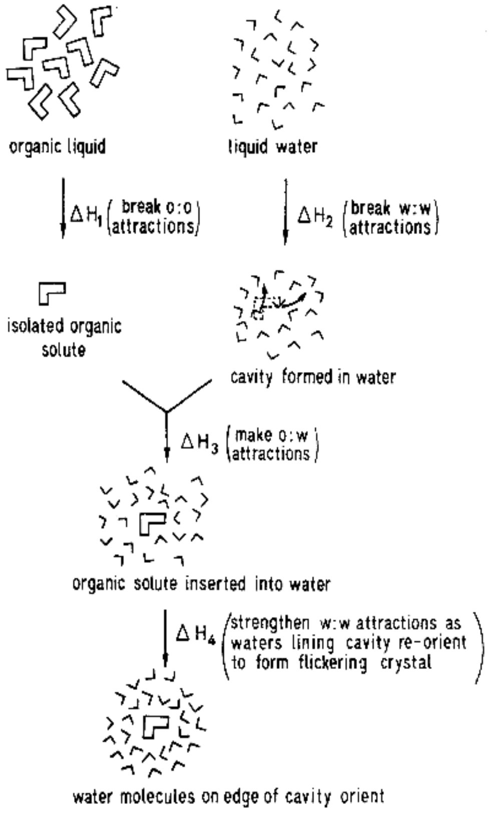
SOLUBILITY

Aqueous solubility is the concentration of the chemical in the aqueous phase, when the solution is in equilibrium with the pure compound in its usual phase (gas, liquid or solid) at a specified temperature and pressure (e.g., 25°C, 1 atm). We then speak of a saturated solution of the chemical, the concentration of which we will denote as C_w^{sat}. Whether an organic molecule 'likes' or 'dislikes' being surrounded by water molecules is one of the key factors in determining its environmental behavior. It is necessary, that we try to understand the molecular forces and interactions involved when an organic compound dissolves in water *(1).*

Molecular Description of Dissolution

When an organic solute dissolves in water, there are a number of steps involved that contribute to the overall energetics of the system. Firstly, the solute molecules must be separated from one another so that they can be freely dispersed in the solvent and surrounded by solvent molecules. The magnitude of these forces will depend on the size and structure of the solute. Secondly, the solvent molecules must become partially separated form one another to create a cavity large enough to accommodate the solute. The larger the solute to be dissolved, the greater the size of the cavity that must be created. These processes are both endothermic (i.e., $\Delta H > 0$).

Once the solute occupies the cavity and is surrounded by water molecules, there will be new attractive forces between solute and solvent. These may be London Dispersion and dipole type forces depending on the nature of the solute and their magnitude will depend on factors such as size, polarity and potential H-bonding. Finally, the water molecules in the salvation shell will form extra strong H-bonds to neighbouring water molecules similar to those found in solid ice. These later two processes will be exothermic ($\Delta H < 0$) as new attractive forces are formed. The figure below schematically represents the molecular reorganization that takes place upon dissolution.



Thermodynamic Description

Enthalpy of Dissolution

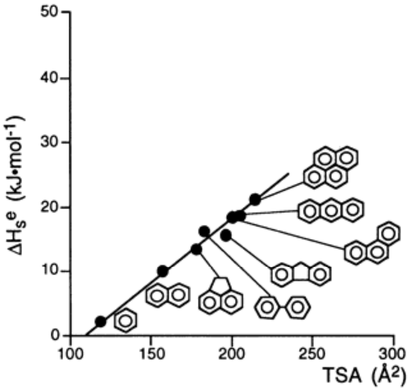
The enthalpic contributions to the excess free energy of solution (ΔG_s^e) reflect the changes in interactions between solute:solute, solvent:solvent and solute:solvent molecules when the liquid organic compound is dissolved in water. Ideal solutions exhibit identical attractions for all combinations of these molecular interactions, and so the excess enthalpy of solution (ΔH_s^e) for ideal solutions is zero. There are four enthalpy terms in the process of forming a solution from pure solvent and pure solute and they are:

