ESSENTIAL PHYSICO-CHEMICAL PROPERTIES

Pollutants in the environment may occur as solids, liquids or gases. Their mobility depends on their viscosity (for liquids), their water solubility (if they travel in water) and vapor pressure (for transport in air). These properties also determine which phase (gas, water, solids) the compounds prefer and where they tend to accumulate and thus are decisive for the design of remediation techniques. In the following you find a brief overview about the essentials, for a comprehensive description please see: Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M., 3rd edition, 2017: Environmental Organic Chemistry. An electronic version can be found at the UT library: https://ebookcentral.proquest.com/lib/unitueb/detail.action?docID=4717383

1. BASIC PROPERTIES

1.1 VAPOR PRESSURE

The tendency of a compound to escape its liquid or solid phase determines its saturation vapor pressure ($P°$). Thus, compounds with low molecular weight have high vapor pressures and vice versa (Fig. 1.1). Vapor pressure comes in many different units (atm, mmHg, etc.), here Pascal (Pa) are used. For practical purposes (e.g., comparison with legal limits) concentrations may be preferred, which can be easily calculated from pressures based on the ideal gas law:

$$C_{g,sat} = \frac{P_i^\circ}{R\,T}\ [\text{mol l}^{-1}] \text{ or } C_{g,sat} = \frac{P_i^\circ\, M_i}{R\,T}\ [\text{g l}^{-1}] \qquad (1.1)$$

$P_i°$ and M_i denote the saturation vapor pressure [here in kPa] and molar mass of compound i [g mol^{-1}]. R is the ideal gas law constant (e.g. 8.3144 J mol^{-1} K^{-1} (= m^3 Pa mol^{-1} K^{-1}) or 0.082075 atm L mol^{-1} K^{-1}) depending on the pressure units (kPa vs. atm).

With increasing temperature, the tendency to escape to the gas phase obviously increases which leads to increasing vapor pressure. The latter is described by van't Hoffs law which relates the saturation vapor pressure ($P°$) of a compound to temperature (T [K]):

$$P_i^\circ = A \exp\left(\frac{-\Delta H_{vap}}{R\,T}\right) \qquad (1.2)$$

ΔH_{vap} denotes the enthalpy of vaporization (e.g. in kJ mol^{-1}, typical values for organic compounds are around 50 kJ mol^{-1}) and A is a constant.

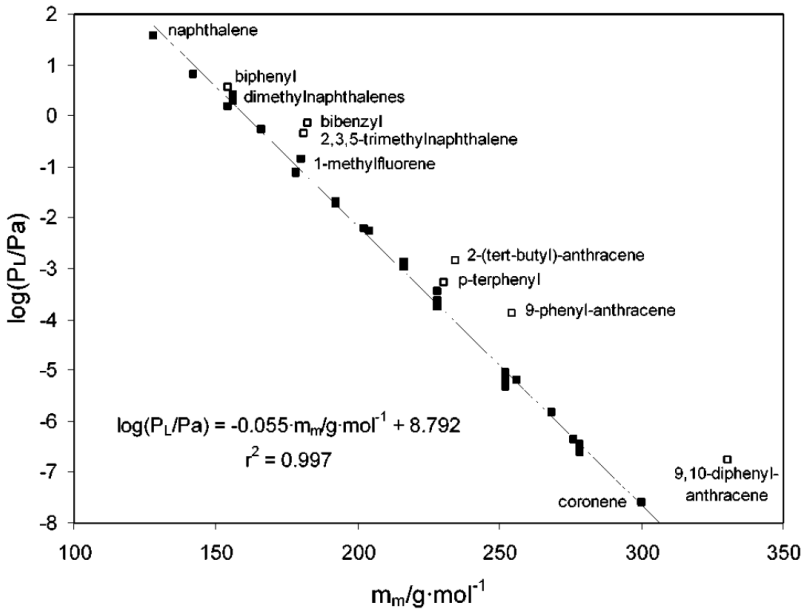


Fig. 1.1: Plot of sub-cooled vapor pressures P_L [Pa] (or $P_i°$) versus molar mass [g mol^{-1}] of some polycyclic aromatic compounds (PAHs). Figure from Lei et al. (2002).

