

Electrokinetic potentials of metal oxides in highly concentrated electrolyte solutions

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The sign and the magnitude of the surface charge at the solid/liquid interface define the adsorption behavior of ionic species. The surface charge and the point of zero charge derived from potentiometric titrations are frequently used in adsorption modeling, while the electrokinetic potential is used chiefly in assessment of colloid stability, and very seldom in adsorption modeling. Limited usefulness of electrokinetic data was partially due to the fact that older-generation zetameters produced reliable results only at low electrolyte concentrations. This situation has changed over the recent decade, namely the new-generation instruments are able to measure the zeta potentials at electrolyte concentrations in excess of 1 M. The instruments based on electroacoustic method (electric sonic amplitude ESA or colloid vibration current CVI) are especially useful for this purpose. The problem with electroacoustic method is that electrolyte solutions also produce ESA and CVI signal, which is roughly proportional to salt concentration. At high electrolyte concentrations the ESA and CVI signal of salt is higher than the signal produced by a colloid. This problem is solved by electrolyte background subtraction procedure, which is a standard feature in commercial instruments. Thus, the zeta potentials are obtained as a result of subtraction of two large and almost equal numbers, and the value of the difference is very uncertain.

We suggest an alternative method to solve the problem of electrolyte background correction in electroacoustic measurements. By mixing two salts with common ion (e.g., LiNO₃ and LiCl), which give electroacoustic signals of opposite signs we prepared electrolytes, which give negligibly weak electroacoustic signal. Electroacoustic measurements in such electrolytes do not require electrolyte background correction, even at very high electrolyte concentrations, when the proportions of the components of mixed electrolyte solution are properly adjusted.

The electrokinetic potential of anatase (pristine isoelectric point IEP at pH 6.8) was studied as a function of pH in 1.73 m Li(NO₃,Cl) solution. The zeta potential at high ionic strength was positive at pH up to 10.5. This result confirms the phenomenon reported by several research groups, namely, Li salts at high concentrations induce a shift in the IEP of anatase and of other metal oxides to high pH. Such a shift is due to preferential adsorption of Li, which is observed at high salt concentrations, and which is absent at low concentrations. This preferential adsorption is cation-specific, and the role of the anion is less significant. Very likely, in the studied system there is no IEP at all, and the zeta potential of anatase is positive also beyond the data range.

Aspects of deep biosphere in intertidal sediments from the Wadden Sea (southern North Sea, Germany)

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Holocene intertidal sediments deposited in the backbarrier tidal system south of Spiekeroog Island (Northwest Germany) show similarities to those of the deep biosphere in various aspects. The research group on "BioGeoChemistry of Tidal Flats" sampled sediment cores down to a depth of about six metres by means of a vibration corer and studied them with microbiological and geochemical methods.

Sediment sequences and pore water profiles differ between the study sites. The sediments become anoxic at a few centimetres depth. Sulphate concentrations decrease within the upper several decimetres, but zones with a maximum of pore water sulphate were observed at greater depth. Methane concentrations mirror those of sulphate. Molecular biological analyses and the presence of intact phospholipids containing archaeol and hydroxyarchaeol show the presence of ANME-2 consortia and suggest that anaerobic methane oxidation occurs in the sulphate-methane-transition zones.

Organic matter is present throughout the core, but the content strongly varies with grain size. Mud-rich sediments contain up to 2% total organic carbon. With increasing depth organic matter shows a more terrestrial geochemical signature, becomes more recalcitrant and thus is harder to degrade. Molecular biological analyses of the microbial community composition shows clear depth zonations which reflect the pore water chemistry and organic matter quality and availability. Bacteria in the upper parts of the sediment sequences are dominated by *Proteobacteria*. In deeper layers, *Chloroflexi* and other groups of non-cultivated bacteria often found in the deep biosphere prevail indicating that subsurface tidal flat sediments harbour similar prokaryotic populations as those found in the deeper sub-seafloor biosphere.

Resting, inactive cells present as bacterial endospores represent up to 10% of total bacterial cells. The spore numbers, estimated from the content of dipicolinic acid as a spore-specific biomarker, strongly depend on the type of sediment. Pure cultures obtained from deeper samples were dominated by the spore forming *Firmicutes*.

The results show that various aspects of the deep biosphere can be studied in a relatively easily accessible but complex environment.