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Solubilization control by redox-switching of polysoaps

P. Anton[2,*], **A. Laschewsky**[1,**], **M. D. Ward**[3]

[1] Université Catholique de Louvain, Dépt. de Chimie, Place L. Pasteur, 1,
B-1348 Louvain-la-Neuve, Belgium
[2] Universität Mainz, Institut für Chemie, D-55099 Mainz, Germany
[3] University of Minnesota, Department of Chemical Engineering and Materials Science,
151 Amundson Hall, 421 Washington Avenue S.E., Minneapolis, MN 55455-0132, USA

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Summary

Reversible changes in the self-organization of polysoaps may be induced by controlling their charge numbers via covalently bound redox moieties. This is illustrated with two viologen polysoaps, which in response to an electrochemical stimulus, change their solubility and aggregation in water, leading from homogeneously dissolved and aggregated molecules to collapsed ones and vice verse. Using the electrochemical quartz crystal microbalance (EQCM), it could be shown that the reversibility of this process is better than 95% in 16 cycles.

Introduction

Monomeric and polymeric surfactants that respond to external stimuli such as temperature, electrical charge or irradiation with light offer the possibility of controlling surfactant properties such as solubility, solubilization capacity or emulsification properties right on the spot. As examples, Saji et al. could disintegrate micelles of low molecular weight ferrocene surfactants by oxidation. Thin films of hydrophobic compounds that had been solubilized by these surfactants were thus deposited onto the electrode surface [1]. N. Kuramoto et al. demonstrated that the lower critical solution temperature of poly(N-acryloylpyrrolidine-co-vinylferrocene) depends on the concentration and oxidation state of the ferrocene moieties [2]. Recently, we synthesized a series of redox-active micellar polymers, whose solubility can reversibly be influenced by a redox moiety [3]. We were now interested in further consequences of the redox state on the polysoap properties. In this context, two viologen polysoaps **P-1** and **P-2** (Fig. 1) were investigated in more detail.

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[*] *Present address:* AKZO Research Laboratories, D-63784 Obernburg, Germany

[**] Corresponding author

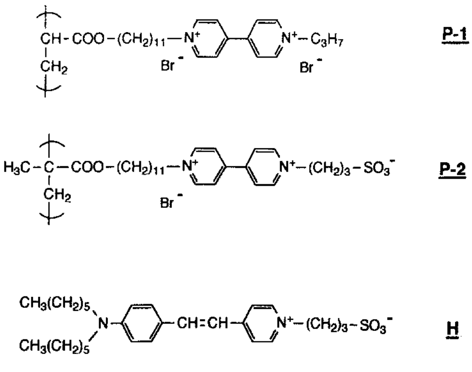

Fig. 1: Chemical structures of the viologen polysoaps **P-1**, **P-2** and the hemicyanine dye **H** used for solubilization experiments

Results and discussion

Cyclic voltammetry shows that **P-1** and **P-2** are reduced in two steps (Fig. 2). As judged from the charges, this process is highly reversible. For **P-1**, the peak potentials measured against a SCE reference electrode in 0.1 M KCl are -0.53 V/-0.48 V for the first redox step, and -0.76 V/-0.71 V for the second redox step. Separations of the oxidative and reductive peak potentials range between 0 mV and 56.5 mV at 25°C. This indicates, together with the shape of the peaks, that the redox moieties of the polymer are at least partially adsorbed onto the electrode [4].

