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SELF-ASSEMBLY OF MOLECULES AND COLLOID PARTICLES IN THE DESIGN OF ADVANCED MATERIALS AND PRODUCTS

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Abstract

Here, we present a review on the state of the art and our contributions to the theory and experiment on molecular and colloidal self-assembly. This includes self-assembly of amphiphilic molecules (surfactants) in micellar aggregates; growth of giant wormlike micelles and their effect on solution viscosity; micelle structuring in liquid films (stratification); particle self-assembly on liquid interfaces and in liquid films driven by capillary forces. The results have applications for the design of personal-care and house-hold products, and nanostructured materials.

Keywords: surfactant micelles, wormlike micelles, stratifying liquid films, capillary forces, convective self-assembly.

1. Introduction

By definition, self-assembly is a process, in which a disordered (chaotic) system of pre-existing components spontaneously forms an ordered structure or pattern due to specific, local interactions among the individual components. The constitutive components can be either molecules (molecular self-assembly) [1,2] or colloidal particles (colloid self-assembly) [3]. The colloid self-assembly is a *bottom-up* technique for the creation of nanoscale structures. In that respect, it is a much cheaper alternative of the *top-down* techniques, e.g., lithography, in which material is deposited or chiseled away to make nanoscale objects [4].

As a rule, the self-assembly is driven by attractive forces. In the case of self-assembly of amphiphilic molecules in aqueous solutions (Fig. 1), the driving force is the hydrophobic attraction between the hydrocarbon chains of the molecules in aqueous environment. In general, the entropy contribution to the standard adsorption free energy of surfactants is several times greater than the enthalpy contribution; see e.g. [5,6]. Thus, it turns out that the physical origin of the hydrophobic force is the structuring of water molecules near hydrocarbon chains in the aqueous phase [5]. The self-assembly process leads to chain transfer from aqueous into hydrophobic environment, accompanied by disappearance of the ordering of water molecules near the chains. As a result, the entropy increases and the system's free energy decreases, which in its own turn engenders spontaneous self-assembly.

In the case of colloid particles at a liquid interface, the attractive capillary force between the particles originates from the interfacial deformation [7-10]. The particle (surface) aggregation minimizes these deformations as well as the surface energy, which again results in spontaneous ordering [10-13].

Apart from the attractive force, a repulsive force is also needed to obtain stable equilibrium structures. The repulsive forces are usually of steric or electrostatic origin. The knowledge of the driving forces is crucial in order to understand and control the self-assembly of molecules and colloid particles.

In this article, we present a brief overview of the state of art and of our contributions in the fields of self-assembly of amphiphilic

molecules (Section 2); growth of giant micellar aggregates (Section 3); micelle structuring in liquid films (Section 4) and particle self-assembly on liquid interfaces driven by capillary forces (Section 5).

2. Self-assembly of amphiphilic molecules

As already mentioned, the amphiphilic molecules exhibit the remarkable property to form self-assembled aggregates in aqueous solutions. A typical amphiphilic molecule (surfactant, detergent) consists of hydrophilic headgroup and hydrophobic tail. The driving force for self-assembly is the natural tendency of the surfactant molecules to bring their hydrophobic tails out of contact with the water phase. Depending on the shape and size of the molecular headgroups and tails, aggregates of different shape and structure can be formed [1]. Some of them are illustrated in Fig. 1 and are briefly considered below.

The *spherical micelles* (Fig. 1a) are the most typical aggregates formed from surfactant molecules. Their existence was first discovered by McBain in 1913 in carboxylate (soap) solutions; see e.g. [14].

The most popular property of the micellar solutions is their washing action, which finds numerous applications in the everyday life (personal-care and house-hold detergency) and in various industrial processes. One of the washing mechanisms is the uptake of oil in the micelle core (solubilization of oil) and the formation of "swollen" micelles (Fig. 1b) [15].