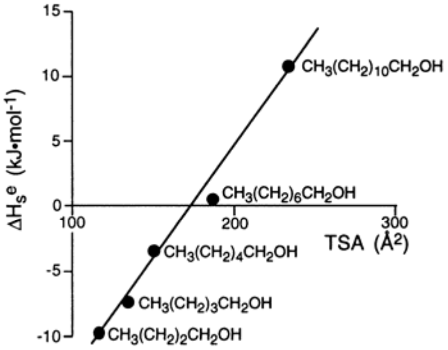
1. ΔH_1: the energy to overcome solute:solute interactions to produce an isolated organic solute.
2. ΔH_2: the energy to overcome solvent:solvent interactions to produce a cavity (hole) in the solvent (water) that can accommodate the organic solute. The size of the cavity will depend on the size of the organic solute and this term is important when dealing with large organic molecules.
   Both ΔH_1 and ΔH_2 are positive (require energy).
3. ΔH_3: the energy gained from the intermolecular attractions between the organic solute and water molecules, when the organic solute is transferred into the cavity. The net excess enthalpy change resulting resulting from breaking and forming intermolecular forces upon introduction of the organic solute into the aqueous cavity is referred to as ΔH_{cav}.
   $$\Delta H_{cav} = \Delta H_1 + \Delta H_2 + \Delta H_3$$
4. ΔH_4: "iceberg formation". The water molecules immediately surrounding the organic solute have strong polar interactions with nearest-neighbor water molecules only on the side away from the organic molecule. This situation appears to result in a "solidifying of positions and orientations" of these cavity-lining water molecules. The "freezing" effect gives rise to an enthalpy term ΔH_{ice}. This enthalpy effect will also be related to the size of the organic solute.

The total excess enthalpy associated with solute dissolution is given by;

$$\Delta H_s^e = \Delta H_{cav} + \Delta H_{ice}$$

and is related to the size (or more precisely to the surface area) of the solute molecules. As the nonpolar surface area of the organic solute increases, ΔH_s^e increases, the solutions become less ideal and the organic molecules have a lower aqueous solubility. See the figures below for the polycyclic aromatic hydrocarbons (PAH) and for a series of alcohols. Note that the experimentally determined heats of solution for the larger PAH's must be corrected for the corresponding heats of melting since they are solids (and not in the reference state, the pure liquid) at 25°C.





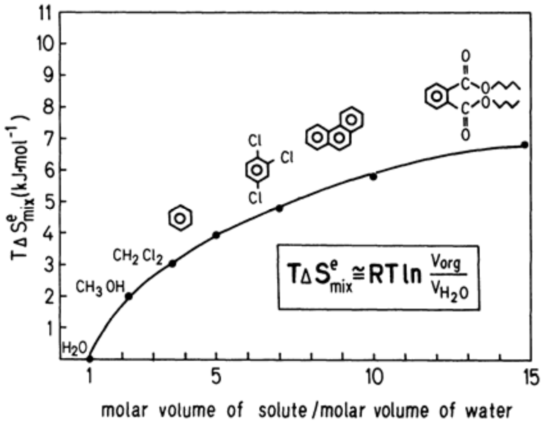
Entropy of Dissolution

Since ΔS_{mix} embodies the increased system randomness that results from mixing materials, this entropy change will always promotes dissolution. When solute and solvent have the same shape and size, this energy term is given by ΔS_{mix}^{ideal}, and is called the ideal entropy of solution. Organic molecules do not, however, have the same sizes and shapes as a water molecule, and the difference or the excess entropy of mixing relative to the ideal case must be considered and the following expressions can be derived:

$$\Delta S_{mix}^{real} = \Delta S_{mix}^{ideal} + \Delta S_{mix}^{e}$$

and $\Delta S_{mix}^{e} = -R\ln\frac{V_{org}}{V_{H_2O}}$ for a mole of organic solute.

V_{org} is the molar volume of the organic solute and V_{H2O} is the molar volume of water.
The figure below shows the contribution of molecular size to the entropy of dissolution of an organic compound in water.



Free Energy of Dissolution

An ideal solution is one where the intermolecular forces between the component molecules are identical to those they would experience in the pure state, thus the pure liquid standard state is defined as ideal. The intermolecular forces resulting from an organic compound dissolved in water are very different from the pure organic liquid (mainly London Dispersion) and pure water (mainly Hydrogen Bonding) and aqueous solutions of organic solutes are far from ideal.

