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Phase behaviour and self-assembly patterns of surfactant mixtures in solutions

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Abstract. Modern trends in studies of solutions of surfactant mixtures are discussed. The emphasis is placed on thermodynamic and molecular-statistical modelling of the phase behaviour and self-assembly patterns. The methods for prediction of properties of mixed micellar solutions based on the data for solutions of individual surfactants and the methods for calculation of the size, shape and composition distribution of micelles using the quasi-chemical models that take into account the molecular characteristics of components are analysed. Recent studies of surfactant solutions using computer experiments are surveyed. Theoretical approaches to the description of self-assembly phenomena in solutions of amphiphilic polymers and of their mixtures with low-molecular-mass surfactants are discussed. The bibliography includes 309 references.

I. Introduction

Self-organised solutions of surfactants are the most common nanostructured liquid systems; their studies started in 1913 with the discovery of micelles by McBain. Over the last decades, the substantial progress in understanding the nature of phenomena occurring in such systems and diversity of their behaviour has been made owing to the development of novel experimental techniques, methods of theoretical simulations and computer-assisted calculations.[1–3] The range of surfactants under study has extended significantly. Surfactants with complex molecular architectures attract ever increasing interest, in particular, the gemini surfactants that combine two polar head groups and two non-polar tail groups linked through a bridge in one molecule.[4] Surfactants with fluorocarbon and siloxane hydrophobic chains, biological surfactants [5] and surfactants with head groups modified by introduction of specific substituents bearing chemical or biological functions [6,7] are the subjects of intense investigations. For instance, the self-assembly of surfactants designed by introduction of peptides and oligopeptides gives rise to structures that mimic natural objects, such as biological membranes. Solutions containing two or more surfactants are of particular interest [3,8–10] since mixtures rather than individual surfactants are most abundant in practice. By combining different surfactants one can deliberately adjust properties of the system without recourse to the synthesis of new substances. Another important factor is that technological processes adopted in industry typically afford surfactant mixtures. Isolation of individual components from such mixtures can prove too time-consuming and costly and thus it is desirable to learn the effect of different admixture surfactants on the main component in order to produce formulations with optimum properties.

Mixtures of surfactants with water-soluble polymers have been attracting growing interest over the last two decades. The majority of industrial and household surfactant compositions contain polymers. Amphiphilic water-soluble polymers can be considered as modified surfactants. Such polymers can substantially reduce surface tension of the solution, be adsorbed at interfaces, form micelles in the solution, solubilise non-polar species and be assembled into liquid-crystalline structures. Furthermore, they tend to form mixed micelles with low-molecular-mass surfactants.[1]

The recognition of the similarity between the self-assembly phenomena in colloid systems, polymers and biological structures stimulated emergence of an interdisciplinary field of science that, in terms of physics, chemistry, materials science, biochemistry and engineering, deals with soft matter, *i.e.*, diverse systems manifesting an intermediate degree of ordering between crystalline solids and ordinary liquids. These include micellar solutions, gels and liquid crystals. Hamley, the author of one of the first books devoted to soft matter, expressed confidence that the soft-matter materials will play an ever increasing role and largely replace solid nanostructured materials in the future due to development of new design methods, which can now be only dreamed about.[11]

The modern applications of surfactant solutions encompass production of detergents, drugs, cosmetics, nutrition products and dyes, oil production technologies, chemical, biochemical and pharmaceutical industries where surfactants can control the rate and direction of chemical processes, perform syntheses of mesoporous materials, nanocrystals and periodic composites, produce gels with desired morphology, etc. Furthermore, surfactants are applied to affect colloids stability, emulsification, flocculation, structuring, suspension formation and rheological properties. Micellar and vesicular polymeric systems acquire growing importance in pharamacology (in particular, for incapsulation of drugs)

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and chemical catalysis. Polymer gels with different structures are being actively investigated and widely used.

Strictly speaking, mixed micellar surfactant solutions are systems composed of two or more surfactants with each component capable of micelle formation in its own solution. In a broad sense, these are solutions where mixed micelles are formed. This definition also includes the case where only one component is capable of micelle formation, whereas the second diphilic component (*e.g.*, a fatty alcohol or acid) does not form micelles in its individual solution but can penetrate into micelles of the first component. The mixed micellar systems considered in the present review fall into the latter, extended definition. The emphasis is placed on the self-assembly in aqueous solutions of low-molecular-mass surfactants; studies of similar phenomena in solutions of block-copolymers and of their mixtures with surfactants are also cited. The review discusses results of experimental studies as well as problems of the thermodynamic and molecular-statistical modelling of mixed micellar systems.