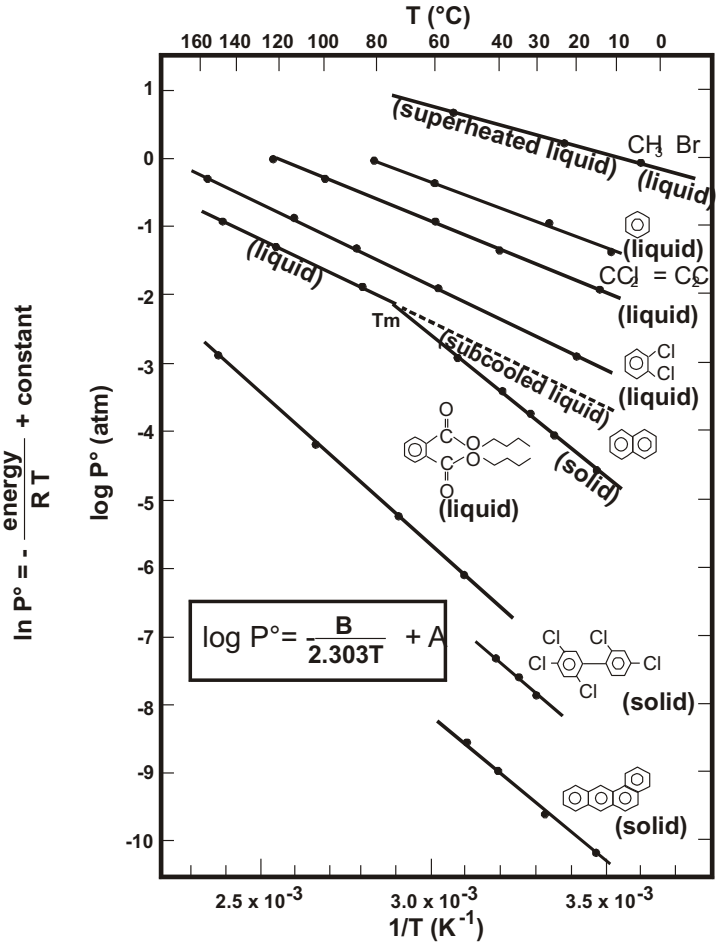


Fig. 1.2: Temperature dependency of saturation vapor pressures for different compounds; note the extrapolation to subcooled vapor pressure of naphthalin. Figure from Schwarzenbach et al. (1993).

Mixtures. Many organic compounds occur in organic mixtures such as fuels, e.g. benzene in gasoline. The vapor pressure of in constituent of an organic mixture can be calculated by Raoult's law:

$$P_i = \chi_{i,o}\, \gamma_{i,o}\, P_i^{\circ} \tag{1.3}$$

where $\gamma_{i,o}$ and $\chi_{i,o}$ denote the activity coefficient and mole fraction of compound i in the organic phase, respectively. In ideal mixtures $\gamma_{i,o}$ is 1 and in non-ideal cases larger than 1.

1.2 WATER SOLUBILITY

Dissolution of neutral organic compounds such as benzene in water is very different from dissolution of a salt. They do not dissociate and solubilities depends on several steps: Space is needed in water to host the organic compound (i) and thus the water molecules form a cage (ii) which leads to reorganization (iii) of the water molecules (structuring) causing a decrease of the system entropy. Solubility thus depends very much on the size of the organic molecule (and surface properties) and is attributed to "hydrophobic" interactions. Since the size (of the molecule and cage in water) does not much change with temperature, the solubility of liquid compounds does not change much, but follows again van't Hoffs law:

$$C_{w,sat} = S = A \exp\left(\frac{-\Delta H_{sol}}{R\,T}\right) \tag{1.4}$$

S and $C_{w,sat}$ here are used synonymously and denote the water solubility of a compound. ΔH_{sol} is the enthalpy of solution (A is a pre-exponential factor); Fig. 1.3 shows some examples for temperature dependency of common organic compounds.