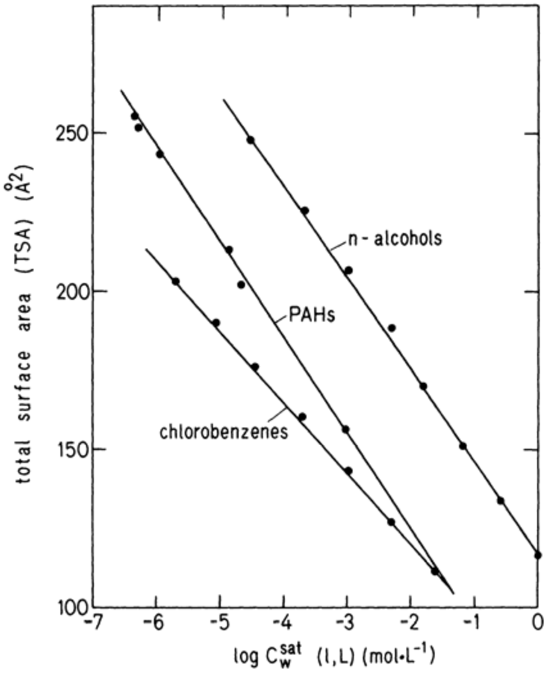
The excess free energy of solution of an organic compound dissolved in water is the additional free energy that a compound is carrying in a nonideal mixture or solution as compared with the *reference state*, or ideal solution (e.g. the pure liquid compound). The excess free energy of solution ΔG_s^e will have enthalpic, ΔH_s^e, and entropic, ΔS_s^e contributions.

We can now assemble the terms that contribute to the excess free energy of solution in water of the organic compound from its pure liquid phase:

$$\Delta G_s^e = \Delta H_s^e - T\Delta S_s^e$$

We find the excess free energy is dependent on the molecular size of the organic solute and good correlations are obtained for a given class of compounds between the aqueous solubilities of liquid organic compounds, C_w^{sat}, and molecular size.

See the figure below:



Consider;

$$X_{(l)} \quad ==== \quad X_{(aq)}$$

where X is an organic solute.

The familiar form of the equilibrium expression is; $K_{eq} \approx \frac{[X\,(aq)]}{1}$

However, the equilibrium expression is actually a ratio of *activities* not concentrations, where { } is used to denote activity and the activity of a compound in a pure liquid (*the reference state*) is equal to unity.

$$K_{eq} = \frac{\{X\,(aq)\}}{\{X\,(l)\}} = \frac{\{X\,(aq)\}}{1}$$

The activity is defined as the product of the activity coefficient γ and concentration, expressed either as a molar concentration, [X(aq)] or the mole fraction either χ.

$$\{X\,(aq)\} = \gamma'_w\,[X\,(aq)] \qquad \text{or} \qquad \{X\,(aq)\} = \gamma_w\,\chi_w$$

It can be shown that the overall free energy change for the dissolution reaction is given by;

$$\begin{aligned} \Delta G_s &= RT \ln \{X(aq)\} \\ &= RT \ln \gamma_w \chi_w \\ &= RT \ln \chi_w + RT \ln \gamma_w \end{aligned}$$

But at equilibrium, $\Delta G_s = 0$

So, $$RT \ln \chi_w = - RT \ln \gamma_w$$

And $$\ln \chi_w = - \ln \gamma_w$$

$$\chi_w = \frac{1}{\gamma_w}$$

Mole fraction concentrations are converted to molar units using the molar volume of the solvent. Thus;

$$C_w = \frac{\chi_w}{\overline{V}_{H2O}}$$

So;

$$C_w = \frac{1}{\overline{V}_{H2O}\ \gamma_w}$$

Adding the 'sat' superscript to remind us that we are working with saturated solutions and adding the (L) to remind us that the organic liquid is the reference state, the solubility of organic liquids is inversely related to the aqueous activity coefficient as follows;

$$C_w^{sat}(L) = \frac{1}{\overline{V}_{H2O}\ \gamma_w^{sat}} \qquad \text{or} \qquad \gamma_w^{sat} = \frac{1}{\overline{V}_{H2O}\ C_w^{sat}(L)}$$

where V_{H2O} is the molar volume of water = 0.018 L. Hence, the aqueous activity coefficient of the an organic solute is a direct measure of it's solubility – the larger the activity coefficient, the lower the water solubility. For solids and gases, we also need to incorporate the 'energy costs' associated with melting the solid to the *subcooled* liquid state or condensing the gas to the superheated liquid state. Hence,

