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# Ion specific effects in foam films

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ABSTRACT

Ion specific effects are pronounced at surfaces. Therefore foams and foam films are suitable objects to study ion specific effects. The relative amount of adsorbed ions is ususally indirectly determined by disjoining pressure isotherms. The determined potential of the film surfaces is discussed in context with the surface charge of the neat air/water interface.

## 1. Introduction

Liquid foams are frequently applied in daily life and industrial processes like cleaning agents, personal care products, and products for fire-fighting, flotation and for oil recovery. A general understanding about how to manipulate the foam stability is often missing. Thus, the development of new products is often based on empirical evidence and experience. In order to control the processes one has to distinguish between *foam-ability*, i.e. the highly dynamic process at the beginning of foam formation and the *foam stability*, dominating at a later stage when the drainage of the foam lamella (or foam films) slows down and surface forces come into play. The present review addresses single foam films in thermodynamic equilibrium where the disjoining pressure, i.e. the excess pressure between film and bulk, compensates the capillary pressure. Some publications show that the stability of foam films is directly correlated to the stability of the respective foam, e.g. [1,2], and in foams with pronounced foam-ability, the correlation is much more complex [3].

In general, the surface forces in foam films can be described by the well-known DLVO theory. The disjoining pressure is the sum of repulsive electrostatic, attractive van der Waals and repulsive steric pressure. Based on these interactions two different types of thin films can be distinguished: common black films (CBF) with thicknesses between 10 and 100 nm which are mainly electrostatically stabilized and Newton black films (NBF). In a NBF no free water except hydration water around the surfactant headgroups is left between the film interfaces. Hence, the film thickness corresponds to twice the surfactant length.

The properties of foam films can be tuned with respect to the type of surfactant, surfactant concentration, ionic strength of the system (electrolyte concentration), and pH of the solution. However, in applications usually mixtures of several components are used. The main foaming agents used in these processes are beside non-ionic surfactants anionic alkyl sulfates, alkyl carboxylates, and quaternary ammonium surfactants. Besides the main foaming agents the mixtures contain a vast number of additives (electrolytes, alcohols). It turned out that in the mixtures not only the nature of the components but also the specific interaction between the dominating surfactant and the additive are important with respect to foam film properties [4]. Therefore, the specific interactions between the most frequently used additives (electrolytes) and surfactants are regarded within this review. The film thickness and stability of foam (and wetting films) are linked to the effect of ion adsorption at the air/water interface and to a specific interaction between headgroups and ions in the wider frame of Hofmeister effects. The term "Hofmeister series" is a synonym used for specific ion effects. Originally, it dates back to Franz Hofmeister, who investigated the ability of ions to precipitate egg-white proteins [5]. Hofmeister classified anions in series like the following, ordered along their efficiency to salt-out proteins:

$$SO_4^{2-} > F^- > CH_3COO^- > Cl^- > Br^- > I^- > SCN^-.$$

Related to the Hofmeister series, especially hydrophobic interfaces, e.g. the air/water interface are of interest. In this context the surface charge plays an important role. It is controversially discussed in

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literature, whether the air/water interface is negatively or positively charged [6•,7•]. Furthermore, many experimental on one hand — and theoretical results on the other hand contradict each other concerning the ion adsorption at the air/water interface, since they are sensitive for different length scales. Some methods are only sensitive for the surface layer and not for the subsurface layers and others are sensitive for both.

The aim of this review is to contribute to the clarification of such fundamental questions about interfacial ion effects. A general understanding of specific ion effects at interfaces is important in many fields like in life science and for technical applications, e.g. the disposal of nuclear waste. In addition: Thin liquid films are good model systems for studying interactions in colloidal systems.

In order to observe which and how ions influence the properties of the air/water interface, asymmetric wetting films of electrolyte solutions on a bare silicon substrate were investigated. Wetting films with two different interfaces give the opportunity to determine the sign of the surface charge of the air/solution interface (Section 2).

In the following, specific ion effects on the properties of symmetric foam films stabilized by anionic, nonionic or cationic surfactant are considered (Section 3). Specific ion effects can be studied by the addition of different electrolytes to a surfactant solution or/and by varying the counterion of the surfactant. Due to replacing inorganic ions by organic electrolytes, the impact of the hydrophobicity of the ions on foam film properties is identified.

Although the topic “ion specific effects in foam films” is of high impact for many applications, the number of papers addressing this issue is rather low. In the following we will give the state of the art approach of the current research, and we want to point out the importance of this topic.

### *1.1. Ion specific effects measured by interfacial forces*

The disjoining pressure is an excess pressure within the thin film with respect to the pressure of the liquid in the meniscus. Most of the studies presented in this review were carried out with a Thin Film Pressure Balance (TFPB). The TFPB measures the disjoining pressure $\Pi(h)$ in dependence of the film thickness $h$ resulting in a disjoining pressure isotherm $\Pi(h)$. The TFPB with porous plate technique was developed by Exerowa [8]. It is mainly used to study foam films, but it has been also extended to study wetting films [9•]. Thereby the foam film is formed over a 1 to 2 mm hole that is drilled into a porous glass plate. It is enclosed within a pressure-controlled cell and connected to the outer atmospheric pressure. The film thickness is measured interferometrically. More detailed information about TFPB and interaction in foam films are given in former reviews (e.g. [10] and references therein).

