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THE DISTRIBUTION COEFFICIENT CONCEPT AND
ASPECTS ON EXPERIMENTAL DISTRIBUTION STUDIES

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SUMMARY

Aspects on the distribution coefficient concept, sorption mechanisms and measurements of sorption phenomena are given.

(This is an <u>introductory summary</u>; a full revised Technical Report with the same title will be issued in late 1983).

CONTENT

SORPTION PROCESSES

Various kinds of processes can be recognized which would remove a dissolved substance from an aqueous phase, either by adsorption or by other mechanisms. Some basic processes, somewhat arbitrarily defined, are summarized below.

1. Physical adsorption

Physical adsorption will occur due to non-specific forces of attraction involving the entire electron shells of the solute and the adsorbent. These forces, which are denoted as van der Waals forces, have a very short range. The process is rapid and reversible and does not require any activation energy. It is fairly independent of the chemical nature of the adsorbent. There is usually no specific adsorption site. Several consecutive layers of adsorbed particles can be developed, and the selectivity is poor. Thus, the process is fairly independent of ionic strength and even solute concentrations at low total concentrations. However, the composition of the aqueous phase in terms of pH and concentrations of complexing agents would be decisive for the sorption process, since these parameters would determine the chemical state of the solute in the aqueous phase.

2. Electrostatic adsorption

Electrostatic adsorption (ion exchange) will occur due to the action of attractive coulombic forces between electrically charged solute species and oppositely charged sorbent surfaces. The range is much greater than for physical adsorption processes. The process is usually rapid and largely reversible and may require some activation energy. It is strongly dependent of the chemical nature of the sorbent, and specific adsorption sites may sometimes be recognized.

Charge and size restrictions can result in a certain selectivity in some systems. The process is generally highly dependent on the ionic strength of the aqueous phase as well as of the chemical state and concentration of the solute.

Ion exchange reactions can take place between non-complexed cations (e.g. M^+, M^{2+}) in the solute and ions having the same charge forming part of the surface crystal layer of the sorbent, or which are present in the outer

part of the electric double layer existing on most sorbent surfaces. Thus, ion exchange reactions can be considered as isomorphous ion replacements, specific of the solid sorbent or as non-specific adsorption processes that can occur on most solid sorbents, depending on magnitude and polarity of the total charge of the electric double layer.

The electrostatic adsorption processes may frequently be considered as replacement reactions involving displacement of hydrogen ions from non-dissociated surface groups of the sorbent. Thus, ion exchange reactions may be observed on solids which have a very low or negligible charge or even a charge of the same sign as the adsorbed ion, according to this concept.

3. Chemisorption

Chemisorption will occur due to the actions of specific chemical forces, and can be considered as a chemical bonding involving a sharing or possibly transfer of electrons. Energies associated with chemisorption are large. The process may be slow and partly irreversible, and highly selective. A large activation energy may be required, leading to a pronounced temperature dependence. The reaction is insensitive to the ion strength but highly dependent of the solute concentration, often with a characteristic saturability, related to the formation of a single adsorption layer.

4. Precipitation, coprecipitation and substitution

The removal of dissolved material due to precipitation, because the solubility product is reached should be recognized as one mechanism that would reduce the total solute concentration in solution. Many of the long-lived elements in spent nuclear fuel would form sparingly soluble complexes with OH^-, CO_3^{2-}, F^- and PO_4^{3-}, e.g. the actinides in their lower oxidation states. Thus, due to changes in pH or the redox potential the solubility product may be exceeded, even at total solute concentrations as low as 10^{-8}-10^{-9} M in some cases.

Coprecipitation is generally defined as the precipitation of a solute, at concentrations below the solubility product of any sparingly soluble compound, in conjunction with the precipitation of some other macro component. The microcomponent is incorporated or attached to the solid precipitate either by the formation of isomorphous mixed crystals or by the adsorption on the precipitate or occlusion.