Surfactant molecules with two tails, including phospholipid molecules, can form another kind of self-assembled structures, *vesicles*; see Fig. 1c. In the living organisms, such phospholipid bilayers are the main structural unit in the cell membranes [1]. In concentrated surfactant solutions (e.g. in liquid soaps), the amphiphilic molecules can form mesophases of different structure, e.g. lamellar phases (Fig. 1d), as well as hexagonal, cubic and disordered sponge phases [2]. At intermediate surfactant concentrations, the spherical micelles undergo transitions to rodlike (and flexible, wormlike) micelles; see Fig. 1e. The hexagonal liquid-crystalline phase represents an array of parallel rodlike micelles with hexagonal packing in the cross-sectional plane [2].
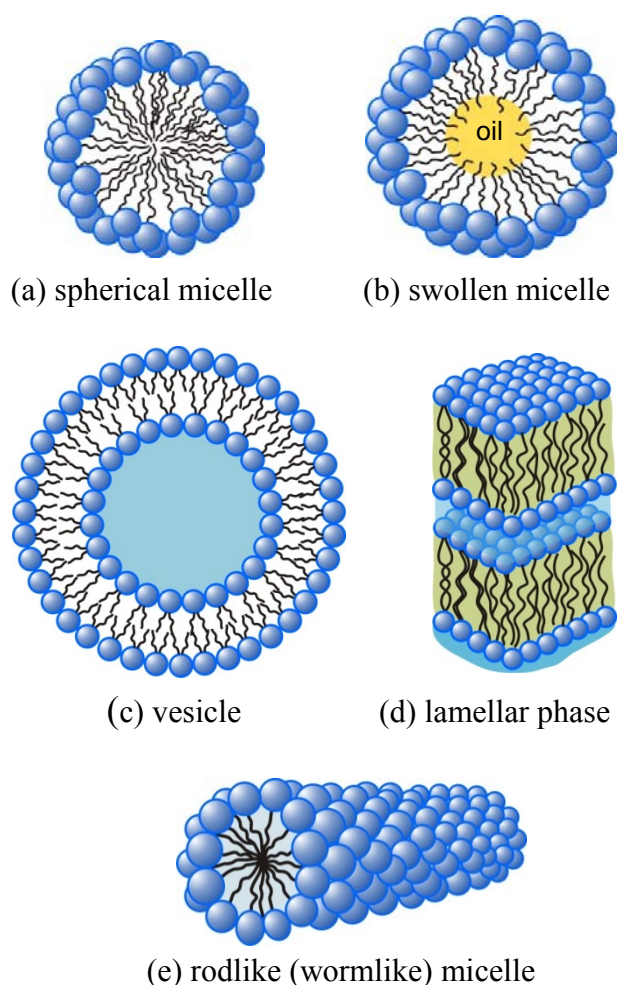

(a) spherical micelle   (b) swollen micelle

(c) vesicle   (d) lamellar phase

(e) rodlike (wormlike) micelle

Fig. 1. *Examples for self-assembled structures from amphiphilic molecules (surfactants, phospholipids, etc.)*

The interactions of the micellar solutions with solid surfaces (including the human skin and hair in personal-care applications) are related to the concentration of the free surfactant monomers, which are in equilibrium with the micelles. In the studies of our group, a complete system of equations, based on a detailed physicochemical model, was formulated that describes the equilibrium between micelles and monomers in solutions of ionic surfactants and their mixtures with nonionic surfactants [16,17]. The equations of this system represent mass balances, chemical and mechanical equilibria. Each nonionic surfactant is characterized by a single thermodynamic parameter – its micellization constant. Each ionic surfactant is characterized by three parameters, including the Stern constant that quantifies the counterion binding. In the case of mixed micelles, each pair of surfactants is characterized with an interaction

parameter. The solution of this system of equations gives the concentrations of all monomeric species, the micelle composition, ionization degree, surface potential and the mean area per headgroup. Upon additional assumptions for the micelle shape, the mean micelle aggregation number and electric charge can be also estimated. The theoretical model predicts quantitatively the dependence of the critical micellization concentration (CMC) of ionic surfactants on the ionic strength; of the CMC of mixed surfactant solutions on the input composition and of the electrolytic conductivity of micellar solutions on their concentration. It turns out, that in the absence of added salt the conductivity is completely dominated by the contribution of the small ions: monomers and counterions. The theoretical predictions are in good agreement with the experimental data [16,17].