In most of the studies described in the review, the adsorption of ions at the foam film surface is deduced from changes in the surface potential calculated from the disjoining pressure isotherms. Therefore the electrostatic contribution of the disjoining pressure isotherm is analysed and the non-linear Poisson–Boltzmann equation has to be numerically solved

$$\in_0 \in_r \nabla^2 \Phi = -e c_{i0} exp\left(\frac{-z_i \Phi}{kT}\right) \tag{1}$$

considering the boundary conditions and assuming a constant potential or constant charge density ($\Phi$: surface potential, $e$: elementary charge, $c_{i0}$: concentration of a specific ion type $i$, $z_i$: valency of ion type $i$). The surface charge density can be calculated by the Grahame equation from the potentials and the ionic strength resulting from the PB calculations.

### *1.2. The air/water interface is negatively charged*

Before describing ion specific effects in foam films one has to consider ion specific effects at the free air/water interface.

Since new surface selective spectroscopic techniques and computational methods enable the investigation of aqueous interfaces on a molecular level, a remarkable progress was achieved for the understanding of ion effects at the air/water interface. Furthermore, such studies showed that cation effects are less pronounced than anion effects since anions are larger and the difference in their radii is larger, as well [11••–13]. Experimental and theoretical studies indicated the adsorption of large anions (with low ion charge density) to the outermost layer of the liquid/air interface (e.g. [11••–15]). The driving force for ion adsorption at hydrophobic surfaces might be the hydrophobic effect: The solvation of ions corresponds to the creation of a cavity which pertubs the hydrogen network structure of water molecules and cost free energy. At the surface the cost in free energy is drastically reduced. The reduction in free energy is pronounced for water breaking (chaotropic) ions. Obviously, strongly hydrated ions are rather repelled form the interface, while less hydrated ions are attracted. In the case of halides the ability to structure water (kosmotropic) or to break water structure (chaotropic) correlates well with their size and their polarizibility.

Often, the ion affinity for an interface is related to the interplay of the polarizability of the ion with the interfacial electric field due to the dipolar orientation of interfacial water molecules [16,17]. This is in contradiction with simulations showing that non-polarizable ions adsorb at the interface as long as their radius is large enough [18–20]. This could even lead to a reverse adsorption behavior: $Li^+$ is repelled less than the larger $Na^+$. It is assumed that $Li^+$ appears larger due to its strongly bound first shell of water molecules [21•]. The Hofmeister series can be partially or fully reversed depending on the adjacent interface and the counterions, in other words, it depends on the ion's environment [22]. The advantage of the approach from Schwierz et al. [22] is that surface polarity, and in specific the crossover from hydrophobic to hydrophilic surfaces, is treated realistically and the changes of ion hydration and surface hydration as an ion approaches the surface are included in the potential of mean force. While the reversal of the Hofmeister ordering of ion adsorption on polar and nonpolar surfaces is already apparent from the potential of mean forces the additional Hofmeister series reversal with respect to the surface charge is a collective effect which only comes out from the full Poisson Boltzmann treatment.

All findings described so far mention an excess of ions at the air/water interface. This is in contradiction with the textbook description of ions being repelled from the interface and the outermost surface layer being depleted of ions [23]. The first interpretation from Onsager and Samaras was based on the consideration of the interface as a sharp discontinuity between two continuous dielectric media and the ions as point charges, which are repelled from the interface due to image charge repulsion. This traditional interpretation is based on macroscopic measurements of increasing surface tension with the concentration (activity) of many inorganic salts, including the alkali halides. According to the Gibbs model the increase in surface tension dictates a negative surface excess in presence of salts. The interpretation of the macroscopic results in terms of a non monotonic ion density profile with surface enhancement and subsurface depletion shows that the theoretical and experimental findings mentioned above do not contradict the surface tension measurements and thermodynamic arguments [24].

In literature, there is still a strong debate about the sign of charge of the air/water interface (e.g. [6•,7•]). The strong decrease in surface tension due to the addition of acids (hydronium ions) [25,26] leads to the conclusion that the air/water interface is positively charged. As mentioned above, the correlation between the surface charge and surface tension measurements is not that simple.

One possibility to determine the potential of the air water interface is to measure disjoining pressure isotherms of wetting films (e.g. Silicon/water/air). Wetting films are asymmetric. In contrast to foam film experiments wetting film experiments give the possibility to determine the sign of the surface potential of the air/water interface if the sign of the surface potential of the opposing Silicon/water interface is known. The values of the surface potential can be independently determined