene ( $\sigma_i^c = 3.0$ , see above). Insertion of the according values into Eq. 5-28 then yields:

$$\log \gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.3) = 7.15 - (5.25) (0.1) = 6.63$$

or

$$\gamma_{il}^{\text{sat}} (f_{v,\text{MeOH}} = 0.3) = 4.2 \times 10^6$$

which is about 75 times smaller than  $\gamma_{iw}^{\text{sat}}$ . Hence, the corresponding mole fraction solubility is about a factor of 75 larger (Eq. 5-31), that is:

$$x_{il}^{\text{sat}} = (75) (7.2 \times 10^{-9}) (0.018) = 9.7 \times 10^{-9}$$

and by analogy to case (a):

$$C_{il}^{\text{sat}} (f_{v,\text{MeOH}}) = (9.7 \times 10^{-9}) / (0.022) = 4.4 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}$$

## 5.5 Availability of Experimental Data; Methods for Estimation of Aqueous Activity Coefficient and Aqueous Solubility

### Experimental Data

We have already seen from our above discussions that organic chemicals cover a very wide range of aqueous solubilities, that is, from completely miscible down to  $10^{-10} \text{ mol} \cdot \text{L}^{-1}$  and below (see Appendix C). Because of these low solubilities and owing to the analytical limitations in the past, many organic substances have acquired the reputation of “being insoluble in water” (e.g., Lide, 1995). From an environmental point of view such a statement is, of course, not correct at all because water is one of the major transport and reaction media for organic compounds in natural systems. Hence, for assessing the behavior and the effects of organic pollutants in the environment, accurate data on aqueous solubilities and aqueous activity coefficients are of utmost importance.

The conventional method of determining *aqueous solubility* is to equilibrate an excess amount of the pure chemical of interest with water in a batch reactor. Equilibrium is achieved by gently shaking or by slowly stirring with a magnetic stirrer. The aim is to prevent formation of emulsions or suspensions and thus avoid extra experimental procedures such a filtration or centrifugation which may be required to ensure that a “true” solution is obtained. This method, which is commonly referred to as *shake flask method* works quite well for more soluble compounds. For more sparingly soluble chemicals such as higher alkanes, PAHs, PCBs, polychlorinated dioxins, and dibenzofurans, however, experimental difficulties can still occur because of the formation of emulsion or microcrystal suspensions, and because of adsorption phenomenon if filtration is necessary. For such compounds, the *generator column method* has been found to produce much more accurate solubility data. In this method, a solid support (e.g., glass bead) is coated with the chemical, packed in an open tubular column, and

water is run through at a precise flow rate to achieve equilibrium. Subsequently, the aqueous effluent is assessed for the organic solute by using an appropriate analytical technique. For a more detailed discussion of the various aspects of the experimental determination of aqueous solubilities, we refer to Yalkowsky and Banerjee (1992) and to the handbooks published by Mackay et al. (1992–1997). These latter handbooks also contain large compilations of water solubilities of a variety of important compound classes. Additional experimental data may be found in smaller compilations reported by Ruelle and Kesselring (1997a,b), Montgomery (1997), and Mitchell and Jurs (1998). As with our comments on experimental vapor pressure data (Section 4.4), we should point out that, particularly for sparingly soluble compounds, aqueous solubilities determined by different methods and/or different laboratories may vary by as much as a factor of 2 to 3, and in some cases even by more than an order of magnitude. Such data should, therefore, be treated with the necessary caution. Again, one way of deciding which solubility value should be selected is to compare the experimental data with predicted values using other compound properties or solubility data from structurally related compounds.

Several experimental methods are available to determine activity coefficients of organic compounds in dilute aqueous solution. A critical review of the various direct and indirect measurement methods can be found in the article by Sherman et al. (1996). For compounds exhibiting small  $\gamma_{iw}$  values (i.e., high water solubilities), differential ebulliometry or dewpoint techniques are frequently used. Here, the effect of the solute on the boiling point of the solvent (i.e., water), or on the dewpoint of the solvent vapor, respectively, is determined under constant pressure. The measured changes then allow us to derive the activity coefficient of the compound in the solvent. For compounds that exhibit larger  $\gamma_{iw}$  values, particularly for the more volatile compounds, the techniques of head space gas chromatography and gas stripping seem to provide reliable activity coefficients in dilute aqueous solution. Among the indirect approaches, derivation of  $\gamma_{iw}$  values from experimental evaluation of the partitioning of a compound between an organic solvent (e.g., hexadecane, *n*-octanol) and water is the most widely used method. We will come back to this issue in Chapter 7.

