

**COMPARISON OF ADSORPTION BEHAVIOR OF FATTY ACIDS
ON MERCURY DROP ELECTRODE AND ON ALUMINUM OXIDE**

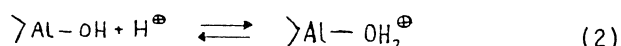
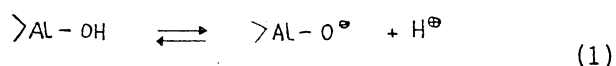
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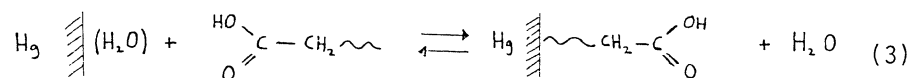
Solute adsorption on interfaces in aquatic systems is of great importance in understanding the fate of reactive solutes and the factors that regulate their composition. The net energy of interaction of the surface with the adsorbate may result from various chemical and physical forces.

Data will be presented on a case study on the adsorption of fatty acids on two model surfaces: (1) the mercury electrode and (2) δ -Al₂O₃ colloids. The Hg electrode has a uniform, reproducibly renewable and smooth surface; its surface potential can be adjusted with a potentiometer. The extent of adsorption is accompanied by a change in the capacity of the double layer at the electrode surface and can be determined by measuring the capacity current e.g. by alternating current polarography. δ -Al₂O₃ may serve as a model of a polar surface, representative of many suspended particles encountered in natural waters. Its surface potential (or surface charge) depends on the pH of the solution, primarily on the extent of surface protonation of the surface groups



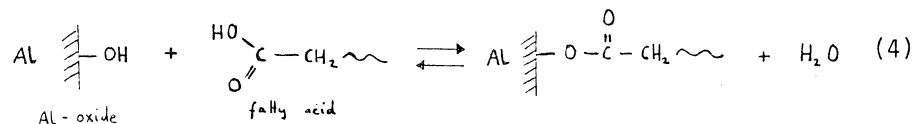
Colloidal δ -Al₂O₃ with a high specific surface area (100 m² g⁻¹) permits sensitive determinations of solute adsorption, e.g. with C-14 labeled substances.

For the adsorption of fatty acids on Hg, the affinity of the surface for the fatty acids plays a subordinate role in comparison to the (negative) affinity of the aqueous solvent; i.e. the fatty acids become displaced from the water. Because of the hydrophobic effect, these substances tend to reduce the contact with water and become adsorbed at interfaces.



This adsorption equilibrium (3) increases with increasing chain length, i.e. increasing hydrophobicity of the fatty acid.

At the polar Al₂O₃ surface, however, the carboxylic group is capable to undergo a coordination reaction with the surface hydroxogroup (ligand exchange).



This surface complex formation equilibrium obeys the mass law equation

$$\frac{[>\text{AL}-\text{O}-\overset{\text{O}}{\parallel}\text{C}-\text{R}]}{[>\text{ALOH}] [\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{OH}]} = {}^sK \quad (5)$$

Eq. (5) describes the pH dependence of adsorption (maximum tendency is observed near the pK (acidity) value of the fatty acid). Note that the orientation of the molecule in (4) and (5) is opposite to each other. With increasing hydrophobicity of the fatty acid molecule, sK decreases, and above a certain chain length, the hydrophobic effect outweighs the tendency for surface coordination; furthermore, the orientation of the adsorbed fatty acid changes in such a way that the carboxylic group is oriented away from the surface.

Adsorption caused by the hydrophobic effect is impaired if the adsorbate is present as an anion (conjugate base). At higher pH values, hydrophobic association of fatty acid anions to micelles, containing counter ions within their double layers, renders - at higher total concentrations - their adsorption possible.

References

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- STUMM W., KUMMERT R. and SIGG L. (1980) A ligand exchange model for the adsorption of inorganic and organic ligands at hydrous oxide interfaces. *Croatica Chimica Acta* 53, 291-312.