GB481
Geochemie minerálních povrchů

4
Adsorpce

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Povrchové interakce

| Table 4.1	Intermolecular Interactions at the Solid-water Interface (Modified from Westall, 1987)
A	*Chemical Reactions with Surfaces*
	Surface hydrolysis
	Surface complexation
	Surface ligand exchange
	Hydrogen bond formation
B	*Electrical Interactions at Surfaces*
	Electrostatic interactions
	Polarization interactions
C	*Interactions with Solvent*
	Hydrophobic expulsion

Adsorpční izotermy
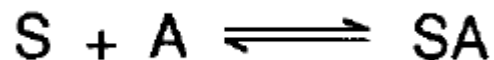
Langmuirova

$$S + A \rightleftharpoons SA$$

S = surface site of adsorbens
A = adsorbate in solution
SA = adsorbate on surface sites

$$\frac{[SA]}{[S]\,[A]} = K_{ads} = \exp\left(-\frac{\Delta G^{o}_{ads}}{RT}\right)$$

$$[S_T] = [S] + [SA]$$

maximum concentration of surface sites, S_T

$$[SA] = [S_T]\,\frac{K_{ads}\,[A]}{1 + K_{ads}\,[A]}$$

Adsorpční izotermy

Langmuirova

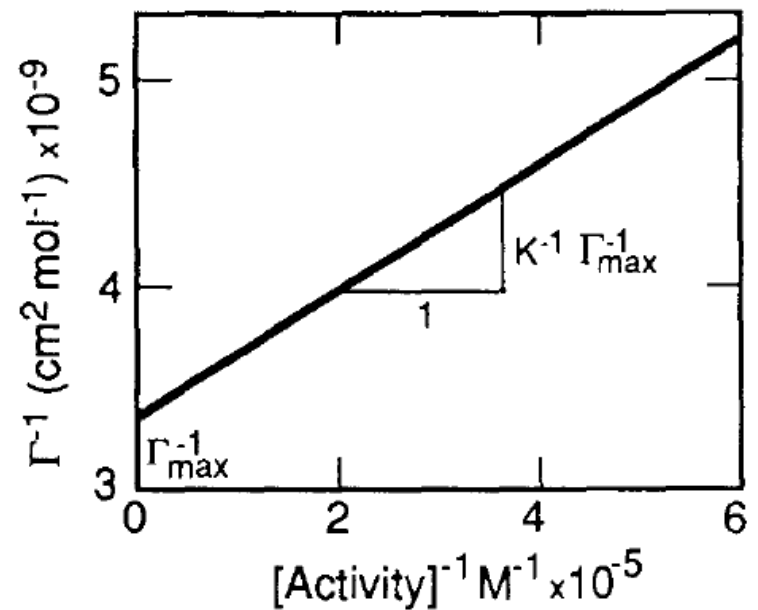$$\Gamma = [SA] \,/\, \text{mass adsorbent} \qquad\qquad \text{surface concentration}$$
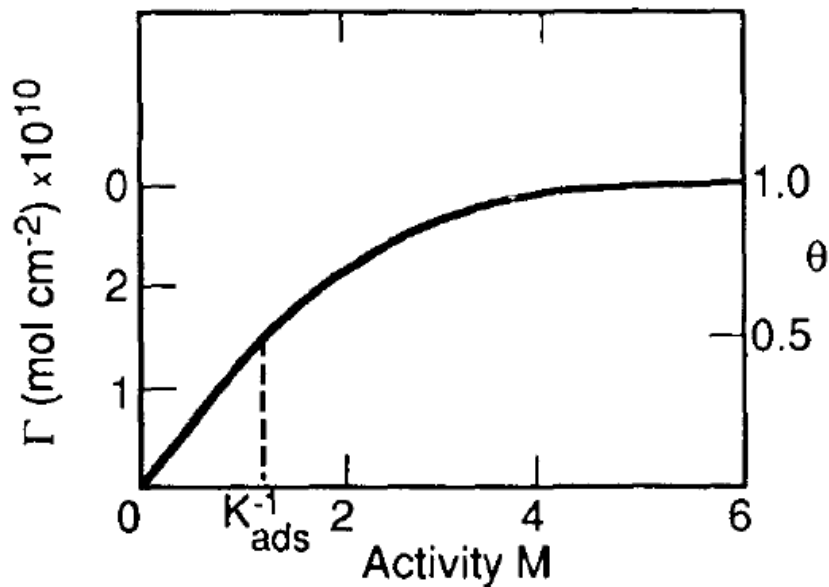
$$\Gamma_{max} = [S_T] \,/\, \text{mass adsorbent}$$