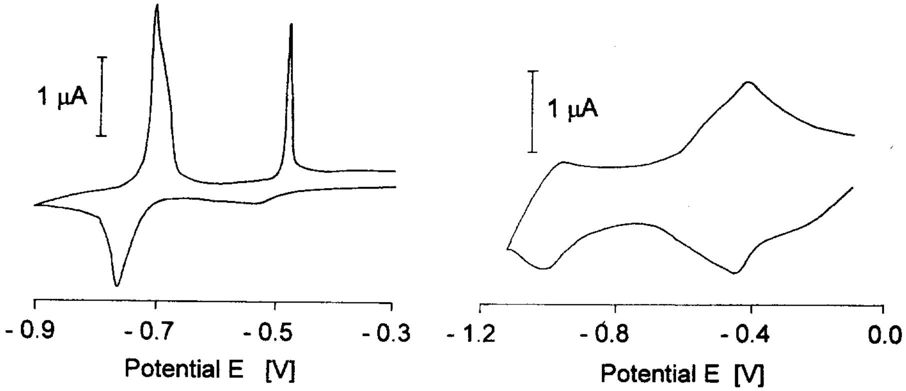

Fig. 2: Cyclic voltammograms of **P-1** (left) and **P-2** (right) in 0.1 M aqueous KCl, c = 1.0 mM, v = 100 mV/s; working electrode: mecury coated Pt wire, reference electrode: SCE; T = 20°C, pH = 5.5

Similar observations are made for **P-2**. However, the cyclic voltammograms of the two polysoaps differ noticeably in shape, which may be due to different morphologies of the adsorbed films [5]. Moreover, the peak potentials of **P-2** are shifted to more positive values for the first redox step (-0.44 V/-0.41 V), and to more negative values for the second one (-1.00 V/-0.95 V). These shifts may be attributed to different coulombic interactions between the redox moieties, as the redox reactions of **P-1** and **P-2** lead to different overall net charges. Potential shifts have also been observed for viologen amphiphiles in organized media, e.g. cast films and Langmuir-Blodgett films [6]. Noteworthy, the cyclic voltammograms of **P-2** and its acrylate homologue are almost identical with respect to their shape and position of the peak potentials [3].

Reversibility of the redox reaction and adsorption of the reduced species was examined more closely with an electrochemical quartz crystal microbalance (EQCM). This method relies on the frequency decrease of a quartz crystal bearing a gold electrode, when redoxactive molecules are electro-deposited on its surface [7]. Solutions of the viologen polysoap **P-1** in 0.1 M KCl were adjusted to a pH of 12 to suppress the reductive cleavage of water. Thin layer chromatography of the solutions after the experiment did not indicate any ester cleavage, but the initially colourless solutions turn slighly yellow after 2-3 days. This may probably be due to a reaction of the viologens with hydroxyl anions to form fluorescent pyridones at this high pH value [8]. However, the reaction is not fast enough to exert any influence on the measurements, if freshly prepared solutions are used.

These solutions were inserted into an EQCM set-up described earlier [9]. The electrode potential was periodically changed between 0 and -0.7 V, and the frequency change of the quartz crystal was monitored (Fig. 3).

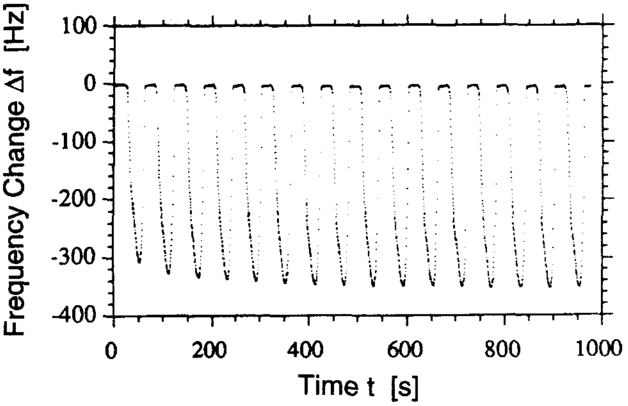

Fig. 3: Frequency change of the EQCM during adsorption and desorption cycles of P-1 in 0.1 M KCl. The potential was periodically changed between 0 and -0.7 V; c = 1.0 mM, v = 10 mV/s; working electrode: gold (vapour-deposited onto quartz), reference electrode: SCE; T = 20°C, pH = 12