In summary, we can conclude that there is quite a large experimental database on aqueous solubilities and/or aqueous activity coefficients of organic compounds available in the literature. In this context, we should recall that for compounds exhibiting  $\gamma_{iw}$  values greater than about 100, we may assume that  $\gamma_{iw}$  is concentration independent (Section 5.2). Thus, if only  $\gamma_{iw}$  is known for a given compound (either experimentally determined or predicted; see below), we can estimate its aqueous solubility by using Eqs. 5-6, 5-10, or 5-15, respectively (see also Illustrative Example 5.2). If neither the aqueous solubility nor the aqueous activity coefficient is known for a given compound (e.g., for a new chemical), we may use one of the various methods that have been developed for estimating these important compound properties.

### **Prediction of Aqueous Solubilities and/or Aqueous Activity Coefficients**

Any general approach (i.e., any approach that is not restricted to a confined set of structurally related compounds) for prediction of aqueous solubilities and/or aqueous activity coefficients has to cope with the intrinsic difficulty of describing precisely

what is happening when introducing an organic compound in water. We have discussed this problem in detail in Section 5.3, where we have also seen that by using molecular descriptors such as the solvatochromic parameters we are able to model the aqueous activity coefficient of any kind of organic compound with reasonable success. The problem with these and similar approaches (Yalkowsky and Banerjee, 1992) is only that often not all required descriptors are readily available for a given compound.

Therefore, similar to the attempts made to estimate vapor pressure (Section 4.4) there have been a series of quite promising approaches to derive topological, geometric, and electronic molecular descriptors for prediction of aqueous activity coefficients from chemical structure (e.g., Mitchell and Jurs, 1998; Huibers and Katritzky, 1998). The advantage of such quantitative structure property relationships (QSPRs) is, of course, that they can be applied to any compound for which the structure is known. The disadvantages are that these methods require sophisticated computer software, and that they are not very transparent for the user. Furthermore, at the present stage, it remains to be seen how good the actual predictive capabilities of these QSPRs are.

A completely different method that has been shown to be particularly useful for estimating activity coefficients in *nonaqueous* solutions is based on a group contribution approach. The best known and most widely used version of this approach is the UNIFAC method (Hansen et al., 1991; Kan and Tomson, 1996). A similar approach that is, however, focused on aqueous solutions is referred to as AQUAFAC (Myrdal et al., 1993). The basic idea of this type of approach is to express enthalpic and entropic contributions to the excess free energy by summing up interactive terms of parts of the solute and solvated molecules, particularly of their functional groups. A large number of such interaction parameters have been derived from a statistical analysis of experimental data on vapor–liquid partitioning. As already mentioned above, UNIFAC works best for nonaqueous mixtures or mixtures that contain only a very limited amount of water. When dealing with solutions exhibiting significant amounts of water, the present limitations of UNIFAC, but also of AQUAFAC (Sherman et al., 1996; Fan and Jafvert, 1997), are probably due primarily to the difficulties in properly expressing the entropic contributions resulting from the unique properties of the solvent water.

We conclude our short discussion of estimation methods for aqueous solubilities and aqueous activity coefficients by restating that simple one-parameter relationships [e.g., relationships between liquid aqueous solubility and molar volume (Table 5.4) or octanol–water partition constant (Section 7.4)] may also be quite powerful predictive tools, provided that we confine a given equation to a set of *structurally closely related* compounds. In this context, we should emphasize again (and again!) that only with a sufficient understanding of the molecular interactions that determine the excess free energy of a given compound in a given molecular environment (here in aqueous solution) will we be able to define which compounds are structurally related with respect to a given partitioning process. This will become even more evident in the following chapters.

## 5.6 Questions and Problems

### Questions

#### Q 5.1

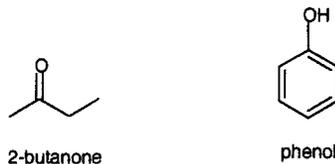
What is meant by the term *water solubility* or *aqueous solubility* of a given compound? What is the range of aqueous solubilities encountered when dealing with environmentally relevant compounds?

