Assembly modulates dissociation: electrokinetic experiments reveal peculiarities of the charge formation at monolayer films

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Self-assembled monomolecular films of alkanethiols chemisorbed on gold were used as a two-dimensional model system to study the effects of spatial confinement of surface functional groups on their acid–base behaviour; reduction of the surface charge density by mixed assemblies revealed an increase of the acidity of carboxy groups; surfaces with low amounts of charged groups show the interplay of dissociation of functional groups and preferential adsorption of ions in terms of surface charge formation.

Ionization of natural and synthetic molecules originates inter- and intramolecular forces of key importance: ion–ion and ion–dipole interactions determine structural features and transitions within and between polymers, complexes or supramolecular assemblies enabling a wealth of dedicated functions in artificial settings as in nature. Prominent examples comprise the universal principle of specific (*e.g.* receptor–ligand) binding or phase transitions of polymer gels in response to environmental stimuli as involved in muscle function.[1–3] Ionization in that context very often occurs in confined molecular geometries which can cause substantial deviations of the acid–base equilibria from those of isolated, ideally dispersed functionalities. Two-dimensional assemblies, *i.e.* self-organized thin films of amphiphilic molecules, represent an example of spatially confined molecules in which interactions of the charged species are restricted to a defined geometric plane. Various simple two-dimensional model systems such as insoluble fatty acid monolayers at the air–water interface,[4,5] self-assembled monolayers (SAMs) on solid supports[6–10] and micelles[11] provided evidence that the acid–base equilibrium of charge determining groups such as carboxylic acid and amine functions is shifted in favor of the uncharged moieties, if these ionizable groups are densely packed. The p*K* value of a functional group determined in solution was concluded to be no longer valid to describe the charging characteristics of a densely confined array of functional groups. However, rather different explanations were suggested for this reduced acidity/basicity including electrostatic in-plane interactions,[6,7,10] hydrogen bonding between the uncharged ionizable moieties[12] or reduced ion hydration due to a highly oriented solvent structure at the interface,[9,13] and a systematic analysis of the environmental factors altering the acid–base behavior has been lacking so far. Additionally, recent evidence proves that interfacial charging by unsymmetrical ion adsorption needs to be considered as a ubiquitous effect in aqueous electrolyte solutions.[13–17] This communication reports on a novel approach to these fundamental phenomena using streaming current measurements to characterize the electrosurface behavior of binary SAMs. Two sets of binary self-organized films were prepared by coassembly of a carboxy-modified alkanethiol (11-mercaptoundecanoic acid; MUA or 16-mercaptohexadecanoic acid; MHA) with a second component of equal methylene chain length providing either polar (11-mercaptoundecanol; MUOH) or non-polar (hexadecanethiol; HDT) environments to scrutinize the aforementioned possible origins of altered acid–base equilibria (surface coverage of dissociating sites, hydrophobicity, hydrogen bonding) of interfacially confined functionalities (Fig. 1). Surface charging of the SAMs in aqueous environments was directly monitored by the electrokinetic technique of streaming current measurements across rectangular microchannels formed by the sample surfaces using an in-house developed instrument, the Microslit Electrokinetic Setup.[18–21] In contrast to the widely applied chemical force microscopies[6,10,15] which provide rather local electrostatic forces, this method yields a well-defined average of the effective interfacial potential. Addtionally, this method provides the isoelectric point (pH at which the electrokinetic potential vanishes) of the monolayer surface as a measure of its net acid–base characteristics. As we have already reported previously, MUA and MHA SAMs show strongly attenuated acidity obvious from isoelectric points (IEPs) of about pH 4.3 in KCl solutions[20] which is about 2 units of pH higher than IEPs of polymeric systems bearing more isolated and sterically flexible COOH functionalities.[22,23] Further, hydrophobic

