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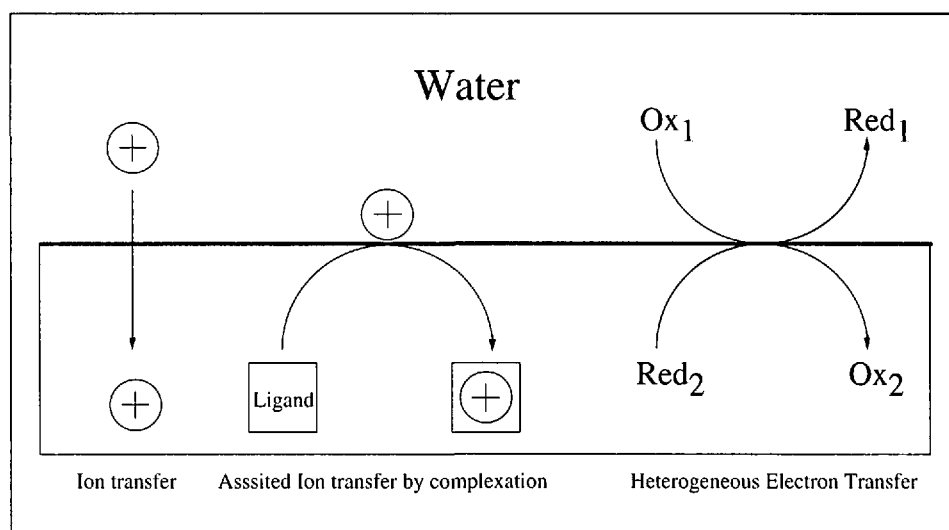
that hydration of the phenyl moiety is a function of the group in the *para* position [2].

Recently, we have studied the acid-base properties of dyes at the air/water interface and showed that even in the absence of specific adsorption the degree of dissociation is reduced due to the higher potential energy of the ions in the top nanometer-thick layer. Also, picosecond time-resolved studies allow to probe the solvent friction in the interfacial layer, and *e.g.* we have measured that in the case of Eosin B the rotational relaxation time decreased from 350 ps in the bulk to 90 ps at the interface showing that both solvation and friction are reduced at the interface.

Ion-transfer reactions are very fast and the strategy followed by the group has been to devise new experimental approaches aimed at increasing the rate of mass transfer to the interface. The gist of the approach is to support micro liquid/liquid interfaces either at the tip of glass micropipettes or in microholes laser micromachined in thin polymer sheets. In both cases, the interfacial area has been reduced to few square micrometers so that the mass transport of the reactants to the interface was controlled by spherical diffusion, and apparent rate constants as high as $1 \text{ cm} \cdot \text{s}^{-1}$ have been measured [3]. It is important to know how ions can exchange their solvation shell upon transfer from one phase to the next. Of course, ion-transfer reactions are multi-step processes which involve co-transport of solvent from the solvation molecules. Ion-transfer reactions are very important to understand not only the passive transport of ions (*e.g.* ionic drugs) across biological membranes but also industrial processes such as solvent extraction.

Assisted ion-transfer reactions involve primarily an ion-molecule complexation in the interfacial layer. These reactions are also extremely fast, and in this case, the mass transfer of both reactants to the interface has to be considered in order to obtain some kinetic information. Using the same methodology as for ion-transfer reactions, we have studied the transfer of potassium ions facilitated by complexation with dibenzo-18-crown-6 [4].

Assisted proton-transfer reactions are a special class of assisted ion transfer, as any base can act as a proton acceptor. We recently studied the partitioning of quinidine at different aqueous pH and we proposed a novel approach of representation named **ionic partition diagrams** [5]. An important conclusion of this work is that for an aqueous pH of 12 and more, the



Figure

more stable form of quinidine is the anion obtained by deprotonation of the alcohol group, this anion being in the organic phase. This has important consequence for some mechanisms in phase-transfer catalysis [6].

The understanding of electron-transfer reactions at a simple molecular interface is of prime importance to understand biological **heterogeneous electron-transfer reactions** taking place in biological lipid membranes. Research at the Laboratoire d'Electrochimie in the last couple of years has focused on photo-induced electron transfer, and we endeavoured for this purpose to develop new experimental methodologies such as time-resolved laser-induced fluorescence in the evanescent wave created by Total Internal Reflection [7]. For example, we have studied the quenching of aqueous excited Eu^{III} in the evanescent wave obtained by total reflection of a nanosecond laser beam at a water/1,2-dichloroethane interface, in the presence of an organic quencher located in the adjacent phase. The interfacial quenching yielded a rate constant of *ca.* $0.1 \text{ cm} \cdot \text{s}^{-1}$. We also studied the interfacial quenching of a series of porphyrins monitoring by transient absorption the disappearance of the reactants.