$$\Gamma = \Gamma_{max} \frac{K_{ads}\,[A]}{1 + K_{ads}\,[A]}$$

$$\frac{\theta}{1 - \theta} = K_{ads}\,[A] \qquad\qquad \theta = \frac{[SA]}{[S_T]}$$
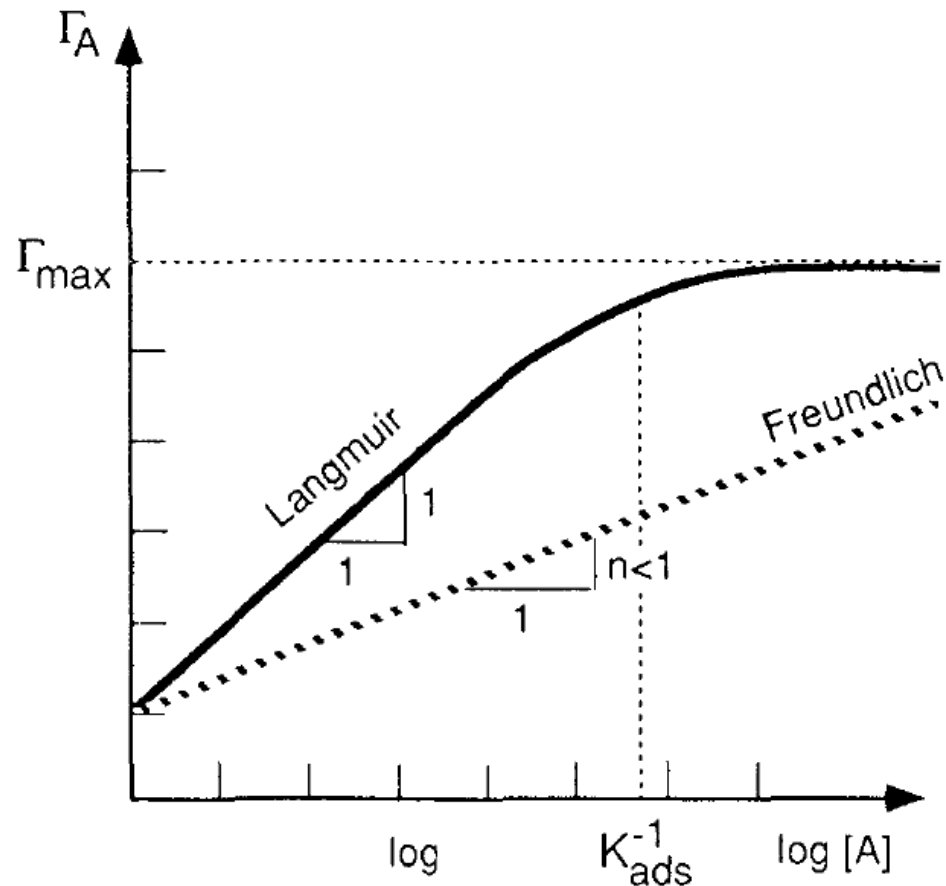
Adsorpční izotermy

Langmuirova

Langmuir adsorption isotherm
From the adsorption isotherm [plotted in accordance with (4.10a)], the equilibrium constant K and the adsorption capacity, Γ_{max}, is obtained by plotting Γ^{-1} versus the reciprocal activity of the sorbate (Eq. 4.10c).
(From Stumm and Morgan, 1981)

Adsorpční izotermy

Freundlichova

$$\Gamma = m[A]^n$$

Plot of adsorption data in a double logarithmic plot. In a Langmuir isotherm the initial slope is unity. A Freundlich isotherm shows in a double log plot a slope of n < 1. Such a Freundlich isotherm is obtained if the adsorbent is heterogeneous (decreasing tendency for adsorption with increasing θ).
(Modified from Morel, 1983)