Formation of mixed crystals due to substitution reactions, replacements of ions in the lattice of a crystalline compound or interstitial incorporation of the microcomponent into the lattice are related phenomena.

5. Differentiation of sorption mechanisms

It is evident, that the sorption of a trace component would be the result of several different processes. It is rarely possible to unambiguously differentiate the various mechanisms outlined above since many mechanisms would be involved simultaneously. Generally, the probability of physical adsorption and chemisorption increases with increasing degree of hydrolysis of e.g. a trace metal, whereas the probability of ion exchange decrease. Still there is always an element of electrostatic interaction in almost any sorption process.

The role of hydroxy groups, both on the solid and on the solute species, make a distinction between physical adsorption, electrostatic adsorption and chemisorption somewhat arbitrary or superficial. In some systems the hydrogen ion displacement concept appears to give a better explanation.of observed phenomena, while the electric double layer concept would be more suitable under other conditions. The increasing tendency for sorption with increasing degree of hydrolysis, e.g. on solids with very low ion exchange capacity, may possibly be due to lower hydration of the hydrolyzed ions, causing an enhanced ion uptake or exchange. An increased degree of hydrolysis would, however, stimulate the action of van der Waals forces or possibly permit the formation of hydrogen bonds between the hydrolyzed solute and electronegative atoms on the surface of the solid.

As a conclusion, it can be stated that

o   the over-all sorption of a solute on a sorbent can rarely be defined in terms of one single well-defined mechanism,

o   to strictly differentiate between various mechanisms is generally difficult, or even impossible,

o   a gradual change from one predominant sorption mechanism in a system to another one is feasible, e.g. by the change of pH,

o   there are a large number of physical and chemical parameters that would have significant influence on the over-all sorption of e.g. a trace element.

FACTORS INFLUENCING TRACE ELEMENT SORPTION

Some major parameters that would significantly affect the sorption of trace element, e.g. in conjunction with geologic storage of spent nuclear fuel are summarized below.

1. Effects of pH

The pH of the aqueous phase is one of the principal parameters affecting sorption, both due to the effect on the properties of the sorbent (surface charge, surface alterations) and the solute (chemical state, hydrolysis).

The adsorption of cations at trace concentrations is generally small at low pH, but increases with increasing pH above a certain level. If the adsorption increase were due only to the decreasing H^+-concentration, the following reaction would be valid:

$$n\overline{H^+} + M^{z+} = \overline{M^{z+}} + nH^+ \qquad (1)$$

where species adsorbed on the solid are denoted by bars. This exchange reaction can be defined by

$$k_{ex} = \frac{[\overline{M^{z+}}][H^+]^n}{[M^{z+}][\overline{H^+}]^n} = K_{ex}/f \qquad (2)$$

where f is the activity coefficient ratio and K_{ex} the corresponding thermodynamic constant.

Assuming high exchange capacity (C) of the solid and a negligible change of the composition due to the exchange with M^{z+} the following relations would be valid

$$C = [\overline{H^+}] + z[\overline{M^{z+}}] \approx [\overline{H^+}] \qquad (3)$$

$$k_{ex} = \frac{[\overline{M^{z+}}]}{[M^{z+}]} \cdot \frac{[H^+]^n}{C^n} = D \cdot \frac{[H^+]^n}{C^n} \qquad (4)$$

where D is the distribution ratio, $[\overline{M^{z+}}]/[M^{z+}]$.

Thus $\log D = npH + n\log C + \log k_{ex}$ (5)

or $\log D = npH + const.$ (6)

assuming constant C and f. At low pH the following pH-dependence would be expected:

o   log D vs pH would have a slope of n, which is equal to or proportional to Z

o   the increase in sorption would shift towards lower pH if n or k_{ex} increases, i.e. with the charge and/or the affinity for the adsorbent.