#### Q 5.2

How is the aqueous activity coefficient of a compound related to the aqueous solubility, if the compound is (a) a liquid, (b) a solid, and (c) a gas under the prevailing conditions? Comment on any assumptions that you make when answering this question.

#### Q 5.3

The excess enthalpy in aqueous solution ( $H_{iw}^E$ ) of 2-butanone is smaller than that of the similarly sized phenol (Table 5.3), although one can assume that phenol has stronger polar interactions with the water molecules. Try to explain these findings.



#### Q 5.4

The excess entropy in aqueous solution ( $S_{iw}^E$ ) of *n*-hexane is significantly more negative as compared to the similarly sized naphthalene (Table 5.3). Try to explain this difference.



#### Q 5.5

Figure 5.2 and Table 5.4 show that, for a given class of structurally closely related compounds, a linear relationship exists between liquid aqueous solubility and size of the molecule (Eq. 5-18). Note that in both Fig. 5.2 and Table 5.4 decadic instead of natural logarithms are used:

$$\log C_{iw}^{\text{sat}}(\text{L}) = -c \cdot V_{ix} + d$$

Try to answer the following questions:

- (a) Why are the slopes  $c$  of the regression lines quite similar for the *n*-alkanes and the alkanols (Fig. 5.2a), and why do these two groups of compounds exhibit such different intercepts  $d$ ? Why are there any significant differences in the intercepts between primary, secondary, and tertiary alkanols?

- (b) Why do the chlorobenzenes and PAHs (Fig. 5.2b) exhibit different slopes?
- (c) Why is there such a large scatter in the data of the halogenated C<sub>1</sub>- and C<sub>2</sub>-compounds (Fig. 5.2c)?

### Q 5.6

Explain qualitatively how the aqueous solubility of a (a) liquid, (b) solid, and (c) gaseous compound changes with temperature. Which thermodynamic quantity(ies) do you need to know for quantifying this temperature dependence?

### Q 5.7

Explain in words how environmentally relevant inorganic salts affect the aqueous solubility of a (a) liquid, (b) solid, and (c) gaseous compound. Is it true that the effect is linearly related to the concentration of a given salt? What is the magnitude of the effect of salt on the aqueous activity coefficient of organic compounds in typical seawater?

### Q 5.8

Explain in words how organic cosolvents affect the activity coefficients in water-solvent mixtures? Which organic solvents are most effective? Is it true that the effect of an organic cosolvent is linearly related to its volume fraction in the solvent-water mixture? Below which volume fraction can the effect of an organic cosolvent be neglected?

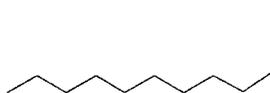
### Q 5.9

Derive Eq. 5-34 by realizing that the number of moles of a given compound present in a given volume,  $V_L$ , of the pure liquid of that compound is given by  $V_L / \bar{V}_L$ .

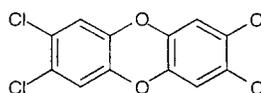
## Problems

### P 5.1 *Calculating Aqueous Activity Coefficients and Excess Free Energies in Aqueous Solution from Experimental Solubility Data*

Calculate the aqueous activity coefficients,  $\gamma_{iw}^{\text{sat}}$ , and the excess free energies in aqueous solution,  $G_{iw}^E$  (in kJ·mol<sup>-1</sup>), of (a) *n*-decane (n-C<sub>10</sub>H<sub>22</sub>), (b) 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, and (c) bromomethane (CH<sub>3</sub>Br) at 25°C using the data provided in Appendix C.



*n*-decane



2,3,7,8-tetrachloro-*p*-dioxin



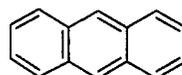
bromomethane

### P 5.2 *A Tricky Stock Solution*

You work in an analytical laboratory and you are asked to prepare 250 mL of a 0.5 M stock solution of anthracene in toluene ( $\rho^{20}$  (toluene) = 0.87 g·cm<sup>-3</sup>) as solvent. You look up the molar mass of anthracene, go to the balance, weigh out 22.3 g of this compound, put it into a 250 mL volumetric flask, and then fill the flask with toluene. To your surprise, even after several hours of intensive shaking, there is still a substantial portion of undissolved anthracene present in the flask, although your

intuition tells you that these two aromatic compounds should form a near-ideal liquid mixture.