Mastné kyseliny a povrchově akt. látky
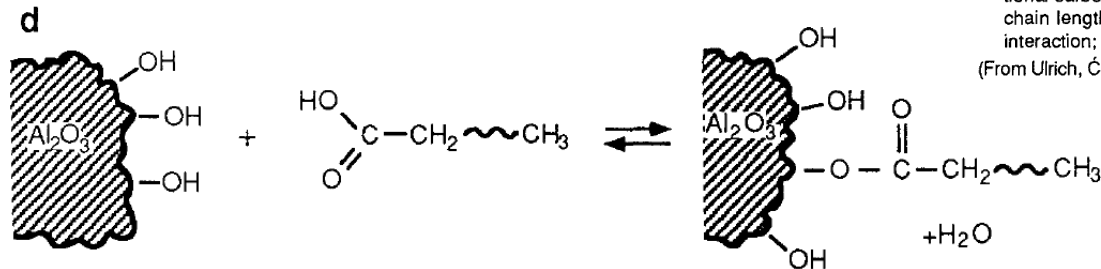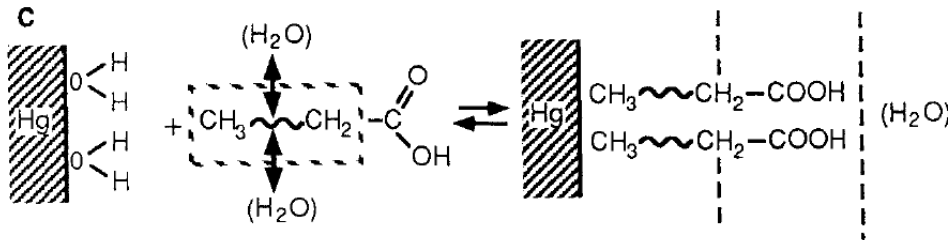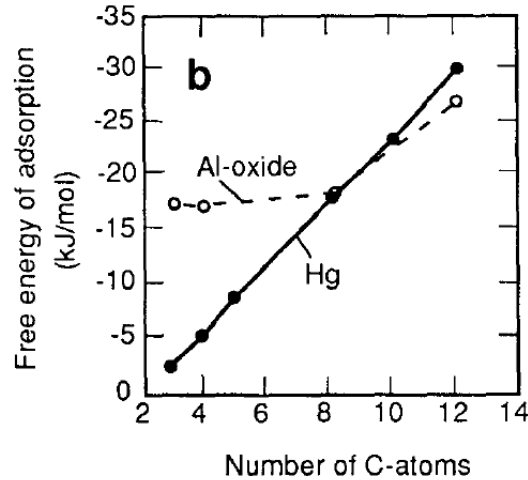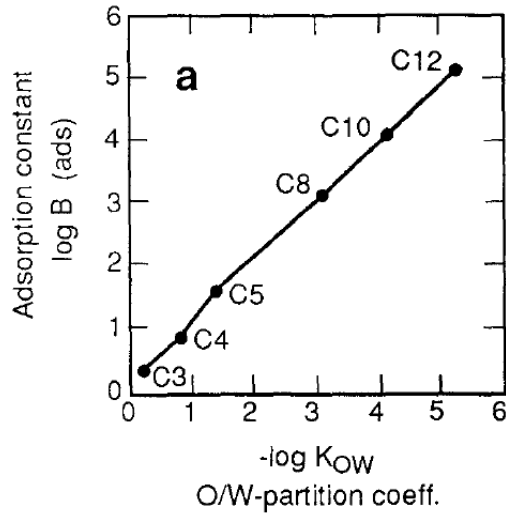
a) Adsorption on the mercury electrode vs hydrophobic properties (as measured by the octanol/water partition coefficient) of adsorbing species at pH 4. B_{ads} is the adsorption constant (M^{-1}) (Eq. 4.13).

b) The free energy of adsorption as a function of the number of carbon atoms (n_c) in the fatty acid, on the mercury electrode and on the alumina.

Adsorption of fatty acids at two model surfaces.

c) At the nonpolar Hg electrode, the hydrophobic interaction between the hydrocarbon chain and the water phase leads to a displacement of the first-row H_2O molecules and to adsorption at the Hg surface.

d) At the polar aluminum oxide surface, the fatty acid molecules become adsorbed because the functional carboxylic groups exchange for the surface OH groups (ligand exchange). At sufficiently high chain length, adsorption due to the hydrophobic expulsion outweighs adsorption by coordinative interaction; the orientation of the fatty acid molecules may revert.
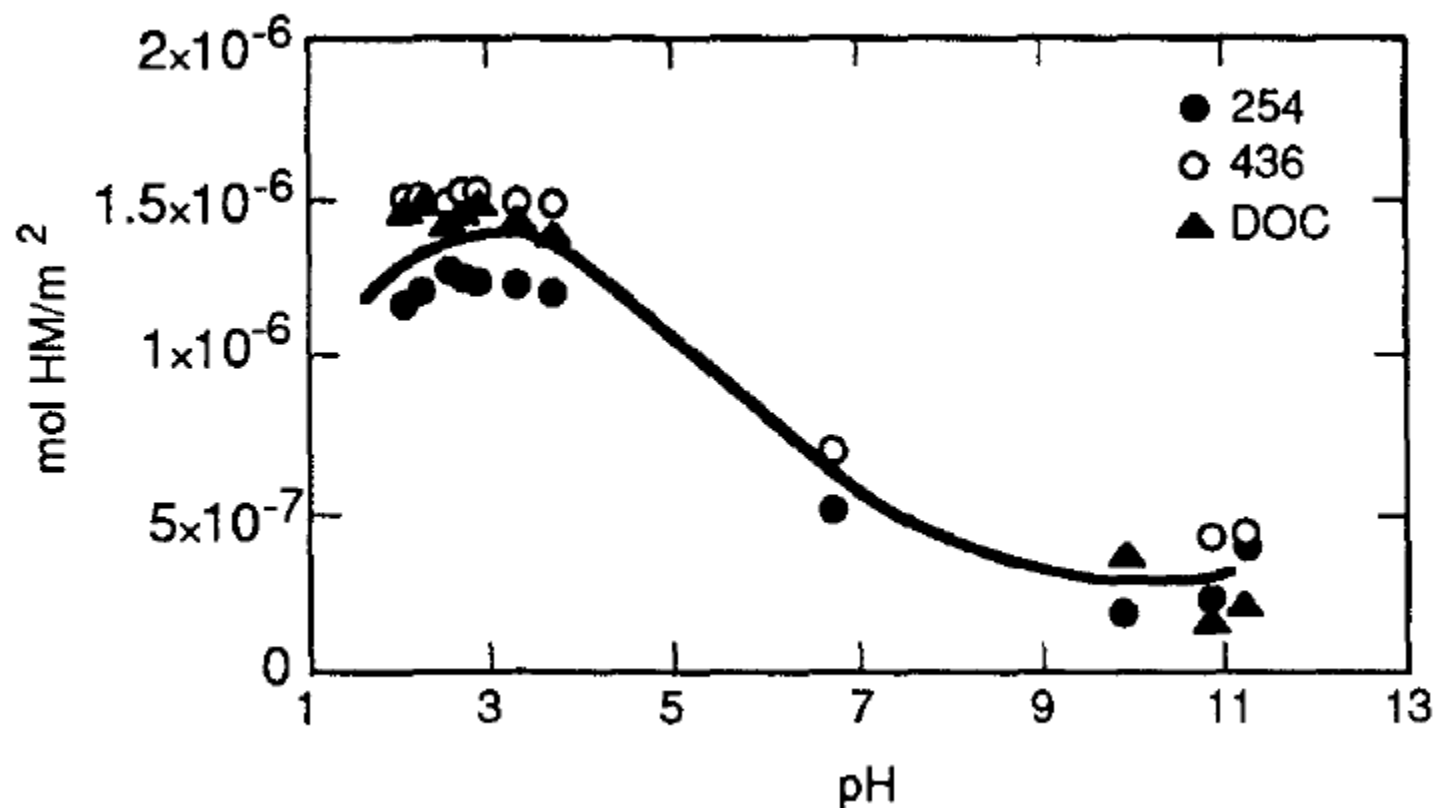
(From Ulrich, Ćosović and Stumm, 1988)