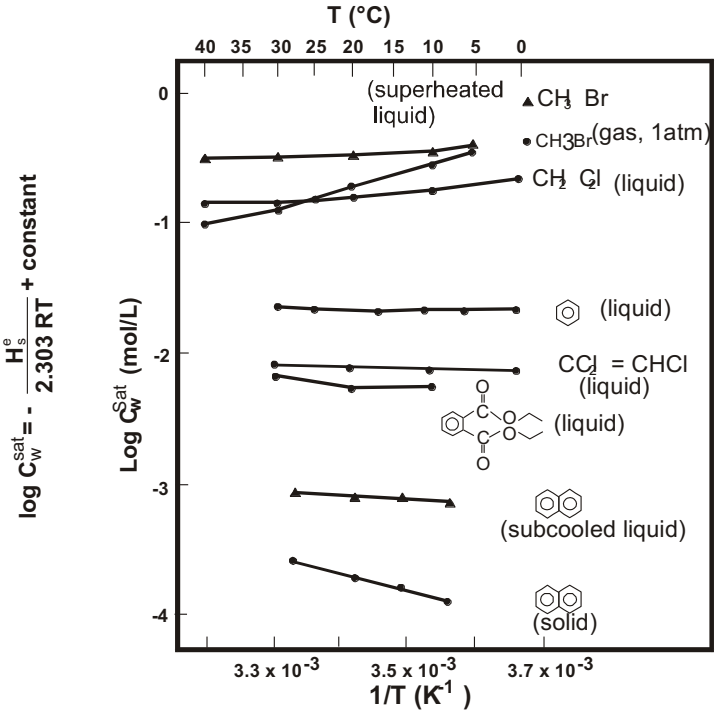


Fig. 1.3: Temperature dependency of water solubility (= saturation concentration in water) for different compounds; note the difference between subcooled and solid naphthaline (two lines at the bottom). Figure from Schwarzenbach et al. (1993).

The solubility of organic compounds may be affected by other water constituents such as ions and other organic compounds. The influence of the ionic strength may be quantified by the so-called Setschenow constant, K^s:

$$\log \frac{C_{w,sat}}{C_{w,sat,sal}} = K^s\, C_{sal} \quad \text{or} \quad C_{w,sat,sal} = C_{w,sat}\, \exp\left(-2.3\, K^s C_{sal}\right) \tag{1.5}$$

$C_{w,sat,sal}$ is the solubility of the organic compound in an aqueous salt solution with concentration C_{sal} in mol l^{-1} (sea water has a NaCl content of about 0.6 mol l^{-1}). Note, such empirical relationships depend on the units used. The "salting out" constant K^s typically is in a range of 0.15 – 0.3.

The presence of highly soluble or even water-miscible organic compounds such as alcohols increase the solubility which maybe again calculated by an empirical relationship:

$$\log \frac{C_{w,sat,co}}{C_{w,sat}} = \sigma\, f_{co} \; or \; C_{w,sat,co} = C_{w,sat}\, 10^{\sigma\, f_{co}} \tag{1.6}$$

$C_{w,sat,co}$ is the solubility of the organic compound in the presence of a volume fraction of cosolvent (f_{co}). σ is the so-called cosolvency power which depends on the compound to be dissolved and the miscibility of the cosolvent with water. For completely miscible solvents such as alcohols σ is in the range of 1-3 (for non-miscible solvents much higher).

Similarly, organic substances such as humic acids or surfactants forming colloids or micelles may lead to an "apparent" increase of the solubility of organic compounds in water:

$$\frac{C_{w,sat,DOC}}{C_{w,sat}} = 1 + f_{DOC}\, K_{DOC} \tag{1.7}$$

$C_{w,sat,DOC}$ is the solubility of the organic compound in the presence of a dissolved organic carbon (DOC). K_{DOC} is a partition coefficient describing the concentration ratio between compound in the organic colloid (or micelle) and water. Eq. 1.7 can be easily derived by a mass balance approach (see upcoming lectures).

1.3 VAPOR PRESSURE AND SOLUBILITY COMBINED: HENRY'S LAW

Organic compounds typically distribute between different phases in the environment (such as solids, water, gas phase). The partitioning between gas phase and water is described by Henry's Law which simply relates the concentration of a compound in gas phase and water C_g and C_w or the respective mole fractions (χ_g, χ_w):

$$H = \frac{C_g}{C_w} \; or \; H' = \frac{\chi_{i,g}}{\chi_{i,w}} \; or \; H^* = \frac{P_{i,g}}{C_{i,w}} \tag{1.8}$$

