Abstract

Sorption of hydrophobic organic compounds (HOCs) to hydrophilic inorganic surfaces in aqueous systems is an important process, because HOCs are common contaminants and the sorption controls their concentration and rate of transport in the environment. Furthermore, in environmental chemistry and analysis, sorption of HOCs to inorganic surfaces, in particular to untreated (uncoated) glass surfaces, causes the loss of analyte and then confuses subsequent data interpretation. For a better understanding of the process and developing a predictive tool, five selected polycyclic aromatic hydrocarbons (PAHs, naphthalene, fluorene, phenanthrene, anthracene and pyrene) and four pairs of n- and cycloalkanes (C5 to C8) have been used as chemical probes. Their sorption behaviors to different hydrophilic inorganic surfaces (e.g. borosilicate glass, silica gel, aluminum oxide and titanium oxide) were systematically investigated.

From a practical point of view, glassware is the commonly used container in analysis. Therefore, sorption coefficients (K_d) of five selected PAHs to the frequently used laboratorial glass surfaces (borosilicate glass) were firstly investigated by using column chromatography. The validation of column method was carried out by comparing the data measured in column chromatography to that obtained in batch experiments. After validation, the influence of environmental factors on K_d, such as ionic strength, pH value, co-solvent, coated surface and temperature, were comprehensively studied. Our data revealed that (1) mass loss caused by sorption on glass walls strongly depends on the ratio of solution volume to contacted surface area (V/S) and (2) use of cosolvent or silane coated glass surfaces is often not sufficient to suppress sorption for large PAHs.

Based on the successful application of column chromatography in glass surface studies, this method was extended to use in the further investigation of sorption to other mineral surfaces (e.g. silica gel, aluminum oxide and titanium oxide). Sorption coefficients (K_d) were determined under different environmental conditions (i.e. ionic strength, pH value and temperature). In particular, the influence of particle size and pore size, which played an important role for the extent of sorption for porous sorbent, was focused on. In this study, the most important observation is that for porous material, not all the N_2-BET determined surface area was effective for sorption in water-mineral systems.

Generally, a linear relationship between log K_d and the corresponding water solubility of the subcooled liquid (log S_w) of the investigated PAHs was found on all investigated inorganic surfaces. It provides a tool to predict sorption behavior of other PAHs to inorganic surfaces. The determined sorption coefficients (K_d) at various environmental conditions on all investigated inorganic surfaces showed that the ionic strength, solution pH and temperature had no significant effect on the sorption process, which indicates that nonspecific interactions (such as van der Waal's forces) dominate the sorption process.

Two sorption modes, adsorption and absorption, are currently considered as sorption mechanisms in sorbent-water systems. The ratio of the sorbent-air/sorbent-water distribution coefficients of n-alkanes to that of cycloalkanes with the same number of carbon atoms (K_n/K_c) was recently demonstrated to be indicative of the mode of sorption ($K_n/K_c < 1$ indicates adsorption, while ~ 1 indicates absorption). Following this approach, four pairs of n- and cycloalkanes (C5 to C8) were investigated with regard to sorption to silica and aluminum oxide surfaces by using batch experiments. After calculating the ratio of K_n/K_c the implications for the sorption mode have been discussed.

To measure in-situ the concentration gradient formed near to inorganic surfaces, a highly spatially resolved electrochemical method, scanning electrochemical microscopy (SECM), was applied. The concentration gradient was represented through an indirect method, measuring the change of conductivity in ionic solutions. The conductivity was observed to decrease significantly with increasing distance between 1 to 300 µm. However, a full explanation of this phenomenon needs further investigations.