Huminové kyseliny
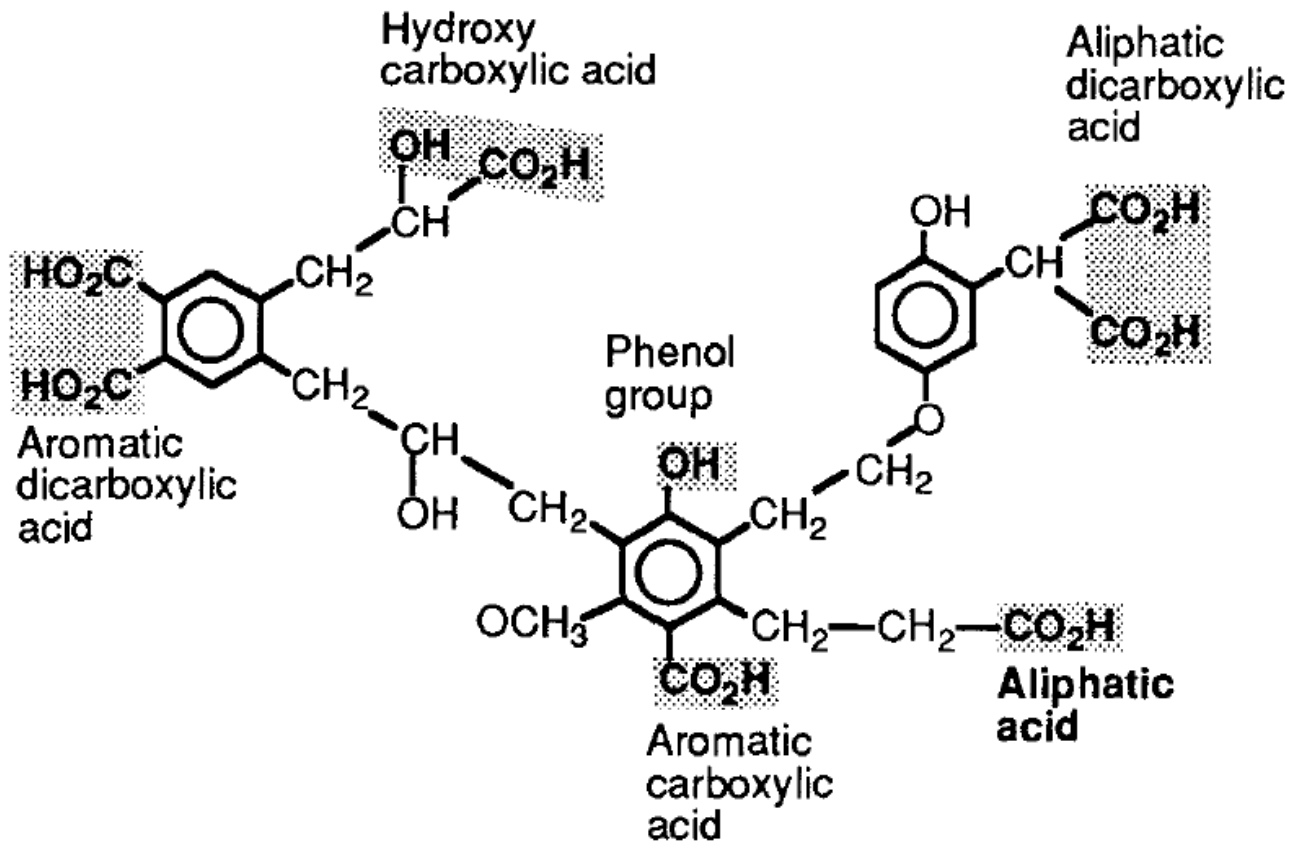
Different types of hydroxy and carboxylic groups present in natural organic substances, exemplified in a hypothetical complex polymer from Thurman (1985).