Note, that first two definitions (H and H') are dimensionless but lead to different numbers. Mol fractions are preferred in pure chemistry, in practical environmental contexts (e.g. comparison with legal limits) concentration ratios (e.g. in µg l^{-1}) are preferred. In Anglo-American literature Henry's law is often defined as the ratio of the partial pressure ($P_{i,g}$) and the concentration in water (e.g. in mol m^{-3}) leading to H^* e.g., in units of atm mol^{-1} m^3. The various definitions of Henrys law constant can be converted into each other; in this lecture we use the dimensionless form (H):

$$H = H' \frac{V_{m,w}}{V_{m,g}} = \frac{H^*}{RT} \tag{1.9}$$

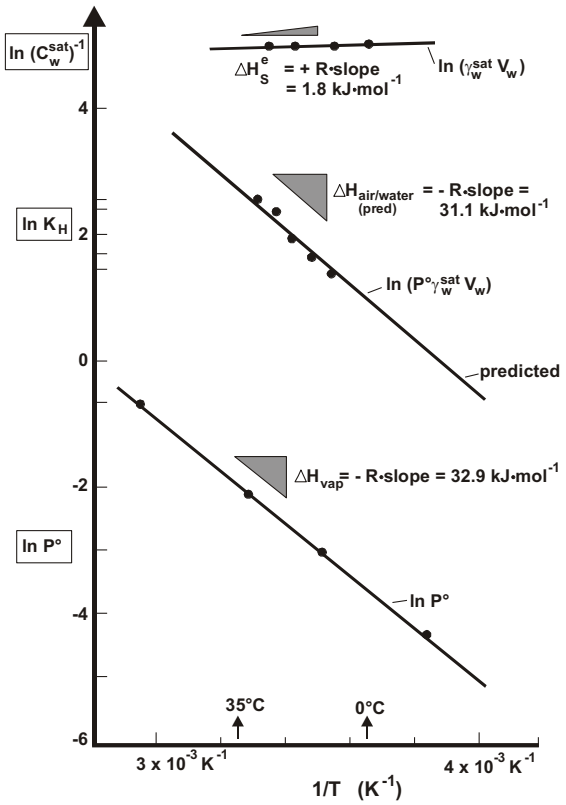


Fig. 1.4: Temperature dependency of Henry's law constant for benzene (ln K_H) compared to solution enthalpy and enthalpy of vaporization; compare to Fig. 1.2 and Fig. 1.3 - solubility is almost independent on temperature; from Schwarzenbach et al. (1993).

Box. 1. shows how to calculate H at different temperatures and Tabl 1 gives a number of examples.

Box 1.1. How to convert to different temperatures?

Henry's law constants but also vapor pressures, water solubilities etc. may be converted from standard to different temperatures based on van't Hoff's law:

$$H_{T_2} = H_{T_1} \exp\left(\frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right)$$

H_{T_1} and H_{T_2} denote Henry's law constants at standard temperate (T_1, e.g. 25°C = 298 K) and at desired higher or lower temperature (T_2). Values for $\Delta H/R$ often are in the range of 4000 K.

Tab. 3. Henry's law constants at 25 °C converted to 10°C (Reisinger und Grathwohl, 1996, Report)

Compound	*H* [-] at 25°C (calc.)	ΔH_{vap}/R [K] (estimated)	*H* [-]10°C calculated
n-Hexane	74,1	(3500)	39,8
Cyclohexane	7,94	(3800)	4,04
n-Heptane	83,2	(4200)	39,4
n-Octane	131,8	(4800)	56,2
Methanol	1,91E-04	5392	7,33E-05
Ethanol	2,57E-04	6377	8,28E-05
n-Propanol	2,75E-04	6777	8,25E-05
Trichloromethane	1,50E-01 *	4612	6,68E-02
Tetrachloromethane	1,24 *	4410	5,72E-01
1,2-Dichloroethane	5,37E-02 *	(4700)	2,33E-02
1,1,1-Trichloroethane	7,03E-01 *	4133	3,40E-01
1,1,2-Trichloroethane	3,72E-02	(5000)	1,53E-02
1,1,2,2-Tetrachloroethane	1,86E-02	(5600)	6,88E-03
1,2-Dichloropropane	1,20E-01	(4200)	5,96E-02
Chloroethene (Vinylchlorid)	1,14 *	3286	6,41E-01
1,1-Dichloroethene	1,07 *	3729	5,56E-01
cis-1,2-Dichloroethene	1,67E-01 *	4192	8,00E-02
trans-1,2-Dichloroethene	3,83E-01 *	4182	1,84E-01
Trichloroethene	3,92E-01 *	4780	1,69E-01
Tetrachloroethene	7,23E-01 *	4918	3,05E-01
Methylbromide	2,63E-01	(2900)	1,57E-01
Tribromomethane	2,75E-02	(5800)	9,81E-03
1,2-Dibromoethan	2,88E-02	(5400)	1,10E-02
Trichlorofluoromethane (F11)	3,96	(3600)	2,09
Dichlorodifluoromethane (F12 ; R12)	17,4	(2400)	11,4
1,1,2-Trichloro1,2,2-trifluoroethane (R113)	13,0	(3800)	6,62
Benzene	2,24E-01	3816	1,14E-01
Chlorobenzene	1,82E-01	(5000)	7,49E-02
1,2-Dichlorobenzene	1,00E-01	(5200)	3,97E-02
1,3-Dichlorobenzene	1,91E-01	(5100)	7,72E-02
1,2-Dimethylbenzene (o-Xylene)	2,19E-01	(5100)	8,85E-02
1,3-Dimethylbenzene (m-Xylene)	2,57E-01	(5000)	1,06E-01
1,4-Dimethylbenzene (p-Xylene)	2,57E-01	(5000)	1,06E-01
1,2,4-Trimethylbenzene	2,34E-01	(5500)	8,81E-02
Phenol	1,62E-05	(6000)	5,58E-06
2-Methylphenol (o-Cresol)	5,01E-05	(6000)	1,73E-05
4-Methylphenol (p-Cresol)	3,24E-05	(6000)	1,12E-05
Naphthalene	1,90E-02	3969	9,39E-03
Phenanthrene	1,17E-03	4570	5,19E-04
Anthracene	2,20E-03	4570	3,21E-04