- What is the problem?
- Give an estimate of how much anthracene has actually been dissolved (in grams).
- What is anthracene's concentration (in molar units) in the stock solution (at 20°C)? The necessary data can be found in Appendix C.

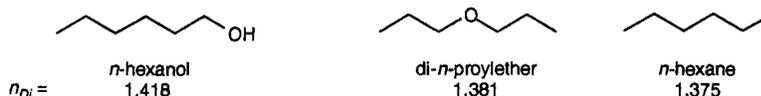


anthracene  
 $T_m = 217.5\text{ }^\circ\text{C}$   
 $T_b = 341.0\text{ }^\circ\text{C}$

**P 5.3 Explaining the Differences in Aqueous Solubility Between *n*-Hexane, di-*n*-Propylether, and *n*-Hexanol**

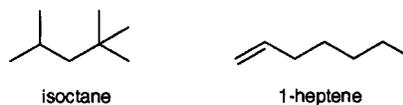
As can be seen from the data in Appendix C, the aqueous solubilities of *n*-hexanol ( $C_{iw}^{\text{sat}} = 6.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) and di-*n*-propylether ( $C_{iw}^{\text{sat}} = 3.0 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ ) exceed that of *n*-hexane ( $C_{iw}^{\text{sat}} = 1.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ ) by more than two orders of magnitude.

- Try to explain the differences in  $C_{iw}^{\text{sat}}$  between the three compounds based on their abilities to undergo intermolecular interactions.
- Use Eq. 5-22 to evaluate the various factors that determine the aqueous solubilities of the three compounds. You can find all necessary data in Tables 4.3 and 5.5 and in Appendix C.



**P 5.4 Estimating Aqueous Solubilities Using Solubility Data of Structurally Related Compounds (adapted from Roberts, 1995).**

As will be discussed in Chapter 7, for estimating the aqueous saturation concentration of a given component of a complex mixture when this mixture is in equilibrium with water (e.g., after a gasoline spill), one needs to know the liquid aqueous solubility of the pure compound of interest. Shown below are the aqueous solubilities of some hydrocarbons present in gasoline that are all liquids at 25°C. Estimate the aqueous solubilities (in molar units) of the two gasoline compounds isooctane (2,2,4-trimethylpentane) and 1-heptene using the experimental data reported below and/or using one of the equations given in Table 5.4. Comment on the selection of the set of reference compounds that you use for your estimates.



Compound	$M_i$ (g · mol <sup>-1</sup> )	$T_b$ (°C)	$C_{iw}^{\text{sat}}$ (25°C) (mg · L <sup>-1</sup> )
1-pentene	70.1	30.0	148
2-methyl-1-pentene	84.2	60.7	78
1-hexene	84.2	63.4	50
4-methyl-1-pentene	84.2	53.9	48
2,2-dimethylbutane	86.2	49.7	12.8
2,2-dimethylpentane	100.2	79.2	4.4
2,2,3-trimethylbutane	100.2	80.9	4.4
3-methylhexane	100.2	92.0	3.3
1-octene	112.2	121.3	2.7
2-methylheptane	114.2	117.6	0.85
1-nonene	126.3	146.9	1.12
3-methyloctane	128.3	143.0	1.42
2,2,5-trimethylhexane	128.3	124.0	1.15

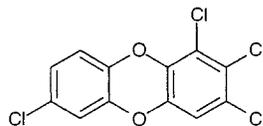
**P 5.5 Evaluating the Effect of Temperature on the Aqueous Solubility and on the Aqueous Activity Coefficient of a Solid Compound**

Living in a cold area, you want to know the aqueous solubility and the aqueous activity coefficient of organic compounds at 1°C rather than at 25°C.

- (a) Estimate  $C_{iw}^{\text{sat}}$  (in molar units) and  $\gamma_{iw}^{\text{sat}}$  of 1,2,3,7-tetrachlorodibenzo-*p*-dioxin at 1°C using aqueous solubilities of this compound determined at more elevated temperatures by Friesen and Webster (1990):
- (b) Also calculate the average excess enthalpy ( $H_{iw}^E$ ) of the compound in water for the temperature range considered (in kJ · mol<sup>-1</sup>). Why are you interested in this quantity? Comment on any assumption that you make.