Over the last few years, micellar solutions of surfactant mixtures have been the subject of extensive investigations, especially, in the USA, Japan and Germany. Many combinations of non-ionic, anionic and cationic surfactants have been studied as well as their mixtures with zwitter-ionic ones. The major results obtained prior to the mid-1990's have been surveyed in several monographs.[2,3,8,12] Of particular interest are synergistic effects, which occur upon mixing of surfactants and result in an increase in the surface activity and viscosity of the solution, decrease in the critical micelle concentration (CMC) and growth of micelles.[9] Recent years are characterised by the increased attention of researchers to the internal structure of aggregates; the capabilities of the experimental elucidation thereof has expanded dramatically due to the modern instrumentation. Novel types of self-assembly in surfactant solutions have been discovered (for instance, formation of multilamellar vesicles). The bulk and quality of the experimental data on the sizes and shapes of aggregates,[13–16] micellar dynamics[17] and, more important, composition of micelles[18–21] have increased substantially. The experimental techniques of structural studies include light scattering, small-angle neutron scattering, electron microscopy, NMR and ESR spectroscopies. Of fundamental imporance in the directional search for systems with desired properties is the establishment of the relationship between the molecular structure of a surfactant and its aggregation behaviour in a solution. The progress in this field relies on the achievments in the thermodynamic and molecular-statistical studies of solutions of individual surfactants,[22–26] but additional complications appear due to a variable composition of the micelles and complex patterns of the interparticle interactions. Computer simulation methods play an increasingly important role in studies of micellar solutions.[27,28] The prediction of properties of mixed solutions based on the data for individual surfactants is of great applied significance. Semiempirical thermodynamical models are often useful in solving this problem.[29]

The present review does not pretend to a comprehensive coverage of the molecular-thermodynamical investigations into the aggregation and phase behaviour of surfactant mixtures. Still, it reflects the major directions of studies and the progress in the field and illustrates the interrelations between the experimental and the theoretical methods.

II. Forms of aggregation. Synergistic effects

Highly dilute solutions of surfactant mixtures as well as solutions of individual surfactants contain the monomeric forms of the surfactant molecules. At the CMC surfactant aggregates. The region of the isotropic micellar solutions extends up to the boundary corresponding to the transition into the liquid-crystalline (mesomorphic) state (Fig. 1). Within the isotropic region, substantial structural transformations can occur, such as transition of spherical micelles to globular (ellipsoidal) and cylindrical ones (Fig. 2 *a–c*), growth of the latter, emergence of worm-like micelles that form a network. Furthermore, vesicles can form, which represent closed (typically, spherical) bi- or multilayer structures with solvent incapsulated (Fig. 2 *d*). Sometimes, especially in the case of non-ionic surfactants, liquid–liquid phase splitting can occur (the solubility diagram has a lower critical point). In the liquid-crystalline region, various structures, such as hexagonal, lamellar, nematic or cubic, can be realised, depending on the nature of the system, concentration of the surfactant and additives, temperature and other parameters (Fig. 3).[1,2,30,31] In some specific cases, a bicontinuous phase is observed. The lower-temperature boundary of existence of a homogeneous surfactant solution is determined by crystallisation of the surfactant (the so-called Krafft boundary) or water. Sometimes, cooling of a micellar solution initiates gelation rather than crystallisation, but such a state is usually unstable.

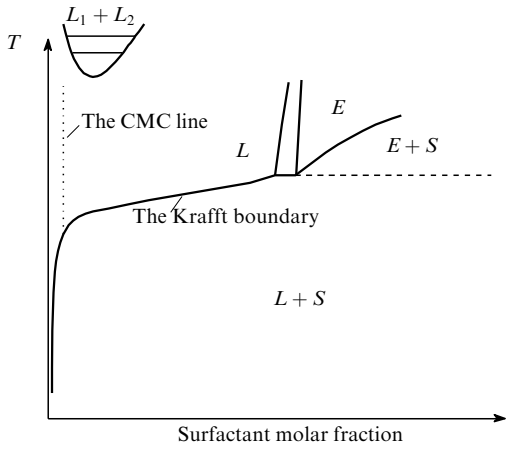


Figure 1. A fragment of a schematic phase diagram composition–temperature for a system surfactant–water.
L is a micellar solution, S is a solid phase, E is a liquid-crystalline phase, L_1 and L_2 are isotropic liquid phases.