For Solids;

$$C_w^{sat}(s) = C_w^{sat}(L)\ \frac{P^o(s)}{P^o(L)}$$

Substituting for C_w^{sat} and rearranging yields;

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w\ C_w^{sat}(s)}\ \frac{P^o(s)}{P^o(L)}$$

For Gases;

$$C_w^{sat}(g) = C_w^{sat}(L)\ \frac{1\,\text{atm}}{P^o(L)}$$

Substituting for C_w^{sat} and rearranging yields;

$$\gamma_w^{sat} = \frac{1}{\overline{V}_w\ C_w^{sat}(g)}\ \frac{1\,\text{atm}}{P^o(L)}$$

As we have seen above, the activity coefficient can be deduced from the aqueous solubilities (together with vapour pressure and melting point data, if necessary). The magnitude of the activity coefficient is a direct reflection of the degree of 'dissimilarity 'of the solute – solvent system.

Activity Coefficients for Selected Organic Solutes in Aqueous Solution

Compound	γ_w^{sat}	γ_w^{∞}
1-butanol	7.0×10^1	5.0×10^1
1-hexanol	9.0×10^2	8.0×10^2
1-octanol	3.7×10^3	3.0×10^3
trichloromethane	7.9×10^2	8.2×10^2
1,1,1-trichloroethane	2.4×10^3	2.2×10^3
phenol	6.3×10^1	5.7×10^1
benzene	2.5×10^3	2.5×10^3
chlorobenzene	1.4×10^4	1.3×10^4
naphthalene	6.7×10^4	6.9×10^4
hexachlorobenzene	4.3×10^7	3.5×10^7
2,2',5,5'-tetrachlorobiphenyl	7.0×10^8	7.5×10^8

From an environmental perspective, it is important to known the activity of an organic solute in *dilute* aqueous solution. The activity coefficient denoted as γ_w^{∞} represents the limiting value at infinite dilution. As can be seen from the data in the table above, the activity coefficient for most compounds is independent of concentration.

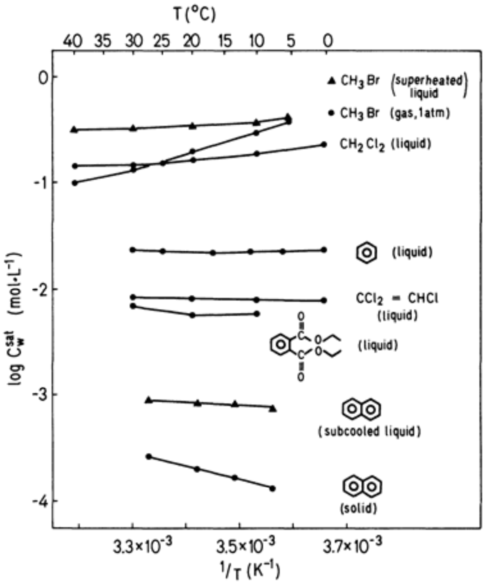
EFFECT OF TEMPERATURE, SALTS AND DISSOLVED ORGANICS

Temperature

The effect of temperature on the solubility of organic solutes depends on the initial state (i.e., s, l or g) of the solute. In general the solubility of organic liquid solutes is almost invariant with temperature, usually changing by less than a factor of 2 times over the ambient temperature range of 0 – 30°C.

$$\ln C_w^{sat}(L) = -\frac{\Delta H_s^e}{RT} + \text{constant}$$

As shown for some liquid organic compounds in the figure below, a plot of $\log C_w^{sat}$ versus 1/T yields information on both the sign and magnitude of ΔH_s^e over a narrow temperature range.