3. Growth of giant micellar aggregates

Above the CMC, surfactants first form spherical micelles and the viscosity of their solutions is close to that of water. However, in the presence of electrolytes or co-surfactants, amphiphilic molecules can assemble into rodlike or wormlike micelles (Fig. 1e) [1,2]. Above a certain micellar volume fraction, the worms intertwine and form a transient micellar network, which gives rise to viscoelastic behavior. In fundamental aspect, the relation between structure and rheology of concentrated micellar solutions has attracted considerable attention [18,19]. In applied aspect, formulations containing wormlike micelles are frequently used as thickeners in cosmetics and homecare [20], and even as drug-delivery vehicles in biomedicine [21].

The most common worm-forming systems consist of (i) ionic surfactant and salt or hydrotrope (amphiphile that does not form micelles) [18]; (ii) ionic surfactant with nonionic and/or zwitterionic additives [22-24]; (iii) two oppositely charged surfactants [25]; and (iv) nonionic, gemini or biological surfactants [26].

Many worm-forming surfactant solutions show complex phase behavior and non-monotonic trends in their viscoelastic properties. It was established that the addition of salts or hydrotropes to cationic surfactant solutions induces micellar growth, and the zero-shear viscosity passes through one or even two peaks as a function of the concentration of additive [18]. Similar non-monotonic rheological behavior was later observed in many other surfactant systems [23-26]. The viscosity typically increases due to a transition from spherical to elongated and then to wormlike micelles. With the increase of surfactant concentration, the wormlike micelles intertwine and form a transient network, which leads to a considerable rise in viscosity. To the right of the peak, the viscosity decreases at higher concentrations, which is counterintuitive. Three of the possible mechanisms are (1) *micelle shortening* − the micelles diminish in size at higher concentrations, which is especially common in catanionic mixtures [25], (2) *micellar branching* – formation of dynamic connections between micelles, which can either slide along the micelle, or form 4-fold ghost-like crossings [27]; and (3) *shape or phase transition* – worms transform into discs, or isotropic micellar solutions are converted into liquid-crystalline mesophases [24,28]. To reveal the mechanism of viscosity reduction in a given system, direct imaging by cryogenic transmission electron microscopy (cryo-TEM) could be applied [25].

In a recent study [29], we examined the rheology–structure relations for ternary mixed micellar solutions, which contain the zwitterionic surfactant cocamidopropyl betaine (CAPB), the anionic surfactant sodium laurylethersulfate (SLES), and the nonionic co-surfactant octanoic acid (HC8). From fundamental and applied viewpoint, such systems are interesting because they exhibit a high and sharp peak ("resonance") of viscosity as a function of fatty acid concentration, which could be applied to control the rheological properties of shampoo-like formulations. To reveal the relations between the complex rheological behavior and the microstructure evolution, we employed cryo-TEM.

For example, in Fig. 2a we show experimental data for the zero-shear viscosity, η_0, vs. the HC8 concentration at a fixed total surfactant (CAPB + SLES) concentration, $c_{tot} = 100$ mM, and at a molar ratio of 7:3 CAPB:SLES. One sees the appearance of a