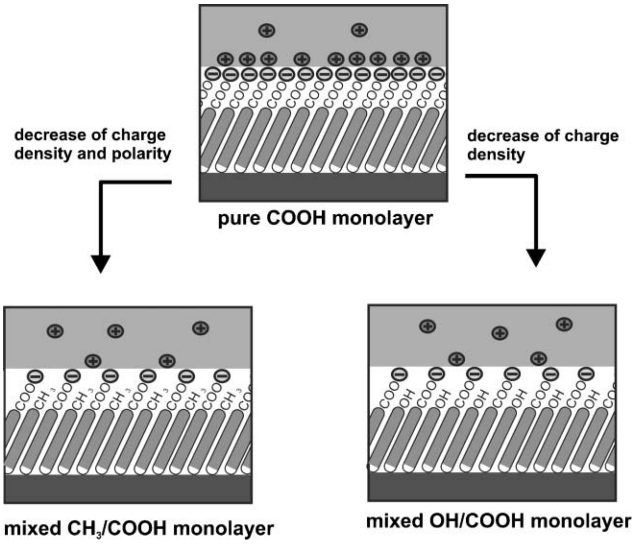

Fig. 1 Schematic view of the control of interfacial charge density and polarity of a two-dimensional layer system by mixed binary self-assembled monolayers as used in this work.

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HDT monolayers revealed a negative charge pH < 4 independent of the background KCl concentration, indicating that the IEP of pH 4 is equivalent to the point of zero charge (PZC).[20] The negative surface charge over a wide range of pH values was, in consequence, attributed to the preferential adsorption of hydroxide ions[19,20] which is supported by theoretical calculations.[14] The IEPs of the two binary systems as a function of the surface composition are summarized in Fig. 2. Whereas mixed monolayers with higher content of MHA show even slightly higher IEPs than a pure MHA monolayer, the monolayers with low surface fractions of carboxy groups (MHA) display a significant shift of the IEP towards the acidic range. For all compositions the IEP of the mixtures is lower than the IEP of pure MUA (IEP = 4.3). For the monolayers with an MUA surface fraction of 10% a pronouncedly acidic IEP of about 2.7 is obtained. The findings indicate that electrostatic interactions of ionized COOH groups are responsible for the lowered acidity in SAMs while the intrinsic p*K* of the surface confined COOH groups is very close to the bulk solution p*K* value. It is noteworthy that the magnitude of this shift is also in line with theoretical approaches based on in-plane electrostatic forces.[24] Hydrogen bonding between the carboxylic moieties can be excluded because otherwise the MUA/MUOH system should not exhibit low IEPs due to stabilization of the uncharged COOH groups by hydrogen bonding. The hydrophobic environment of the carboxy groups in MHA/HDT monolayers might additionally suppress the ionization due to interfacial water ordering at hydrophobic surfaces accompanied by a low permittivity and reduced ion solvation. Another explanation invokes a nanoscale phase separation[25,26] at higher fractions of the acidic component (creating nano-patches of SAM with very similar characteristics as compared to the pure MHA). As recently indicated by STM[25] and AFM[26,27] these domains do not exceed the dimensions of several molecules. Therefore the IEP of the MHA/HDT system hardly varies for COOH surface fractions of 0.25 to 1. In contrast, MUA/MUOH monolayers are expected to show perfect mixing of both components since the MUOH matrix has a surface energy very similar to the pure MUA SAM. Therefore, those binary systems show the lowest IEP due to their uniform distribution of dissociating sites and putatively less perturbed water structure. At fractions of MUA and MHA below 0.05 the IEP increases again. This has to be attributed to the prevailing preferential hydroxide adsorption. Similar to the dilution of the COOH-terminated molecules by implementation of uncharged molecules in the SAMs, the electrostatic interactions among the carboxylate species can be reduced by increasing the ionic strength of the solution. The presence of bivalent background electrolyte cations (Ca^{2+}) also leads to a significant decrease of the IEP as the calcium ions strongly bind to carboxylate groups and therefore effectively screen the electrostatic fields of neighbouring carboxylate groups with increasing concentration. As shown in Fig. 3, the isoelectric point of an MHA SAM scales linearly with the Debye screening parameter κ, N_A being the Avogadro constant, k_B the Boltzmann constant, T the temperature, I the ionic strength, ε_r and ε_0 the dielectric constant of water and the free space respectively [eqn. (1)]. Again, these findings confirm the dominating role of lateral electrostatic interactions in the acid–base equilibria of monolayer films.