During the scan from 0 to -0.7 V, the colour of the gold electrode changes to a copper-like hue. At the same time, the frequency decreases until the minimum potential is reached. The frequence increases again during the reverse scan from -0.7 to 0 V, and the electrode resumes its initial colour. This process is repeated with each cycle and indicates repetitive deposition and stripping of reduced **P-1**. During the 16 cycles shown in Fig. 3, the frequency drop increases from 340 Hz to 360 Hz. If the EQCM showed ideal behaviour [7], the change in the frequency drop would indicate that the amount of mass per unit charge deposited in each cycle increases. Accordingly, some redox groups would become inactive during the deposition and stripping of identical polymer chains within the depletion layer of the electrode. Under these conditions, the loss due to irreversible reactions would be in the range of 5 wt%, calculated on the basis of the Sauerbrey equation [10]. That the redox reaction of **P-1** is at least partially irreversible under the experimental conditions applied, is illustrated by the formation of a very thin, water insoluble red film at the electrode surface in the process of 100 cycles. However, other reasons may also contribute to the different frequency drops, e.g. nonuniform film deposition or viscoelastic behaviour [7]. Indeed, using impedance analysis [7], visco-elasticity could be detected for the films of **P-1**, and consequently, degradation should be well below 5 wt% in 16 cycles.

Thus, the redox reaction of **P-1** is not completely reversible, but the low degree of degradation is highly promising. Similar to other viologen-containing polysoaps [3], a change in the oxidation state of **P-1** leads to a drastic change of its solubility. The question arises if such an effect can be used to control other properties of polysoaps, e.g. their solubilization capacity for hydrophobic substances. To answer this question, solubilizates of **P-1**, **P-2** and a zwitterionic hemicyanine dye **H** (Fig. 1) were prepared as described elsewhere [11]. The amount of dye solubilized at polysoap concentration of 4 g/L was determined with UV/Vis spectroscopy as 301 mg for **P-1** and 547 mg for **P-2**, compared to 8 mg in pure water. To demonstrate the effect of the reduction on the solubilization, these homogeneous, orange-coloured solution were filled into a cuvette and purged with nitrogen. Reduction was then done chemically with sodium dithionite at a pH-value of about 9. Upon the addition of the reducing agent, a purple precipitate forms immediately, while the remaining solution is colourless.

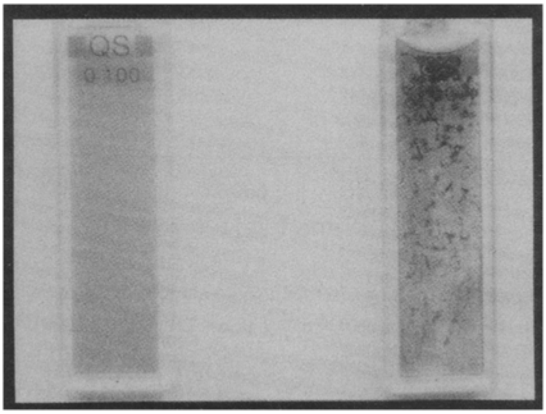

Fig. 4: Solubilizate of **P-2** and the hemicyanine dye **H** with **P-2** in ist native state (left cuvette) and ist reduced state (right cuvette)

When subsequently air or pure oxygen is bubbled through this inhomogeneous mixture, the original homogenous and orange-coloured solution is obtained back. The procedure is illustrated for **P-2** in Fig. 4, and identical observations were made for **P-1**. Switching between the native and the reduced state can be repeated about 3-4 times, until the polysoaps will eventually be salted out by the added electrolyte, the concentration of which increases with each cycle. If, however, the redox process is induced electrochemically, numerous cycles can be run.

These experiments illustrate that the redoxactive viologen polysoap **P-1** and **P-2** respond to an electrochemical stimulus by a change of solubility and aggregation in water, leading from homogeneously dissolved and aggregated molecules to collapsed ones and vice versa. The reversibility of this process is better than 95% in 16 cycles, as determined by EQCM. These properties of the viologen polysoaps, combined with their ability to solubilize hydrophobic dyes, can be exploited to reversibly remove and add hydrophobic substances to an aqueous solution. Under these aspects, **P-1** and **P-2** definitely differ from the low molecular weight ferrocene surfactants investigated by Saji, for which a change in surfactant aggregation goes along with an irreversible deposition of the solubilizate at the electrode surface [1]. For the viologen polysoaps, however, the solubilizates remain trapped in the collapsed hydrophobic domains of the polymer and thus can be redispersed again.

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