For a database on *H* and unit conversions see: https://henrys-law.org/henry/browse/

2. PARTITIONING BETWEEN WATER AND ORGANIC PHASES

2.1 RAOULT'S LAW

If an organic compound *i* is present in an organic phase, the latter may be considered a mixture, and Raoult's law applies, which relates the aqueous concentration of a compound present in the organic mixture to its water solubility S_i. Thus, $C_{i,w}$ can be calculated from the composition of the mixture (and thus from $C_{i,o}$):

$$C_{i,w} = \chi_{i,o}\, \gamma_{i,o}\, S_i \tag{2.1}$$

where $\gamma_{i,o}$ and $\chi_{i,o}$ denote the activity coefficient and mole fraction of compound *i* in the organic phase, respectively. In ideal mixtures $\gamma_{i,o}$ is 1 and in non-ideal cases larger than 1. Partitioning coefficients are simply defined as concentration ratio of a compound *i* in the organic phase ($C_{i,o}$) and in water ($C_{i,w}$):

$$K_{o/w} = \frac{C_{i,o}}{C_{i,w}} \tag{2.2}$$

Inserting eq. 2.1 and expressing $C_{i,o}$ and the mole fraction ($\chi_{i,o}$) and based on the mass fraction ($f_{i,o}$, e.g. in g g^{-1}) and the ratio of the molecular weights (M_o/M_i) the partitioning coefficient simply becomes:

$$K_{o/w}\ [\mathrm{l\ kg^{-1}}] = \frac{C_{i,o}}{\chi_{i,o}\, \gamma_{i,o}\, S_i} = \frac{f_{i,o}}{f_{i,o}\, \frac{M_o}{M_i}\, \gamma_{i,o}\, S_i} = \frac{1}{\frac{M_o}{M_i}\, \gamma_{i,o}\, S_i\ [\mathrm{kg\ l^{-1}}]} \tag{2.3}$$

where $K_{o/w}$ comes now in L^3 M^{-1} [e.g., l kg^{-1}], and the units of S_i are in M L^{-3} [e.g., kg l^{-1}]. This is the most frequent expression for partitioning coefficients in environmental sciences because pollutant concentrations in soils and sediments are usually regulated and reported in mass-based units [e.g., mg kg^{-1}].

A "volumetric" partition coefficient is obtained from the mass-based $K_{o/w}$ (eq. 2.3) by multiplication by the density of the organic phase (ρ_o [kg l^{-1}]):

$$K_{o/w}\ [-] = K_{o/w}[\mathrm{l\ kg^{-1}}]\ \rho_o[\mathrm{kg\ l^{-1}}] = \frac{\rho_o}{\frac{M_o}{M_i}\, \gamma_{i,o}\, S_i\ [\mathrm{kg\ l^{-1}}]} \tag{2.4}$$

M_o/ρ_o may be considered as the molar volume of the organic phase ($V_{m,o}$), then S_i in mol l^{-1} × M_i replaces the mass-based solubility in eq. 2.4 (e.g., in g l^{-1}) and we obtain:

$$K_{o/w}\ [-] = \frac{1}{\gamma_{i,o}\ V_{m,o}\, S_i\ [\mathrm{mol\ l^{-1}}]} \tag{2.5}$$