However, eqn. (6) is rarely fulfilled other than qualitatively because

o   C is not high enough,

o   C is not pH-independent (variation of the surface charge),

o   f is not pH-independent,

o   competition with other cations,

o   the trace element is hydrolyzed above a certain pH.

A steep increase in the over-all sorption of cations is usually observed when pH increases up to and above the level where a significant hydrolysis starts. The state of the trace element changes with pH, and the exchange reaction can not be expressed in any simple form similar to eqn. (3). Moreover, pH in the immediate proximity of a charged surface can differ substantially from pH in the bulk of the solution, and different solute species may exist in the solution layer adjacent to the surface and in the bulk. This phenomenon could be expressed as an enhanced degree of hydrolysis on the surface and the net result would be equal to a precipitation process in the presence of the sorbent surface. The adsorption of hydrolyzed species usually reaches a maximum in the pH-range where neutral hydroxides would dominate, which indicate that the sorption can hardly be considered an ion exchange process. The formation of anionic hydroxy species at still higher pH would usually lead to a reduced sorption.

The theories concerning the sorption of hydrolyzed species on solid sorbents and the various models describing reactions in the double layer, surface reactions etc. are numerous, and it is not within the scope of this report to discuss these in detail. It can be concluded, that it is possible to roughly predict the pH where sorption starts, reaches a maximum and decreases. Calculations of the absolute magnitude of the distribution of a hydrolyzed species between a solid and an aqueous phase can rarely be accomplished without empirical data. Some limits are, however, set by solubility constants.

TERMINOLOGY

The choice of terms selected for sorption processes and the quantitative
description of laboratory results is somewhat arbitrary in the literature.
The very wide variations in the choice of terminology etc adopted by
various authors make it desirable to establish general recommendations in
order to achieve consistency in nomenclature, symbols and definitions.

The fundamental processes in sorption experiments, i.e. the uptake of a
solute from an aqueous phase to a solid phase or the distribution of a
solute between a solid and an aqueous phase, are very similar to liquid-
liquid distribution processes, where a recommended nomenclature has been
adopted. (Liquid-liquid distribution = the process of transferring a
dissolved substance from one liquid phase to another immiscible or partial-
ly miscible liquid phase in contact with it). The following definitions and
terminology are based on the nomenclature for liquid-liquid distribution
recommended by IUPAC:

Distribution   —   the apportionment of a solute between
                                        two phases

Partition   —   synonum for distribution; often but not
                                        invariably applied to the distribution
                                        of one single definite species.

Comment: The two phases are denoted phase I and phase II, corresponding
         to the solid sorbent and the aqueous phase, respectively.

Distribution ratio, D   —   the ratio of the total analytical con-
(Synonum: centration of a substance in phase I
distribution coefficient)   (regardless of its chemical form) to
                                        its total analytical concentration in
                                        phase II.

$$D_A = \Sigma[A]_I / \Sigma[A]_{II}$$

Distribution constant, K_D —   the ratio of the concentration of a
(Synonum: substance in a single definite form in
partition coefficient)   phase I to its concentration in the
                                        same form in phase II at equilibrium.

$$(K_D)_A = [A]_I/[A]_{II}$$

Partition constant, K_D^O —   the ratio of the activity of a given species in phase I to its activity in phase II with which it is in equilibrium.

$$(K_D^O)_A = \{A\}_I/\{A\}_{II}$$

Comment: The distribution ratio (D) is an experimental parameter whose value varies with experimental conditions, and its value does not necessarily imply that partition equilibrium between the phases has been achieved. The ratio should normally be expressed as concentration in phase I divided by that in phase II.

The distribution constant (K_D) is constant for one particular species under specified conditions only.

If the pure phases are taken as standard states, $K_D \longrightarrow K_D^O$ as the total concentrations of dissolved materials decreases.

Distribution isotherm   —   the relationship between the concen-
(Synonym: .   trations of a solute in phase I and the
sorption isotherm)   corresponding concentration of the same solute in phase II at equilibrium with it at some specified temperature.