Huminové kyseliny

Adsorption isotherm of (Aldrich) humic acid (HM) on δ-Al_2O_3 as a function of pH. Extent of adsorption was determined both by measurements of light absorption at 254 and 436 nm, respectively and by measurements of dissolved organic carbon (DOC) of the residual HM in solution (original concentration = 25 mg per liter).

(From M. Ochs, 1991)

Sorpce na organický C

$$K_P = \frac{\text{mol sorbate / mass of solid}}{\text{mol of solute / volume of solution}} \left[\frac{\ell}{kg}\right] \text{ or } \left[\frac{10^{-3} m^3}{kg}\right]$$

partition coefficient K_P

$$K_{OW} = [A_{oct}] / [A_{aq}]$$

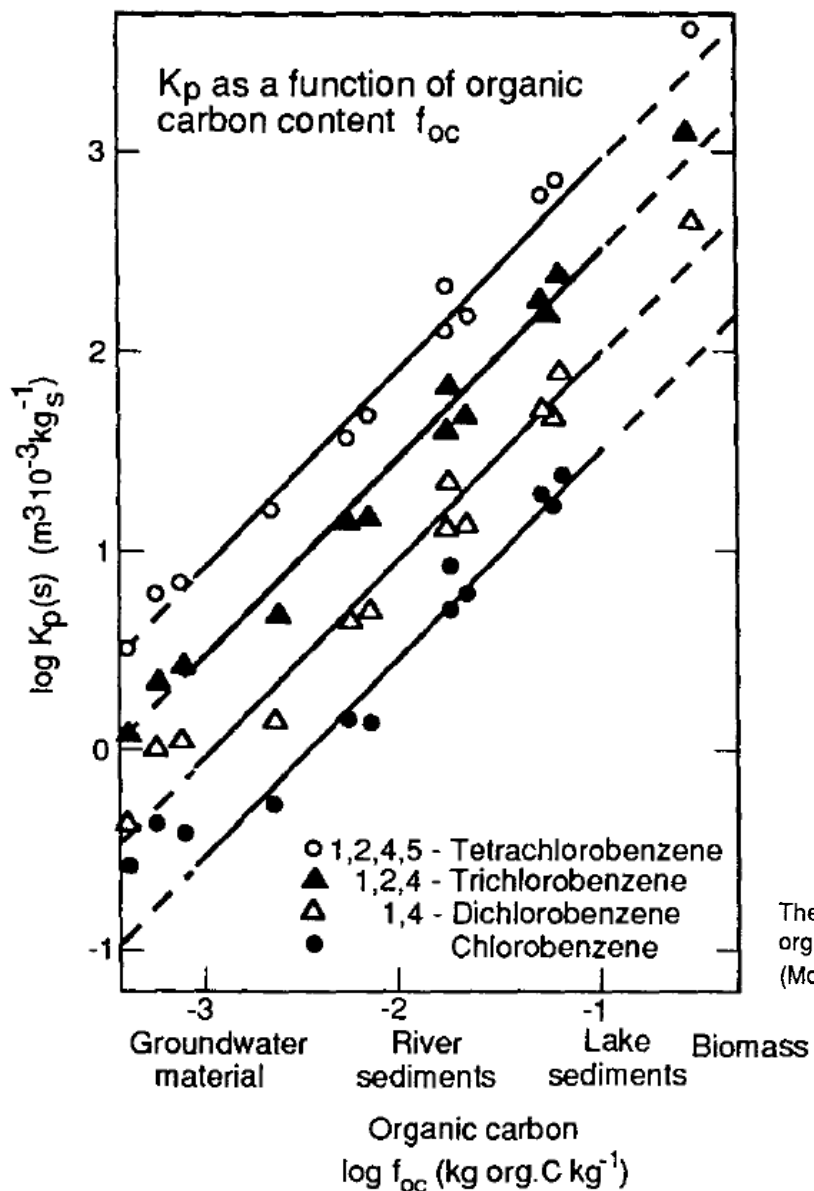octanol-water partition coefficient

$$K_P = bf_{OC} (K_{OW})^a$$
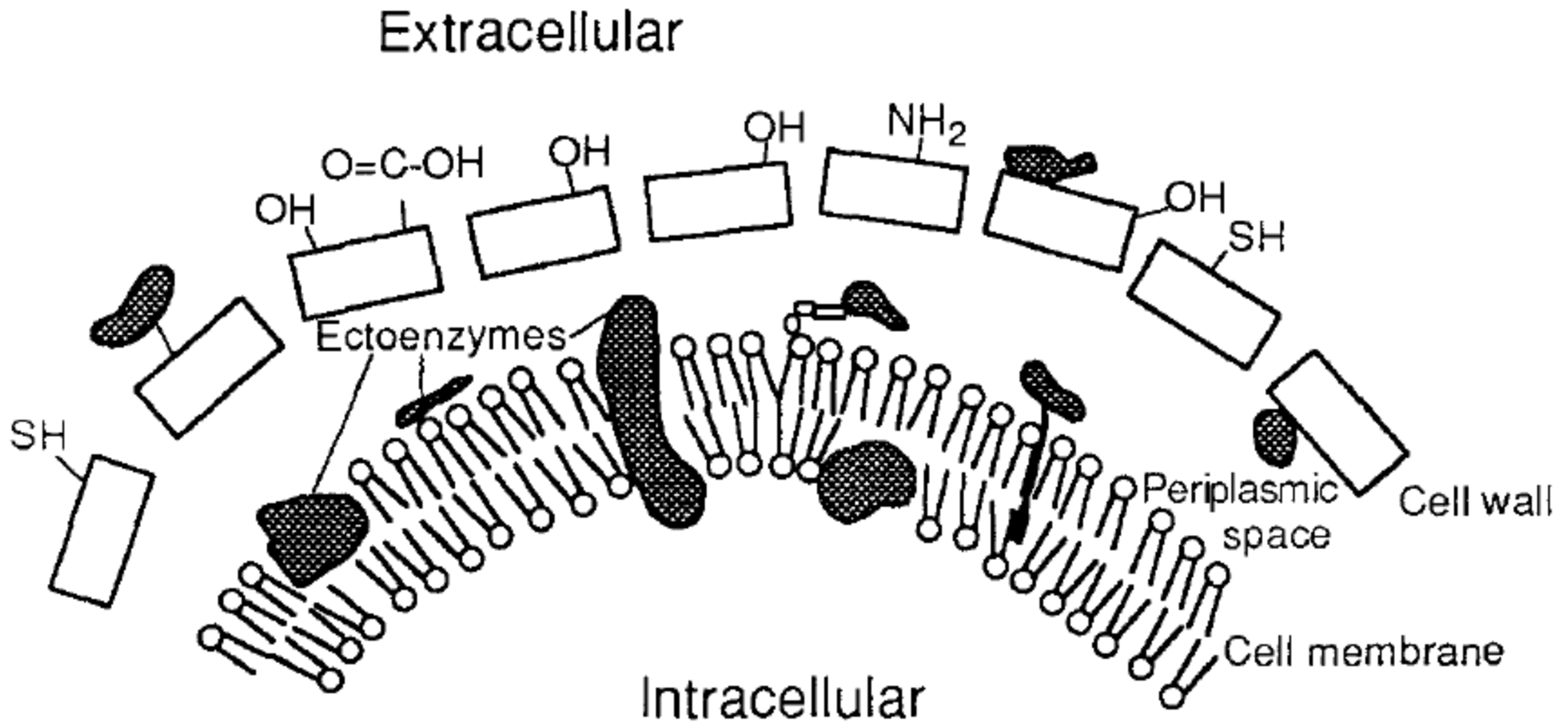
$$\log K_{OW} = a - d \log S_W$$

K_{OW} is inversely related to water solubility, S_W

Sorpce na organický C

The distribution of organic substances between water and representative solid materials of different organic carbon content, f_{oc}.
(Modified from Schwarzenbach and Westall, 1980)

Sorpce na organický C

A conceptualized cross section through a portion of the cell wall (rectangles), periplasmic space, and cell membrane (lipid bilayer with polar head groups in contact with cytoplasm and external medium, and hydrophobic hydrocarbon chains) of an aquatic microbe. Reactive functional groups (–SH, –COOH, –OH, –NH$_2$) present on the wall consitutents and extracellular enzymes (depicted as shaded objects) attached by various means promote and catalyze chemical reactions extracellularly.