This may be directly obtained from eq. eq. 2.3 if $\chi_{i,o}$ is expressed as $C_{i,o}\ V_{m,o}$. Partition coefficients may be derived in different ways (see also below: partition coefficients from fugacities). Since $V_{m,o}$ is constant, an inverse linear relationship with S_i is expected provided that $\gamma_{i,o}$ is constant. In some cases, however, $\gamma_{i,o}$ may be a function of concentration, resulting in nonlinear partitioning.

According to eq. 2.4, $K_{o/w}$ would increase with the molecular weight of compound *i*, but surprisingly almost linear fits are obtained for K_{oc} vs. *S*, as shown by Razzaque and Grathwohl (2002) for soil organic carbon and Lohman (2012) for low-density polyethylene (see next chapter). This

presumably is because increasing molecular weight leads to increasing activity coefficients and this compensates the increase of molecular weight to some extent.

Since we expect an inverse linear relationship of $K_{o/w}$ [l kg^{-l}] vs. S [kg l^{-l}], the product of K times S is more or less a constant (e.g., 0.18 kg/L in octanol for a compound with a solubility of 1 mg l^{-1}: see Fig 2.1, bottom); this is the theoretical max. uptake of a hydrophobic compounds at its solubility limit in octanol (and water). Later we will see how this applies to natural organic matter in soils and sediments (and in synthetic polymers).

As a final remark, remember for pure compounds, which are solids at ambient temperature and pressures, the subcooled liquid state is always used as reference ($S_{i,subcooled}$).

***$K_{o/w}$* from activities or fugacities.** Alternatively, partition coefficients can be derived from fugacities (e.g. in physical chemistry textbooks). At equilibrium, fugacities (i.e., the tendency of a compound to leave a phase) and thus, activities (concentrations relative to a reference state) in both phases have to equal. From Raoult's law (Eq. 2.1), equal solute activities in the aqueous and organic phases can be written as:

$$\left(\frac{C_{i,w}}{S_{i,w}} = \right) \gamma_{i,o}\, \chi_{i,o} \;=\; \gamma_{i,w}\, \chi_{i,w} \left(= \frac{C_{i,o}}{S_{i,o}} \right) \tag{2.6}$$

where $\gamma_{i,o}$, $\gamma_{i,w}$, $\chi_{i,w}$, $\chi_{i,o}$ denote the activity coefficients and mole fractions in the aqueous (w) and organic (o) phases, respectively. At saturation, the relative solubility in both phases (C/S) is unity on both sides. If instead of mole fractions, concentrations are used by introducing the molar volumes ($V_{m,o}$ and $V_{m,w}$ in liters per mol) then Eq. 2.6 becomes (e.g. by replacing: $\chi_{i,w} = C_{i,w}\, V_w$):

$$\left(\frac{C_{i,w}}{S_{i,w}} = \right) \gamma_{i,o}\, C_{i,o}\, V_{m,o} = \gamma_{i,w}\, C_{i,w}\, V_{m,w} \tag{2.7}$$

Note that $C_{i,w}$ (= $\chi_{i,w}/V_{m,w}$) and $C_{i,o}$ (= $\chi_{i,o}/V_{m,o}$) are now expressed in mol L^{-1}. Taking $K_{o/w}$ as the ratio of $C_{i,o}/C_{i,w}$ we get:

$$K_{o/w} = \frac{C_{i,o}}{C_{i,w}} = \frac{\gamma_{i,w}\, V_{m,w}}{\gamma_{i,o}\, V_{m,o}} = \frac{1}{\gamma_{i,o}\;\, V_{m,o}\, S_i \;\; [\mathrm{mol\,l^{-1}}]} \tag{2.8}$$

This is the same solution as shown above for the volumetric partition coefficient (Eq. 2.5). Note, that $\gamma_{i,w}\, V_w$ equals $1/S_{i,w}$ ($C_{i,w}/S_{i,w} = \gamma_{i,w}\, C_{i,w}\, V_{m,w}$ ==> $1/S_{i,w} = \gamma_{i,w}\, V_{m,w}$).