The Laboratoire d'Electrochimie has been very active to develop applications from the hereabove described fundamental investigations. In particular, we have developed a novel electroanalytical method based on the amperometric monitoring of ion concentrations using ion-transfer reactions. This work supported by the **Priority Programme on Biotechnology** has led to the design of new biosensors, for example for urea based on NH_4^+ determination after reaction with urease [8]. The group also has a long-standing collabora-

tion with *Metrohm* (Herisau, AR) for the development of new electroanalytical instruments.

Another activity of the Laboratoire d'Electrochimie is the design and fabrication of micromachined electrochemical systems. In particular, we have developed for Electricité de France a new type of electrolysis cell with an interdigitated coplanar assembly of anode and cathode. The array fabricated using multilayer screen printing techniques has a lateral resolution of 50μ and is designed in the case of sea water electrolysis to produce 160 kg of chlorine per min per m^2 of sea water. This approach has also been used for organic electrosynthesis, *e.g.* for the methoxylation of furane [9].

Recently, we devoted a lot of attention to the micromachining of microcapillaries in plastics for the design of disposable μ -TAS systems.

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Laboratoire de Chimie Physique des Polymères et Membranes

Prof. Dr. Horst Vogel*

The institute concentrates on three major research topics ranging from fundamental studies on the **structure and dynamics of membrane proteins** to the investigation of the **formation of supramolecular structures at interfaces** and applied research in the field of **biosensor development**. All the projects concern interfaces both in a literal sense and in terms of combining different disciplines such as chemistry, physics, and biology. The highly multidisciplinary team works on the synthesis of lipids and polypeptides, the chemical modification of surfaces, the isolation of proteins, the application of recombinant DNA technology, the use of optical spectroscopy (FTIR, fluorescence, circular dichroism) combined with molecular-dynamics calculations as well as with surface-sensitive techniques (surface plasmon resonance, integrated optics, Langmuir film balances, scanning probe microscopies).

In the following, we give some representative examples of our research.

1. Fundamental Studies on the Structure and Dynamics of Membrane Proteins

1.1. Membrane Insertion and Folding of Proteins

Protein integration into or translocation across membranes is a fundamental process in prokaryotic and eukaryotic cells. The biosynthesis of almost all cellular proteins begins in the cytoplasm. The insertion of newly synthesized membrane proteins into cellular membranes is in many

cases directed by *N*-terminal signal (leader) sequences, that are removed from the mature protein after insertion. Complicated protein insertion and translocation machineries composed of water-soluble and membrane-bound proteinaceous components have been characterized genetically and biochemically in prokaryotic and eukaryotic cells, but the detailed molecular mechanism by which the nascent polypeptide chain is driven through the membrane is unknown. However, there are several examples of relatively small proteins which insert into cellular membranes independently of a translocation machinery. Classical examples are the coat proteins of the filamentous phages M13 and Pf3. This suggests that such small proteins must have the structural properties necessary for targeting and translocating within their primary amino-acid sequence.

The project concerns fundamental studies of membrane protein insertion and structural folding using the coat proteins of the filamentous phages M13 and Pf3. The 50-residue-long M13 coat protein is synthesized in *Escherichia coli* cells as a precursor, termed procoat protein, with a classical 23-residue leader sequence at its *N*-terminus. Procoat protein inserts into the plasma membrane as a loop structure in the presence of a transmembrane electrical potential and is finally processed by leader peptidase, yielding the mature transmembrane M13 coat protein. In contrast to M13 coat protein, the 43-residue-long Pf3 coat protein is synthesized without a leader sequence and the protein directly transfers its *N*-terminus across the membrane.



Horst Vogel studied Chemistry at the University of Würzburg/Germany. After his diploma thesis in Physical Chemistry he went to the Max-Planck Institute for Biophysical Chemistry in Göttingen, where he performed his Ph.D. work on the 'Structure of lipid membranes' in the Departments of Profs. *M. Eigen* and *A. Weller*. In the following, he worked at the Max-Planck Institute for Biology in Tübingen/Germany, at the Biocenter of the University of Basel/Switzerland, and at the Karolinska Institute in Stockholm/Sweden, studying the structure and dynamics of membrane proteins. In 1994, he was appointed as a Professor of Physical Chemistry at the EPFL, where he is director of the Institute for Physical Chemistry of Polymers and Membranes.

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