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Concentration polarization effect at the deposition of charged Langmuir monolayers

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ABSTRACT

The review summarizes the results of the recent studies of the electrokinetic relaxation process within the meniscus region during the deposition of charged Langmuir monolayers. Such electrokinetic relaxation is the consequence of the initial misbalance of partial ion fluxes within a small region near the contact line, where the diffuse parts of electric double layers, formed at the monolayer and the substrate surface, overlap. The concentration polarization within the solution near the three-phase contact line should lead to long-term relaxations of the meniscus after beginning and stopping the deposition process, to changes of the ionic composition within the deposited films, to change of the interaction of the monolayer with the substrate, and to dependence of the maximum deposition rate on the subphase composition.

1. Introduction

Mechanisms, leading to regular pattern formation during wetting/dewetting processes, have been intensively studied in the recent years because they are very interesting for both fundamental science and practical applications [1–10]. Such studies can contribute to deeper understanding of wetting phenomena and forces acting between the interfaces of different nature under non-equilibrium conditions. On the other hand, surface patterning during wetting/dewetting processes is a promising alternative to other patterning methods because of its extreme simplicity.

Regular surface patterns can be formed, in particular, during the Langmuir–Blodgett (LB) deposition process [11–19]. The main advantage of this method is related to the possibility of rapid patterning a large (macroscopic) area with lateral resolution in the nanometre range. The properties of such patterned films can be easily controlled by varying the surface pressure within the deposited film, deposition rate, type of the deposited monolayer (which can be also mixed monolayers) as well as by varying the subphase composition.

Regular patterns can be formed spontaneously during wetting/dewetting processes due to interaction of the receding meniscus with the substrate surface. Understanding of this complex physicochemical interaction, which manifests himself under essentially non-equilibrium conditions, is the most important precondition for understanding the mechanisms of pattern formation.

The interfaces between contacting media are usually charged, therefore electrostatic forces and electrokinetic phenomena in a close vicinity to the moving three-phase contact line should also play an important role. Indeed, it was recently shown that electrostatic interactions and electrokinetics are responsible for the regular patterns formation by deposition of charged amphiphilic monolayers [20,21]. Deposition of a charged monolayer to a substrate requires neutralization of surface charges via adsorption (binding) of counterions from the subphase at the ionized surface groups in close vicinity to the contact line. This process is diffusion-limited and is accompanied by formation of ion concentration and electric potential profiles within the meniscus region. Thus, deposition of charged monolayers should be accompanied by concentration polarization of electrical double layers (DL) formed at the interfaces near the contact line. Such concentration polarization is characteristic for other electrokinetic phenomena.

Pattern formation by using charged amphiphilic monolayers instead of electroneutral monolayers has a number of important advantages. In the case of charged monolayers, formation of a structure can be controlled more easily through the monolayer composition, the surface charge and the electrical double layer thickness, which can be simply influenced by regulation of the amounts of different counterions and co-ions within the subphase. In this way, transfer-induced patterns which are characterized by a spatially periodic ionic composition can be produced. Such patterns cannot be obtained by other methods. As well, incorporation of different counterions into the patterned films allows one to obtain films with specific physical and/or chemical properties.

However, despite its obvious importance, the role of electrostatic interactions and electrokinetic phenomena in the mechanisms of patterns formation during wetting/dewetting processes is not sufficiently understood yet. In the present review we summarise the recent achievements in equilibrium and non-equilibrium interactions between

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charged interfaces in close vicinity to the contact line, and in analysis of non-stationary processes of charge and matter transfer within the meniscus region as well as their relationship to the meniscus instability and pattern formation.

2. Equilibrium interactions in the three-phase contact region

Ionisable amphiphilic monolayers spread at the air–water interface are characterized by a net electric charge formed due to dissociation of ionisable groups of the molecules within the monolayer [22,23]. A floating monolayer and the adjacent diffuse layer form a totally electroneutral electric double layer, where the charge of the ionized surface groups is compensated by the opposite charge spread out within the diffuse layer. The ionisable groups at the interface can form surface-active complexes with the counterions dissolved in the subphase. Because of ion exchange with the subphase the degree of monolayer ionization and the interfacial charge density can change. The equilibrium interfacial charge depends on the number of each sort of counterions bound at the monolayer. The number of bound counterions is determined not only by the particular ion concentration in the bulk phase and its individual association (binding) constant, but also by the presence of other ions. A number of models have been developed to describe competitive adsorption or binding of counterions at charged Langmuir monolayers [24–28].

Let us consider a monolayer which contains one sort of (monovalent) ionized groups which can form, however, several complexes of different stoichiometry with the same counterion. Assuming chemical equilibrium for the formation of interfacial complexes we can express the surface molar concentration of the *k*th interfacial complex containing the *i*th ion, X_{ik}, through the surface molar concentration of the ionized amphiphilic molecules, X_I, and the bulk concentration of this ion at the interface, C_{iS}, as

$$X_{ik} = K_{ik} X_I^{\alpha_{ik}} C_{iS}^{\nu_{ik}} \tag{1}$$

where K_{ik} is the equilibrium constant, α_{ik} and ν_{ik} are the stoichiometric coefficients of the respective chemical reaction.