Molar volumes of organic compounds can be calculated with incremental methods or reasonably well approximated simply by the ratio of the molar mass and density of the liquid compound (e.g., for water: $V_{m,w}$ = 18 cm^3 mol^{-1}). $V_{m,w}$ and $V_{m,o}$ are constants and assuming that $\gamma_{i,o}$ is close to one (which is the case as long as the organic phase represents a suitable solvent for the solute) then $K_{o/w}$ depends solely on $1/S_{i,w}$ or γ_w, (i.e., the process is driven by the activity coefficient of the organic solute in water). This is only valid if $\gamma_{i,w}$ is independent on $C_{i,w}$ up to the solubility of the organic compound in water ($S_{i,w}$), which usually is relatively low (e.g., 0.01 mol L^{-1} or < 1 g L^{-1}).

2.2 OCTANOL/WATER PARTITION COEFFICIENTS (K_{OW})

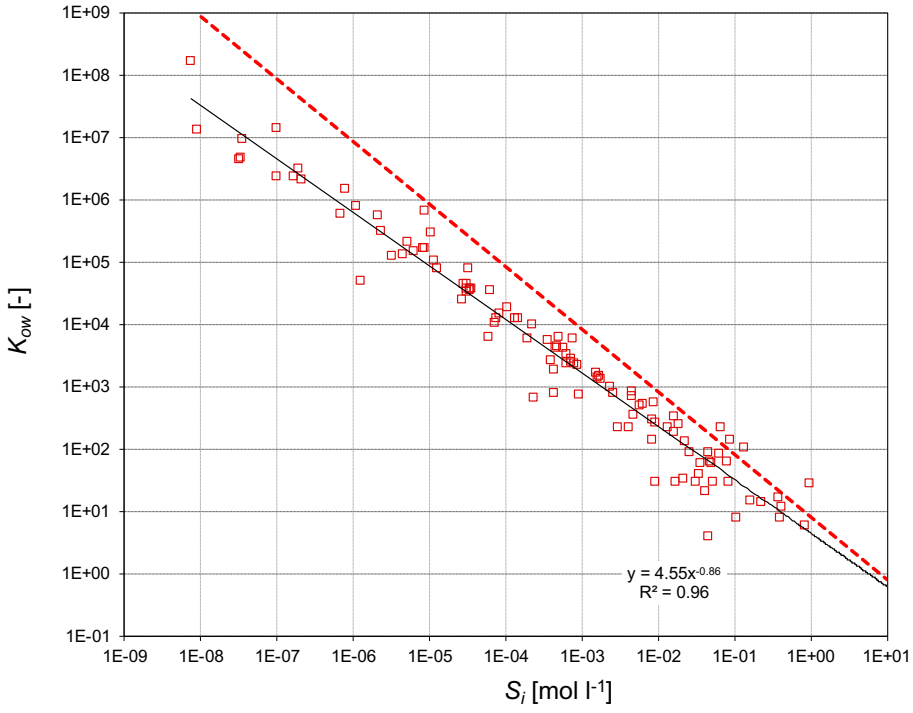
In environmental and medical/toxicological research, octanol is used as equivalent substitute for organic phases in general, such as soil organic matter and biomass (lipids, fats, etc., see Hansch and Leo, 1979; Leo et al., 1971, Chiou et al., 1982). Historically, the octanol/water partitioning coefficient (K_{ow}) was used in medicine to assess the performance of narcotics, such as chloroform. Like other partition coefficients K_{ow} it is simply defined as the concentration ratio of a compound i in octanol ($C_{i,oct}$) and in water ($C_{i,w}$):

$$K_{ow} = \frac{C_{i,oct}}{C_{i,w}} \tag{2.9}$$

Octanol is considered a mixture and thus Raoult's law also applies leading to:

$$K_{ow} = \frac{\gamma_{i,w}\, V_{m,w}}{\gamma_{i,o}\, V_{m,o}} = \frac{1}{\gamma_{i,o}\ V_{m,o}\ S_i\ [\text{mol l}^{-1}]} \tag{2.10}$$

Thus we expect again an inverse linear relationship with respect to S_i (if $\gamma_{i,o}$ is constant). Fig. 2.1 shows K_{ow} vs. S for water-saturated octanol. Note that because water dissolves in octanol, this phase has a molar volume of 0.12 L mol^{-1} instead of 0.16 L mol^{-1} of pure octanol. For low solubility compounds (< 1×10^{-5} mol l^{-1}, such as PAHs), $\gamma_{i,o}$ in octanol goes up to 10 leading to partition coefficients which are a factor of ten lower than expected for ideal conditions (see Fig. 2.1). In literature a multitude of empirical relationships between water solubility of organic compounds and partition coefficients may be found (e.g., Hansch et al., 1968; Allen-King et al., 2002).