narrow peak in viscosity at 18 mM HC8 with height $\eta_0 \approx 41$ Pa·s (41 000 times the viscosity of water!). This value is 4 orders of magnitude greater than the viscosity of the binary surfactant solution (CAPB + SLES) without HC8 and indicates a strong effect of the additive, octanoic acid, at a certain concentration. Using optical microscopy in transmitted-light polarization mode, we did not detect any birefringence, which directly proves that all ternary solutions up to 25 mM HC8 are isotropic micellar, rather than liquid-crystalline. In contrast to a similar system studied in Ref. [28], we can exclude the transition from isotropic micellar solution to liquid-crystalline phase as a probable explanation for the origin of the viscosity peak (Fig. 2a).
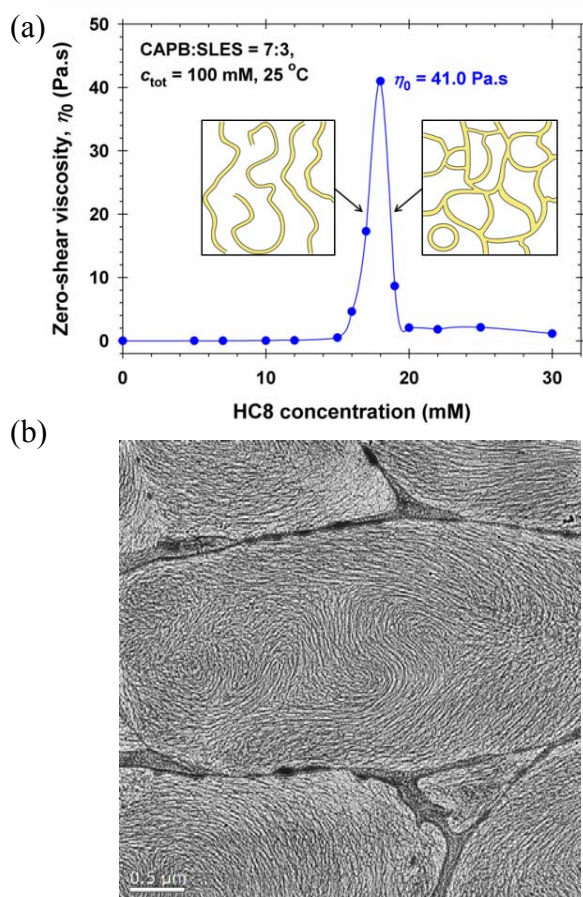
(a)

(b)

Fig. 2. *(a) Peak in viscosity due to growth of giant wormlike micelles. (b) Cryo-TEM micrograph of the entangled wormlike micelles formed at the peak of viscosity. To the left of the peak, the micelles are long and wormlike, whereas to the right of the peak – a network of multiconnected micelles is formed (details in the text).*

The cryo-TEM imaging revealed complex phase behavior: giant entangled wormlike micelles at the peak (Fig. 2b); long wormlike micelles to the left of the peak, and wormlike micelles co-existing with multiconnected micelles to the right of the peak; see the insets in Fig. 2a. In mixed micellar solutions, multiconnected micelles could form due to local inhomogeneities in the micelle composition. Such multiconnected networks provide stress relief mechanisms analogous to those for branched micelles, whose formation is typically associated with the viscosity reduction [27].

The results in Ref. [29] contribute to the understanding of the structure–rheology relation in mixed micellar solutions containing giant micelles. It is demonstrated that small changes in the micelle composition, which affect the molecular packing within the micelle and the intramicellar interactions, could produce tremendous growth of wormlike micelles that leads to a drastic change in both solution's rheology and microstructure. This effect could be utilized to control the physicochemical and rheological properties of surfactant formulations with applications in personal-care and house-hold detergency, and especially, to diminish the total surfactant concentration and to reduce the contamination of the environment by surfactants.

4. Micelle structuring in liquid films

Being self-assembled structures themselves, the surfactant micelles can further self-assemble in ordered layers when confined in the narrow gap between two surfaces, i.e. in a thin liquid film. Stepwise thinning of foam films was observed long ago by Johonnott [30] and Perrin [31]; this phenomenon was called *stratification* [31]. It was explained as a layer-by-layer pressing out of spherical colloid particles, e.g. surfactant micelles or latex beads, contained in the film [32,33]; see Fig. 3. The latter gives rise to an oscillatory force between the films surfaces [1], which was directly detected by the porous-plate-cell method [34,35] and surface-force apparatus [36,37]. Physically, this force is analogous to the oscillatory structural force detected in organic liquids and in aqueous solutions confined between two smooth solid surfaces

[1]. In the latter case, the structural units are molecules of the liquid rather than dispersed colloid particles. The colloid structural forces can stabilize liquid films and disperse systems, since they hamper the film drainage [32-35]. Such forces are observed also in more complex systems like protein solutions, surfactant-polymer mixtures, solutions of polyelectrolytes and amphiphilic block copolymers [38].