The solubility of organic solids <u>increases</u> with increasing temperature since the ‘energy costs’ associated with melting decreases with increasing temperature.

$$\ln C_w^{sat}(s) = -\frac{\Delta H_{fus} + \Delta H_s^e}{R}\frac{1}{T} + \text{constant}$$

Conversely, the solubility of gases <u>decreases</u> with increasing temperature since the ‘energy costs’ associated with condensing a gaseous organic compound increase with increasing temperature.

$$\ln C_w^{1\,atm}(g) = -\frac{-\Delta H_{vap} + \Delta H_s^e}{R}\frac{1}{T} + \text{constant}$$

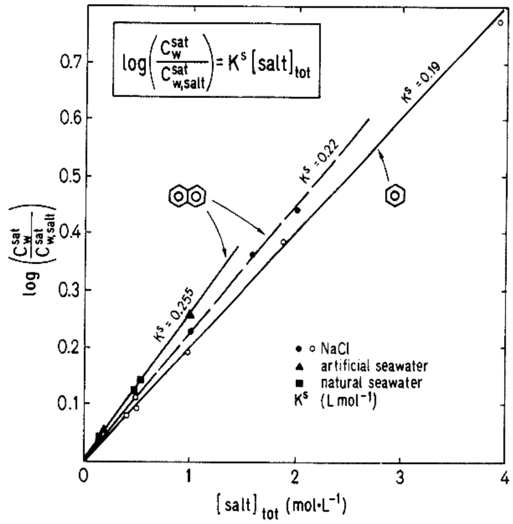
Dissolved Inorganic Salts

In general, organic solutes become less water soluble in the presence of high salt content. The extent of the decreased solubility depends on the intrinsic properties of the solute and total salt concentration.

An empirical formula that relates aqueous solubility in the presence of salts to that in pure water is given below, K^s is a 'salting' constant specific for each organic solute/salt combination and $[\text{salt}]_{tot}$ is the total salt concentration.

$$\log C_{salt}^{sat} = \log C_{w}^{sat} - K^s\,[\text{salt}]_{tot}$$

K^{sea} constants have also been determined which are specific for each organic solute in a standard seawater solution.



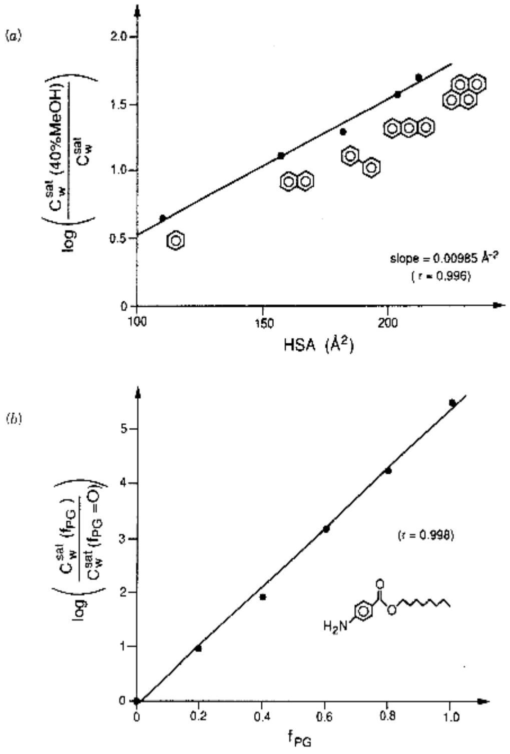
Salting Constants for selected compounds in seawater

Compound	K^s (M^{-1})	Compound	K^s (M^{-1})
trichloromethane	0.20	benzene	0.20
hexane	0.28	napthalene	0.28
phenol	0.13	biphenyl	0.32
chlorobenzene	0.23	benzo[a]pyrene	0.34

As data in the above table confirm, smaller/polar molecules exhibit smaller K^s values that larger/non-polar molecules. At moderate salt concentrations such as seawater (~0.5 M) the aqueous solubility of organic solutes will decrease by a factor between about 1.5 (for small/polar compounds) to about 3 (for large/nonpolar compounds). However, in brines and some wastewaters with high salt concentrations the 'salting out' affect will be more dramatic due to the exponential nature of the relationship.

Organic Co-solvents

As excepted, organic solutes become considerably more soluble in aqueous solutions containing a co-solvent. Common co-solvents for hydrophobic solutes includes methanol, acetonitrile and propylene glycol. As can be seen in the figure below, the solubility enhance is greatest for the most hydrophobic solutes (a) and increases linearly with the amount of co-solvent added (b).