$$\kappa = \sqrt{\frac{2e^2 N_A I}{\varepsilon_0 \varepsilon_r k_B T}} \qquad (1)$$

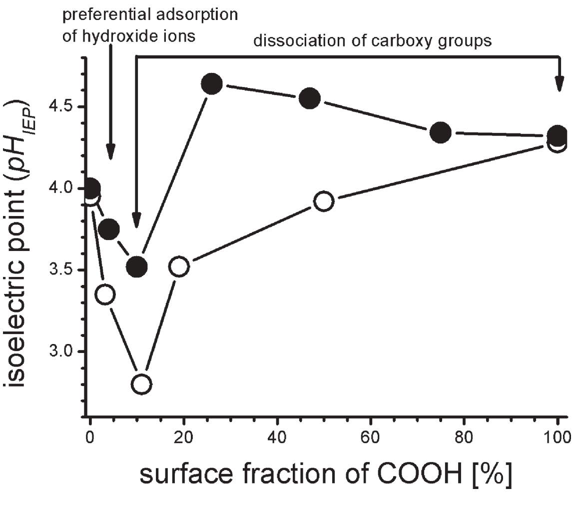

Fig. 2 Isoelectric points (determined in 3 mM KCl solutions) of binary SAMs composed of MUOH/MUA (○) and MHA/HDT (●) as a function of the surface fraction of the acidic component.

In conclusion, electrokinetic measurements could clarify the electrostatic modulation of the acid–base behavior of ionizable surface groups in SAMs. By independent variation of the surface coverage of carboxylic acid groups, the surface tension of the layered substrates and the ionic strength, the p*K*-shift could be unambiguously attributed to lateral electrostatic interactions between the acid anions formed upon dissociation. Due to this attenuated acidity at higher coverage the most pronounced acidic character of the monolayer surfaces was found at SAMs with surface fractions of carboxylic acid groups of about 10% (for the electrolyte solutions investigated in this study). These observations might be generalized for other monomolecular assemblies. For instance, theoretical predictions and surface pressure studies on the penetration of uncharged, insoluble monolayers at the air–water interface by ionic surfactants confirm the importance of in-plane electrostatic interactions for surface thermodynamics.[28,29] Since electrokinetic measurements provide a complete picture of the interfacial charging, the experiments could further reveal the

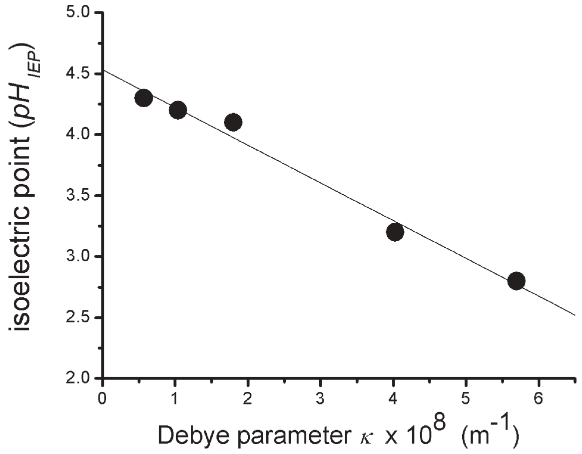

Fig. 3 Isoelectric point of a mercaptohexadecanoic acid SAM on gold as a function of the Debye screening parameter.

increasing contribution of unsymmetrical electrolyte ion adsorption to the monolayer interface at lower amounts of dissociating sites which is often not considered as a surface charge formation process.†

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Notes and references

† Details of the monolayer preparation and characterization are reported in separate publications.[20,26] The zeta potential was calculated from the streaming current by means of the Helmholtz–Smoluchowski equations with respect to the slopes. Further technical details of the Microslit Electrokinetic Setup are given in [18,19].

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