For uncharged particles (e.g. nonionic micelles), the height of the stratification step, Δh, is approximately equal to the diameter of the hard sphere, and is slightly decreasing with the rise of the particle volume fraction [35,37]. Note that Δh coincides with the period of the oscillatory structural force. The studies on stratification with ionic micelles showed that the height of the step is considerably greater than the micelle hydrodynamic diameter. An interesting finding is that the step height, Δh, is practically equal to the mean distance between the micelles in the bulk, δ_l, that is $\Delta h = \delta_l \equiv (c_{m\infty})^{-1/3}$, where $c_{m\infty}$ is the bulk micelle (particle) concentration [32]. Later, the fact that $\Delta h = (c_{m\infty})^{-1/3}$ was confirmed in experiments with charged nanoparticles and Monte Carlo (MC) simulations [39,40].

As demonstrated in our studies [41,42], the above dependence can be used to determine the micelle aggregation number, N_{agg}, from the experimentally measured step height, Δh:

$$N_{agg} = (c_s - \text{CMC})(\Delta h)^3 \qquad (1)$$

where the total surfactant concentration c_s and the CMC are expressed as number of molecules per unit volume. The values of N_{agg} obtained from Eq. (1) are in good agreement with the aggregation numbers determined by other methods.

As an example, in Fig. 3a we show data for the stepwise thinning (stratification) of free foam films containing spherical surfactant micelles comprised of ionic surfactants. The upper experimental curve is for the *cationic* surfactant cetyltrimethylammonium bromide (CTAB), whereas the lower curve is for the *anionic* surfactant sodium dodecylsulfate (SDS). The concentration of both surfactants is 50 mM. Fig. 3b illustrates the micellar structure in the film, which engenders the observed stepwise film thinning. For each

surfactant, at a given concentration the height of the steps is the same, $\Delta h = h_1 - h_0 = h_2 - h_1 = h_3 - h_2 = \ldots$. For the curves in Fig. 3a, substituting the average value of Δh in Eq. (1) we obtain $N_{agg} = 135$ and 65 for CTAB and SDS, respectively. These values are in very good agreement with the micelle aggregation numbers determined by other methods [41,42].
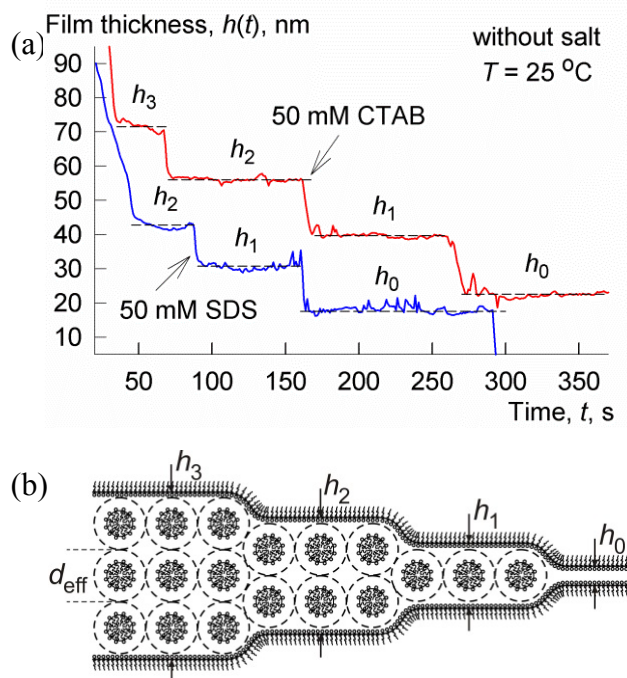

Fig. 3. (a) Stepwise thinning of liquid films formed from micellar solutions of the anionic surfactant SDS and cationic surfactant CTAB. (b) The steps in the thickness correspond to films containing different number of layers of micelles.

A theoretical expression for the effective diameter of the charged micelles, d_{eff}, is proposed [42]. For stratifying films, the theoretical d_{eff} coincides with the experimental Δh. The results allow one to determine the concentration domain, where the films with charged particles stratify, and lead to a convenient method for determining the aggregation number of ionic micelles from the stratification step height; see Eq. (1). The micelle charge, Z, and ionization degree, α, can be also determined [42].