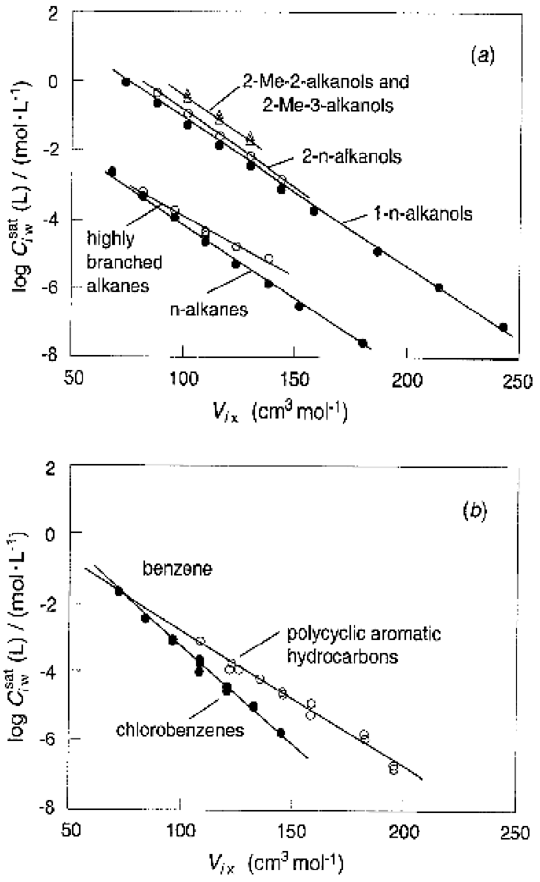


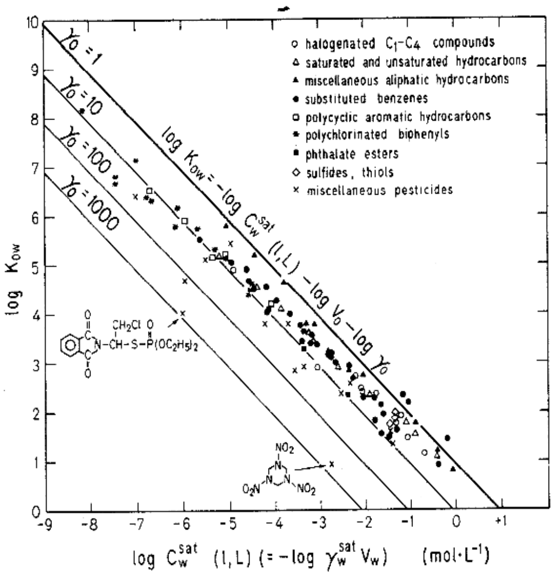
Dissolved Organic Matter

Amphiphlic substances such as anthropogenic detergents or naturally occurring fatty acids and humic substances contain can have a marked affect on the solubility of organic solutes. At higher concentrations amphiphlic molecules will form self-aggregated colloidal suspensions called micelles. The hydrophobic regions of these aggregates can incorporate nonpolar solutes and enhance their solubility. These solubility enhancements vary greatly depending on the source and chemical characteristics of the humic materials.

Predicting Aqueous Solubility and Activity Coefficients

If aqueous solubilities are not known, there are several approaches available for estimating them. Since water solubilities (and therefore γ_w) can be related to molar volumes (V_m) or K_{ow} values for a series of structurally related compounds, these empirical one-parameter relationships can provide powerful predictive tools. However, it should be noted that is not always clear how to define which compounds are structurally related in a given context.





$$\log C_w^{sat}(L) = -c\,V_m + d$$

$$\log C_w^{sat}(L) = -a \log K_{ow} + b$$

where a, b, c and d are constants determined by linear regression of experimental data.

A different method of estimating activity coefficients is based on group contribution approach. In this case, the various enthalpic and entropic contributions for each functional group or structural unit of a molecule (interaction parameters) are summed over the entire molecule. A large number of the various interaction parameters are derived from experimental data and are incorporated into software applications that carry out the necessary calculations. UNIFAC does a good of estimating activity coefficients in nonaqueous solutions, whereas AQUAFAC (AQUeous Functional group Activity Coefficients) has been developed for aqueous solutions.

(1) Environmental Organic Chemistry, R.P. Schwarzenbach; P.M. Gschwend; D.M. Imoden, 1998