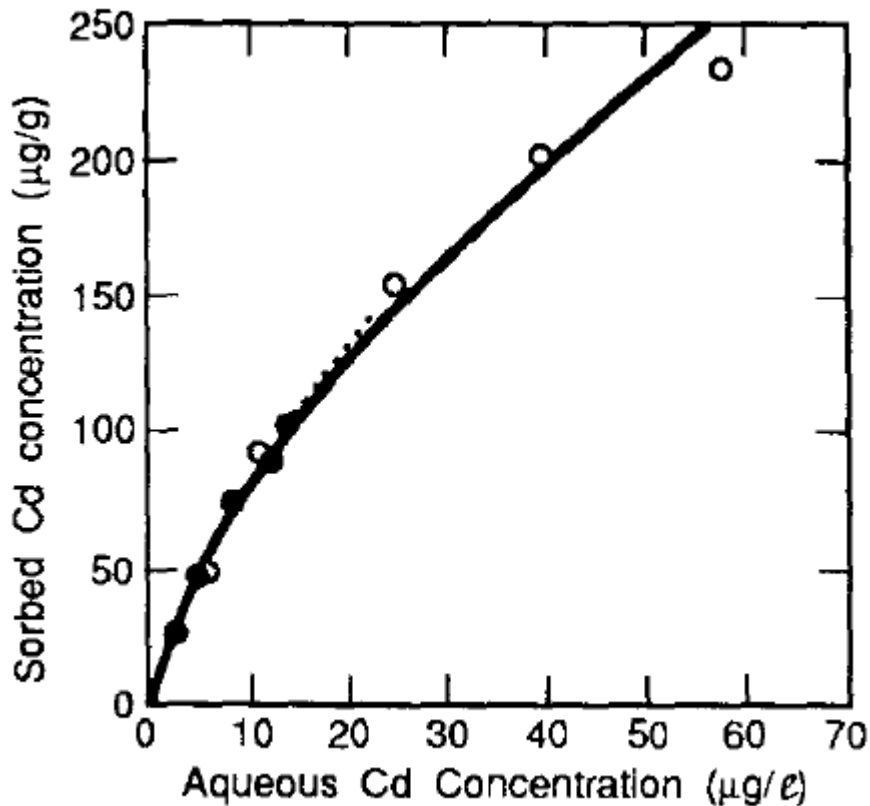(Modified from Price and Morel, 1990)

Reversibilita sorpce

$$S + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} SA$$
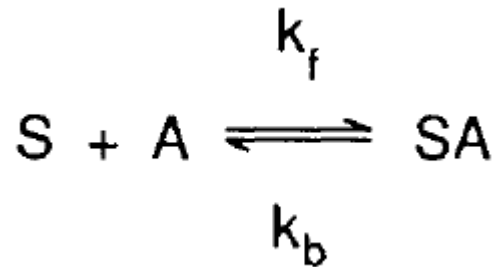
$$\frac{d\,[SA]}{dt} = k_f\,[S]\,[A] - k_b\,[SA]$$

$$\frac{[SA]}{[S]\,[A]} = \frac{k_f}{k_b} = K = K_{ads} \qquad d\,[SA]\,/\,dt = 0$$

Reversibilita sorpce

Adsorption-desorption equilibrium for Cd(II) on illite after 54 days of equilibration. The solution contains HCO_3^-, 2×10^{-3} M Ca^{2+} and has a pH = 7.8. Freundlich isotherms based on separate adsorption (●) and desorption (○) data are given from Comans (1987).

Iontová výměna

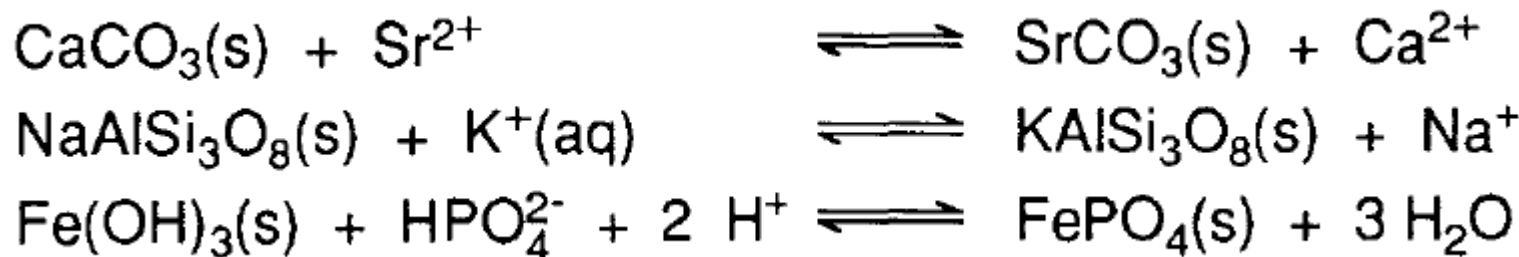$$CaCO_3(s) + Sr^{2+} \rightleftharpoons SrCO_3(s) + Ca^{2+}$$

$$NaAlSi_3O_8(s) + K^+(aq) \rightleftharpoons KAlSi_3O_8(s) + Na^+$$

$$Fe(OH)_3(s) + HPO_4^{2-} + 2\,H^+ \rightleftharpoons FePO_4(s) + 3\,H_2O$$

Table 4.5   Ion Exchange of Clays with Solutions of $CaCl_2$ and KCl of Equal Equivalent Concentration[a]

| | | Ca^{2+} / K^+ Ratios on clay | | | |
| Clay | Exchange capacity (meq g^{-1}) | Concentration of solution $2\,[Ca^{2+}] + [K^+]$ (meq liter^{-1}) | | | |
		100	10	1	0.1
Kaolinite	0.023	–	1.8	5.0	11.1
Illite	0.162	1.1	3.4	8.1	12.3
Montmorillonite	0.810	1.5	–	22.1	38.8

[a] From L. Wiklander, *Chemistry of the Soil*, F.E. Bear, Ed., 2nd ed., Van Nostrand Reinhold, New York, 1964.