5. Particle self-assembly on liquid interfaces

Colloidal particles could self-assemble not only when the particles are confined in a liquid film (Fig. 3b), but also when they are attached to a liquid/gas or liquid/liquid (e.g. oil/water) interface. In the latter case, the self-assembly

is due to attractive lateral capillary forces [7-13]. They appear when the contact of particles or other bodies with a liquid interface causes perturbations in the interfacial shape. The capillary interaction is due to the overlap of such perturbations which can appear around floating particles, vertical cylinders, particles captive in a liquid film, inclusions in the membranes of lipid vesicles or living cells, etc. In the case of floating particles, the perturbations are due to the particle weight; in this case, the force is proportional to the sixth power of particle radius and becomes immaterial for particles smaller than c.a. 10 μm [43]. In other cases, the interfacial deformations are due to the particle wetting properties; the resulting *immersion capillary forces* can be operative even between very small particles, like protein globules [8-10]. Such forces can be responsible for the experimentally observed two-dimensional particle aggregation and ordering. An analogy between capillary and electrostatic forces enables one to introduce "capillary charges" of the attached particles, which characterize the magnitude of the interfacial deformation and could be both positive and negative [8]. Moreover, the capillary interaction between particle and wall resembles the image force in electrostatics [9]. When a particle is moving bound to an interface under the action of a capillary force, one can determine the surface drag coefficient and the surface viscosity, provided that the magnitude of the capillary force is known [44].

Fig. 4a illustrates the physical origin of the immersion capillary forces. The deformations of the liquid surface arise due to the specific wetting (contact angle) of the particles by the liquid phase of the film. The capillary force between two submillimeter particles can be estimated from the expression [8-10]:

$$F \approx 2\pi\sigma\frac{Q_1 Q_2}{L} \qquad (2)$$

where σ is the surface tension of the liquid interface, L is the center-to-center distance between the two particles and $Q_k = r_k\sin\psi_k$, $k = 1,2$, are the "capillary charges" of the respective particles; ψ_k is the meniscus slope angle at the particle surface (Fig. 4a) and r_k is the radius of the particle contact line (denoted by dashed line in Fig. 4a).
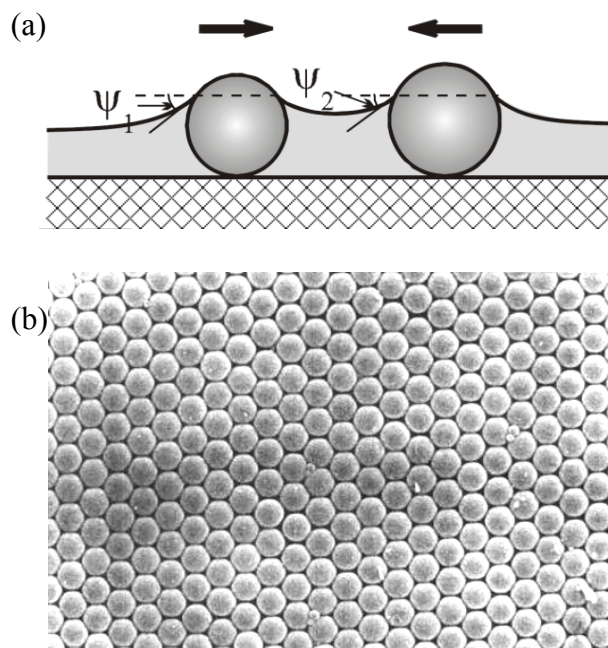

Fig. 4. (a) Illustration of the physical origin of the lateral capillary force acting between colloid particles immersed in a liquid layer [8]. (b) Well-ordered array of polystyrene latex spheres (1.7 μm in diameter) obtained under the action of such capillary forces in the process of convective self-assembly; SEM micrograph [45].

If many particles (like those in Fig. 4a) are immersed in a liquid film, the attractive capillary forces cause particle assembly into ordered clusters. The evaporation of the liquid (e.g. water) gives rise to convective fluxes of liquid toward the clusters. These fluxes bring new particles to the cluster periphery, so that the cluster grows and is transformed into a large ordered domain [11-13,45]; see Fig. 4b. This method for the formation of two-dimensional colloid crystals was called *convective self-assembly*.

