TABLE 5.7  Salting Constants for Benzene and Naphthalene at 25°C for Some Important Salts

<table>
<thead>
<tr>
<th>Salt</th>
<th>Mole fraction of total salt in seawater*</th>
<th>Salting Constant</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>K⁺ (benzene)⁺</td>
<td>K⁺ (naphthalene)⁺</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.799</td>
<td>0.19</td>
<td>0.22</td>
<td></td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0.104</td>
<td>0.70</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>0.055</td>
<td>0.32</td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td>CaCl₂</td>
<td>0.020</td>
<td>0.17</td>
<td>0.19</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>0.018</td>
<td>0.01</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>0.005</td>
<td>0.13</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td></td>
<td>0.10</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>CsBr</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Gordon and Thorne (1967a,b).

McDevit and Long (1952).

A salt mixture as, for example, NaCl does in seawater, it is often sufficient to use the salting constant for that salt as a surrogate for the whole mixture. For example, the error introduced when using $K⁺_{NaCl}$ instead of $K⁺_{tw}$ for predicting the effect of salinity on solubility and activity coefficients of organic compounds in seawater is only about 10% (see examples given Table 5.6).

Based on our simple picture of the dissolution process, the introduction of a polar substituent into a molecule should decrease the salting-out effect. This is because the introduction of a polar group generally decreases the hydrophobic surface area, and favorable interactions of the polar group with the ions present in the water are possible. The very few data available on salting effects on polar organic compounds are consistent with this picture. Table 5.6 shows that the measured $K⁺$ values for phenol, p-aminotoluene, and p-nitrotoluene are generally somewhat lower than the values determined for benzene and toluene. In summary, we have seen that the most important dissolved inorganic salts present in natural waters generally decrease the aqueous solubility (or increase the activity coefficient) of neutral organic compounds. At moderate salt concentrations (e.g., in seawater), the effect of salinity on aqueous solubility is usually less than a factor of 2.

Dissolved Organic Solutes and Solvents

Another aspect of solution composition which can affect the solubility (or aqueous activity coefficient) of organic chemicals involves the inclusion of other organic molecules in the water. As depicted in Figure 5.8, such codissolved organic molecules may influence the aqueous cavity surrounding a solute of interest to us, and in so doing, change the energetic costs of forming such a cavity. Three general cases appear to describe the various observations reported. (1) When the other organic molecules are present in relatively large abundances (more than 10% by volume where there is insufficient water to hydrate most of them), these act as solvent molecules themselves
and partially surround the solute of interest approximately in proportion to their volume fraction in the solution (Yalkowsky et al., 1976). (2) When the other organic compounds are present in somewhat less abundance, these molecules themselves have water-lined cavities surrounding them; and if these hydration shells are somewhat shared by the organic compounds, the overall dissolution cost of the chemical we're considering will be decreased (Banerjee and Yalkowsky, 1988). This situation may be best referred to as an influence of cosolutes. This may be the most appropriate picture of the influence of n-octanol in water at saturation (~4.5 x 10^-3 M or 7 x 10^-4 volume fraction), causing a little more hexachlorobenzene (2x) and DDT (3x) to dissolve (Chiou et al., 1982, 1983). (3) Finally, if the organic chemicals are present at low enough levels (less than 10^-3 volume fraction) that there is a low probability of even their hydration shells overlapping, we can expect no effect on the aqueous activity coefficients or (liquid) solubilities. This is the image we should have for organic compounds that we call "slightly soluble in water" insofar as the molecules of the same kind are too rare to influence one another (Tucker and Christian, 1979; Munz and Roberts, 1986). Similarly, slightly soluble hydrocarbons present in a solution do not appear to enhance the dissolution of other hydrocarbons (e.g., Leinonen and Mackay, 1973).
For the purposes of predicting organic chemical fates in the environment, we are primarily interested in cases where cosolvents are present in relatively large proportions (more than 10% by volume). These are the situations where marked changes in nonpolar chemical activity coefficients occur. To estimate the degree of such effects, we can utilize the conceptualization of Yalkowsky et al. (1976). These workers reasoned that the excess free energy of solution of a compound in a water–organic cosolvent mixture should be a linear combination of the compound’s excess free energies of solution in each solvent alone:

$$\Delta G_{\text{emix}} = (1 - f_c) \Delta G_{\text{ew}} + (f_c) \Delta G_{\text{ec}}$$  \hspace{1cm} (5-24)$$

where

- $f_c$ is the volume fraction of the solution consisting of the cosolvent
- $\Delta G_{\text{ew}}$ is the excess free energy of solution in pure water
- $\Delta G_{\text{ec}}$ is the excess free energy of solution in the cosolvent

It is as if part of the organic solute of interest is dissolved in water, while the remainder is dissolved in the organic cosolvent. Recalling that $\Delta G^e = +RT \ln \gamma$, we can also write

$$\ln \gamma_{\text{mix}} = (1 - f_c) \ln \gamma_w + (f_c) \ln \gamma_c$$  \hspace{1cm} (5-25)$$

or

$$\ln \chi_{\text{sat}} = (1 - f_c) \ln \chi_{\text{w sat}} + (f_c) \ln \chi_{\text{c sat}}$$  \hspace{1cm} (5-26)$$

Yalkowsky and colleagues (1976, and references therein) have reasoned that microscopic-scale situations like that pictured in Fig. 5.8a can be thought of much like a macroscopic-scale counterpart of two liquids contacting one another and exhibiting an interfacial surface tension (e.g., Fowkes, 1964). In this case the solute (shown as an octanol molecule in a blowup of Fig. 5.8a) may be seen as having both hydrophobic surface area (HSA) and polar surface area (PSA). Each of those microscopic surface area types experiences a different interaction energy when juxtaposed to a polar liquid like water or a relatively nonpolar one like acetone or isopropanol. Thus, Yalkowsky et al. (1976) write for $\Delta G_{\text{ew}}$:

$$\Delta G_{\text{ew}} = (\sigma_{\text{HSA}}) \text{(HSA)}(N) + (\sigma_{\text{PSA}}) \text{(PSA)}(N)$$  \hspace{1cm} (5-27)$$

where

- $\sigma_{\text{HSA}}$ is the interfacial energy (e.g., J·cm$^{-2}$) where the hydrophobic solute contacts water,
- $\sigma_{\text{PSA}}$ is the interfacial energy (e.g., J·cm$^{-2}$) where the polar solute contacts water,
- HSA is the solute’s hydrophobic surface area (cm$^2$/molecule),
- PSA is the solute’s polar surface area (cm$^2$/molecule),
- $N$ is Avogadro’s number ($6.02 \times 10^{23}$ molecules/mol), used to put everything on a per mole basis.