Iontová výměna
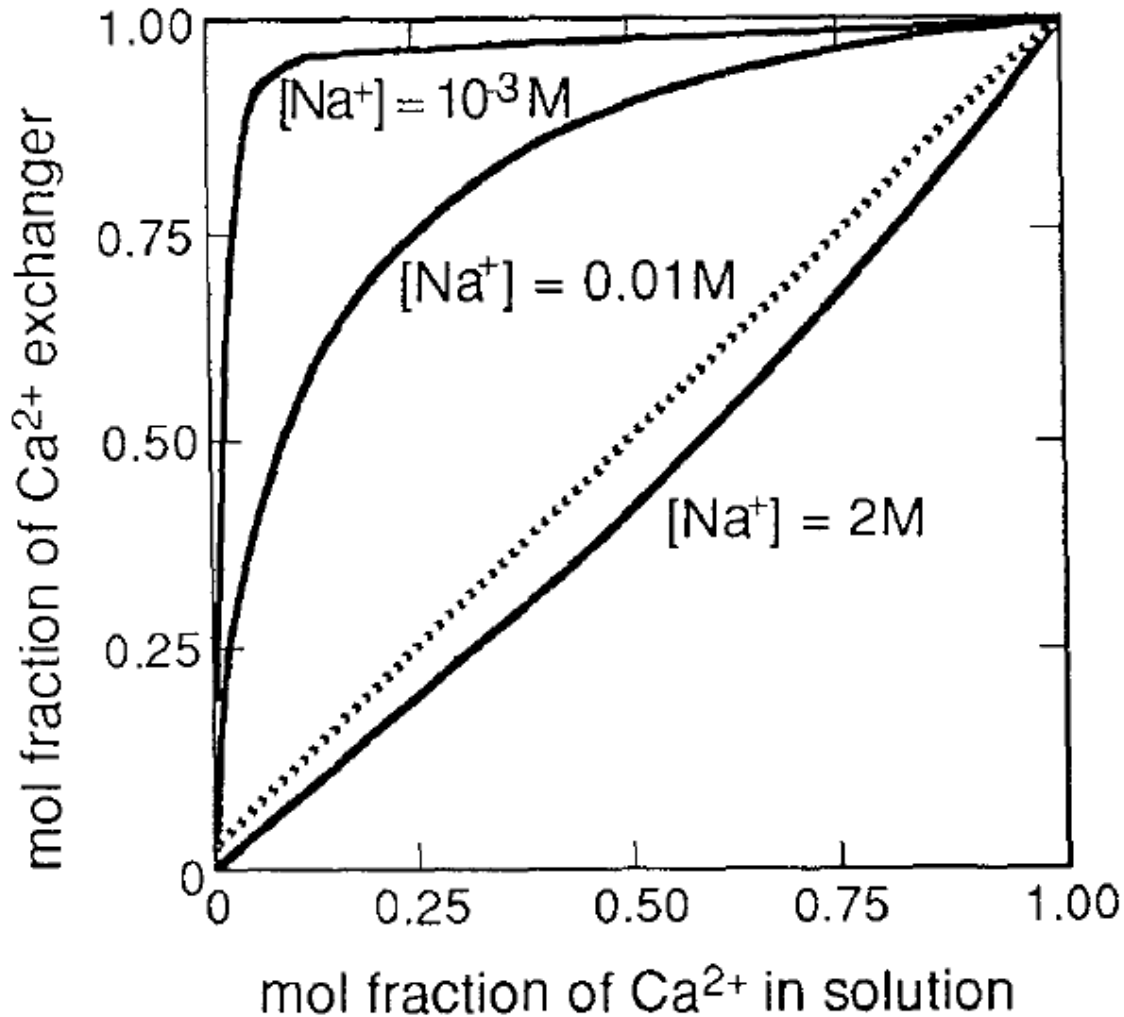
Typical exchange isotherms for the reactions $Ca^{2+} + 2\{Na^+ R^-\} \rightleftharpoons \{Ca^{2+} R_2^{2-}\} + 2 Na^+$. In dilute solutions the exchanger shows a strong preference for Ca^{2+} over Na^+. This selectivity decreases with increasing ion concentration. The 45° line represents the isotherm with no selectivity.