Capillary interactions between particles bound to *spherical* interfaces are also considered by taking into account the special geometry and restricted area of such phase boundaries [9,10]. A similar approach can be applied to quantify the forces between inclusions (transmembrane proteins) in lipid membranes. The deformations in a lipid membrane, due to the inclusions, can be described theoretically in the framework of a mechanical model of the lipid bilayer [9,10].

Other sources of powerful lateral capillary forces are interfacial deformations due to

undulated or irregular contact line on the particle surface, say, engendered by surface roughness. In such a case, the particles interact as *capillary multipoles* [46-49]. Even undulations of nanometer amplitude may give rise to capillary interaction of magnitude greater than the thermal energy *kT*.

In the case of *electrically charged* particles, the interactions between colloids at a liquid interface are affected by both capillary attraction and electrostatic repulsion [50-54]. The surface pressure of monolayers from charged particles was investigated and was found to decay with the interparticle distance as L^{-3} [52-54].

6. Conclusions

Under the action of attractive hydrophobic force, amphiphilic molecules form various self-assembled structures in aqueous solutions: spherical and wormlike micelles; vesicles; lamellar and hexagonal phases, etc. (Fig. 1). In our studies, a quantitative physicochemical model of micelle-monomer equilibria was developed, which allows one to predict the concentration and composition of monomers; the micelle ionization degree, aggregation number and charge, as well as the electric conductivity of micellar solutions [16,17].

Moreover, it was experimentally established that at a given concentration of added fatty acid, the viscosity of ternary mixed surfactant solutions exhibits a high and sharp peak, a "resonance" [24,29]. By cryo-TEM, it was established that to the left of the peak wormlike micelles of increasing length are formed; at the peak itself – entangled wormlike micelles are observed, whereas to the right of the peak the cryo-TEM micrographs show a network of multi-connected micelles [29]. Transitions from wormlike to disclike micelles have been also detected and theoretically analyzed [24]. These results can find applications for the understanding and control of the properties of concentrated micellar systems in personal-care and house-hold detergency, such as shampoos, hair conditioners; formulations for cleaning and dish-washing, etc.

When confined in thin liquid films, spherical surfactant micelles or colloidal particles form ordered layers. If subjected to external pressure, such liquid films exhibit a stepwise (layer-by-layer) thinning of the micellar (particle) structure within the film; see Fig. 3 and Refs. [32-35]. A closed-form semiempirical model of the oscillatory-structural force was applied to interpret the behavior of stratifying liquid films [35,37]. The inverse problem was also solved – it was demonstrated that from the step height Δh one can determine the micelle aggregation number, N_{agg}; see Eq. (1) and Refs. [41,42].

Self-assembly of colloidal particles is also observed when they are attached to a liquid interface (e.g. air/liquid, oil/water, etc.), including the case of the surface of a wetting film; see Fig. 4. In this case, the particle ordering is due to the interplay of attractive capillary forces and convective fluxes due to the evaporation of the liquid (convective self-assembly) [11-13]. Quantitative theory of the lateral capillary forces was developed and applied to systems, where the interfacial deformation is induced by different physical factors: gravitation and wetting [7-10]; undulated contact line [47-49], and electrostatic forces [50,51]. The simultaneous action of capillary and electrostatic forces in monolayers of charged particles at a liquid interface has been also studied, both experimentally and theoretically [52-54].

The attractive lateral capillary forces between similar particles bring about particle aggregation and ordering, and play an important role in the production of various two-dimensional structures, which is the main reason for the growing interest in this area. The obtained structures have found numerous applications for producing photonic crystals; photo- and electro-luminescent semiconductor materials; nanostructured surfaces for photo-electrochemical and photo-catalytic processes; optical elements, such as diffraction gratings and interference filters; micro-patterning by non-densely packed interfacial colloidal crystals; paint coatings of new optical properties; samples for electron microscopy of viruses and proteins; sensors in analytical chemistry; miniaturized immuno-sensors and immunoassays; nano-lithography and micro-contact printing; production of structured porous (incl. nanoporous) materials by using colloid crystal templates; electronic elements

with non-linear electronic, plasmonic or photonic properties, substrates for quantum electronic devices, etc.; for review see Ref. [55].

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