$T / ^\circ\text{C}$	7.0	11.5	17.0	21.0	26.0
$C_{iw}^{\text{sat}} / \text{mol} \cdot \text{L}^{-1}$	$7.56 \times 10^{-10}$	$8.12 \times 10^{-10}$	$12.5 \times 10^{-10}$	$14.9 \times 10^{-10}$	$22.6 \times 10^{-10}$

Hint: You can solve this problem without any lengthy calculations!



1,2,3,7-tetrachloro-*p*-dibenzodioxin

$$M_i = 322.0 \text{ g} \cdot \text{mol}^{-1}$$

$$T_m = 175.0 \text{ } ^\circ\text{C}$$

**P 5.6 Evaluating the Effect of Temperature on the Solubility and/or the Activity Coefficient of a Gaseous Compound (Freon 12) in Freshwater and in Seawater**

For an assessment of the global distribution of persistent volatile halogenated hydrocarbons, the solubility and activity coefficients of such compounds in natural waters need to be known. Warner and Weiss (1985) have determined the solubilities of dichlorodifluoromethane (Freon 12) at 1 bar partial pressure at various temperatures in freshwater and in seawater (35.8‰ salinity):

*Freshwater:*

$T / ^\circ\text{C}$	0.9	9.6	19.9	29.9	40.7
$C_{iw}^{1\text{bar}} / \text{mol} \cdot \text{L}^{-1}$	$9.0 \times 10^{-3}$	$5.6 \times 10^{-3}$	$3.5 \times 10^{-3}$	$2.5 \times 10^{-3}$	$1.8 \times 10^{-3}$

*Seawater:*

$T / ^\circ\text{C}$	4.8	9.2	20.4	29.6	39.9
$C_{iw}^{1\text{bar}} / \text{mol} \cdot \text{L}^{-1}$	$4.9 \times 10^{-3}$	$4.0 \times 10^{-3}$	$2.4 \times 10^{-3}$	$1.7 \times 10^{-3}$	$1.3 \times 10^{-3}$

- Estimate the solubilities (in molar units) of Freon 12 in freshwater and in seawater at 1 bar partial pressure at 5 and 25°C.
- Calculate the activity coefficients of Freon 12 in freshwater and seawater at these temperatures by using the vapor pressure data given in Problem 4.2.
- Derive the average excess enthalpy ( $H_{iw}^E$  in  $\text{kJ} \cdot \text{mol}^{-1}$ ) of Freon 12 in freshwater and seawater for the ambient temperature range (i.e., 0 – 40°C).
- Comment on any differences found between freshwater and seawater.

**P 5.7 A Small Bet with an Oceanographer**

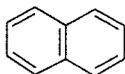
A colleague of yours who works in oceanography bets you that both the solubility as well as the activity coefficient of naphthalene are larger in seawater (35‰ salinity) at 25°C than in distilled water at 5°C. Is this not a contradiction? How much money do you bet? Estimate  $C_{iw}^{\text{sat}}$  and  $\gamma_{iw}^{\text{sat}}$  for naphthalene in seawater at 25°C and in distilled water at 5°C. Discuss the result. Assume that the average enthalpy of solution ( $\Delta_{ws}H_i$ , Fig. 5.1) of naphthalene is about  $30 \text{ kJ} \cdot \text{mol}^{-1}$  over the ambient temperature range. All other data can be found in Tables 5.3 and 5.7 and in Appendix C.

**P 5.8 Evaluating the Effect of Different Cosolvents on the Retention Time of Organic Compounds in Reversed-Phase Liquid Chromatography**

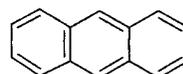
The retention time of an organic compound in reversed-phase liquid chromatography is heavily influenced by the activity coefficient of the compound in the mobile phase, which commonly consists of a CMOS/water mixture.

- Estimate by what factor the activity coefficients of naphthalene and anthracene change when switching the mobile phase from 30% methanol / 70% water (v : v) to 30% acetonitrile / 70% water.
- What is the effect on the absolute and relative retention times of the two compounds when leaving all other parameters invariant?

In the literature (Pinal et al., 1991) you find data showing that the activity coefficient of anthracene is 400 times smaller in 40% acetonitrile / 60% water (v : v) as compared to pure water. All other necessary data can be found in Table 5.8, Illustrative Example 5.5, and Appendix C.



naphthalene



anthracene