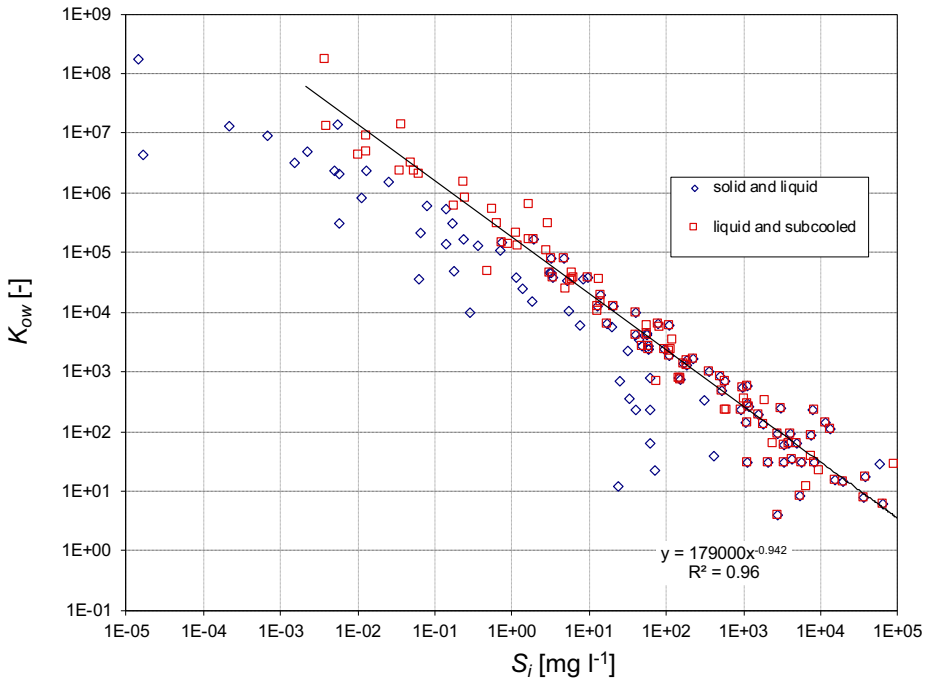


Fig. 2.1: Octanol/water partitioning coefficients (K_{ow}) of various organic compounds *vs.* their water solubility (S) in mol l^{-1} (top) and mg l^{-1} (bottom); the lower plot also includes data on solids solubilities (blue symbols which do not fit that well). The slope of the black regression line in the top diagram (S mol l^{-1}) is significantly < 1, indicating that the activity coefficients for high molecular weight compounds may increase with decreasing subcooled liquid solubility. The dashed red line is calculated for the ideal case ($\gamma_{i,o}$= 1, K_{ow} = 1/($S_{i,w}$ × 0.12) assuming a molar volume of water-saturated octanol of 0.12 l mol^{-1}. To match the observed K_{ow} values, we would need to introduce activity coefficients of 2.7 and 6.8 for benzene and phenanthrene, respectively (see Schwarzenbach et al. 1993, p. 133). In the lower plot, the slope of the regression line is closer to -1 because the increasing molecular weight of the compound compensates for increases in activity coefficients in the organic phase (see eq. 2.4).

Ratios of partition coefficients. In the environment, hydrophobic pollutants are distributed between different "compartments," which include soil and sediment organic matter, plant residues, lipids of organisms, etc... Since there is always a mixture of organic materials in contaminated soils, hydrophobic pollutants will redistribute among the various phases. In ecotoxicology, the ratios of pollutant concentration in lipid and soil organic matter are of concern which may be expressed as:

$$\frac{K_{lipid/w}}{K_{ow}} = \frac{\gamma_{i,ow}\, V_{m,ow}\, S_i}{\gamma_{i,lipid}\, V_{m,lipid}\, S_i} = \frac{\gamma_{i,ow}\ M_{ow}\, \rho_{lipid}}{\gamma_{i,lipid}\, M_{lipid}\, \rho_{ow}} \qquad (2.11)$$

If we would assume that activity coefficients in octanol and lipids are similar and that the densities are similar, then eq. 2.11 can be approximated as the ratio of the molecular weights.

3. LITERATURE

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