Separation factor, $\alpha_{A,B}$ —   the ratio of the respective distribution ratios (D) of two solutes measured under the same conditions.

$$\alpha_{A,B} = (D_A)/(D_B)$$

Loading capacity   —   the maximum concentration of a solute
(Synonymus: in phase I under certain specified
saturation capacity,   conditions.
maximum loading).

BATCH MEASUREMENT TECHNIQUE

The technique discribed has been developed since K_d measurements started at the department in 1976. It has been used for rock (granite, gneiss, diabase etc.), pure minerals (over 30 different), clays, artificially prepared in-organic solids and concrete. In most cases with artificial groundwater, but also with brine, artificial seawater and concrete pore water solutions. A number of species have been studied.

1. <u>Experimental</u>

a. Crush and sieve the solid into desired fractions. Wet sieving is recom-mended for very small fractions (<150 μm).

b. Weigh desired amount of solid in clean vial (a quality that can be centrifuged).

c. Add liquid phase, note weight of vial and solid and liquid.

d. Shake vial to mix the phases, let stand to separate. If phase separation is slow, centrifuge.

e. Remove as much as possible of water, with solid intact. Add new water.

f. Shake to equilibrate solid-liquid (1d - 1w).

g. Centrifuge and repeat e.

h. Add species to be studied in small (but exact) volume of water.

i. Add species to "reference" vials with water but no solid.

j. Shake until sampling time.

k. Centrifuge - take sample. Compare with reference.

l. If possible, put sample back after measurement.

Repeat j. - l. until equilibrium is considered to be reached.

2. Comments to "1. Experimental"

a. Fractions used: 45-63 um, 63-90 um, 90-125 um, 125-250 um. Clays have not been fractionated.

b. 50 ml glass bottles and 25 ml polyetene or polypropene vials used. Amount of solid used 0.2, 0.5, 1.0 g.

c. Amount of liquid used 45 ml or 20 ml.

d.-e. This is done to remove fines and particles that may form pseudo-colloids. A good wet-sieving could make this unnecessary.

h. The species may be added in the last water change. If radionuclides are used, adding of a small amount to each vial may be practical.

i. The use of reference samples corrects for sorption on vial walls and for radioactive decay of the species during measurement. Precipitation of the species with a component in the water will however give results that are difficult to interprete.

DISCUSSION OF MEASURED DATA. FACTORS THAT INFLUENCE K_d.

1. Time dependence

For cesium and strontium the sorption on four different rocks and a large number of minerals has been investigated. For both nuclides a fast rise in "K_d" is observed during the first 24h, the value has increased a little after a week, while it is almost constant after three months. For most systems a fairly stable K_d-value is obtained in one week.

2. Temperature dependence

The temperature dependence of the sorption has been studied for clay and granite with a number of sorbing species. The influence of a temperature change from 25 to 65°C was minor.

3. Liquid/solid ratio

The influence of the liquid/solid ratio has been studied for Cs and Sr with a change in this ratio of a factor 100. This has only given minor changes in K_d.

4. Concentration of sorbing species

The concentration dependence has been studied for Cs over a range from 10^{-1} to 10^{-7} M for granite, orthoclase and hornblende. In all cases a concentration dependence that can be fitted into a Freundlich-type equation, i.e. $g = A \cdot c^{1/n}$, where g = concentration in solid phase at equilibrium, A and n are constants. The value of n ranges between 1.1 - 1.8. The values of A and n changes with time, probably due to the change in sorption mechanism from surface to volume reaction and the alteration of the solid phase.

5. pH-dependence

For all systems studied, K_d has shown to be pH-dependent. This is due to the influence the pH has on ion exchange processes and on hydrolysis.

CONCLUSIONS

To obtain reproducible "K_d" values the most important variables to keep controlled (and to specify when reporting data) are pH, concentration of the studied species and for redox-sensitive elements the redox potential.