The total number of amphiphilic molecules in the monolayer is given by the sum over all interfacial complexes

$$X_R = X_I + \sum_i \sum_k \alpha_{ik} X_{ik} \tag{2}$$

For monolayers in a condensed state, X_R can be assumed approximately constant [29]. From Eqs. (1) and (2) the surface concentration of the ionized molecules, X_I, can be obtained provided that the bulk concentrations, C_{iS}, the equilibrium constants, K_{ik}, and the total number of amphiphilic molecules, X_R, are known.

Under equilibrium conditions the ions are distributed within the diffuse layers according to the Boltzmann equation. Therefore the bulk concentration of the *i*th ion at the interface can be determined as

$$C_{iS} = C_{i\infty} \exp\left(-\frac{z_i F \Psi_S}{RT}\right), \tag{3}$$

where $C_{i\infty}$ is the ion concentration in the solution far from the interface, z_i is the ion charge, F is the Faraday constant, Ψ_S is the surface potential, R is the gas constant, and T is the temperature.

The surface charge density can be obtained as the sum over all charged interfacial complexes

$$\sigma = F\left[z_I X_R + \sum_i z_i \left(\sum_k \nu_{ik} X_{ik}\right)\right] \tag{4}$$

where z_I is the charge of ionized amphiphilic molecules.

As the ion concentrations at the interface, C_{iS}, depend on the surface potential, Ψ_S, then, according to Eqs. (1), (2) and (4), the concentrations of different complexes and the surface charge density should also depend on the surface potential. Thus, Eqs. (1)–(4) establish a link between the surface charge density and the surface potential arising as a result of adsorption (association) of counterions. An increase of the surface potential results in an increase of counterion concentrations at the interface, what leads to their enhanced adsorption and surface charge neutralisation. Such link, usually denoted as charge regulation [22], should be considered as an additional boundary condition for the Poisson–Boltzmann (PB) equation, instead of the conditions of constant surface charge or constant surface potential usually used. Another boundary condition expresses the relationship between the normal electric displacement at the interfaces and the interfacial charge density. The solution of the so formulated problem allows one to obtain the electric potential profile and the ion concentration profiles in the diffuse part of DL along with the concentrations of the interfacial complexes and ionized amphiphilic molecules at the interfaces for a given ionic composition of the subphase.

In a number of studies it was demonstrated that the ion binding model, presented here, can be successfully applied to describe the experimental data on the variation of the monolayer composition with the composition of the bulk solution [24,25,28,31–34]. For non-ideal monolayer behaviour, using activities instead of concentrations in the expressions for the mass action law (Eq. (1)) allows improvements to describe the experimental data [25,28]. However, some practically important systems (e.g. fatty acid monolayers in presence of Cd^{2+} ions [25]) demonstrate an ideal ion binding behaviour. It should be also noted that the behaviour of positively charged monolayers (e.g. fatty amines) in presence of bivalent anions (phosphate, arsenate, etc.) is similar to the behaviour of negatively charged fatty acid monolayers in the presence of bivalent metal ions [35–37].

In the particular case of a fatty acid monolayer being in contact with a subphase containing an inorganic acid and a bivalent metal ion salt (e.g. $HCl + CdCl_2$) the formation of interfacial complexes can be described by the following reactions [29]:

$$R^- + H^+ \leftrightarrow RH \tag{5}$$

$$R^- + M^{2+} \leftrightarrow RM^+ \tag{6}$$

$$2R^- + M^{2+} \leftrightarrow R_2M, \tag{7}$$

where $R^- = CH_3(CH_2)_nCOO^-$ are the fatty acid anions, RH are non-dissociated fatty acid molecules, R_2M and RM^+ are two types of complexes formed by the fatty acid with the bivalent metal ion M^{2+}. There are different opinions in the literature whether bivalent metal ions form with acidic groups of the monolayer only a positive RM^+ complex, or only a neutral R_2M complex, or both of these complexes simultaneously [24,25,30]. Therefore, all three possibilities should be considered [29].

The chemical equilibrium conditions for the reactions (5)–(7) can be expressed as

$$X_{RH} = K_H X_{R^-} C_{H^+}^S \tag{8}$$

$$X_{RM^+} = K_{M1} X_{R^-} C_{M^{2+}}^S \tag{9}$$

$$X_{R_2M} = K_{M2} (X_{R^-})^2 C_{M^{2+}}^S \tag{10}$$

where K_H, K_{M1} and K_{M2}, respectively are equilibrium (association) constants. For this particular system the conservation law for the fatty acid molecules being in all forms (Eq. (2)) and the equation for the surface charge density (Eq. (4)) are specified as

$$X_R = X_{R^-} + X_{RH} + 2X_{R_2M} + X_{RM^+} \tag{11}$$