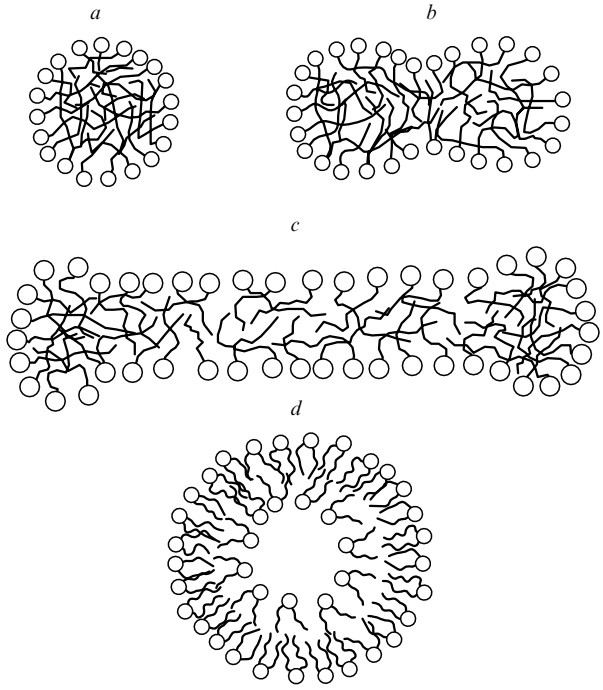


Figure 2. The most typical shapes of aggregates in surfactant solutions: a spherical (*a*), a globular (*b*) and a spherocylindrical (*c*) micelles; a bilayer vesicle (*d*).

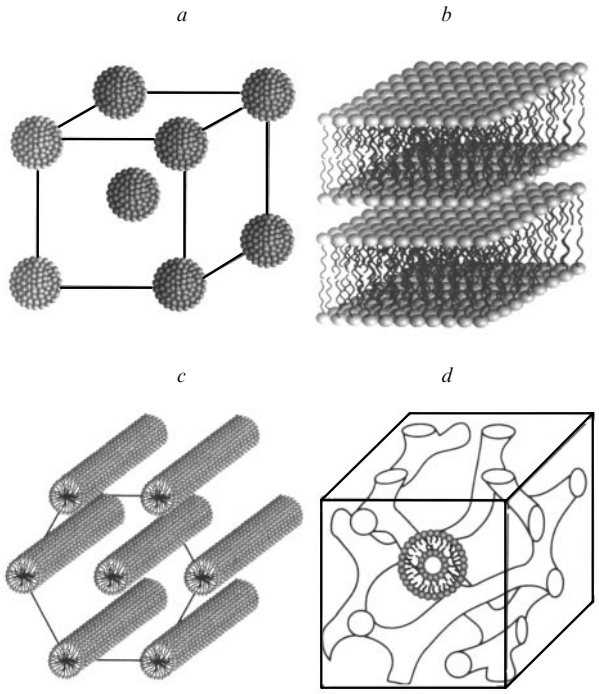


Figure 3. Cubic (*a*), lamellar (*b*) and hexagonal (*c*) liquid-crystalline structures; a bicontinuous structure (*d*).

In overall, the phase and aggregation behaviour of solutions containing two or more surfactants is characterised by diversity and complexity, although their major features can be observed in solutions of individual surfactants. The methods for the determination of CMC, phase boundaries and structures of aggregates and mesomorphic phases for mixed micellar systems are the same as for solutions of individual surfactants.[3] What is problem specific to mixed systems is the compositional analysis of aggregates. To solve the problem, such techniques as NMR,[32,33] small-angle neutron scattering,[18] ESR,[34] potentiometry with electrodes selective to the surfactant ions,[35,36] ultrafiltration through a membrane that allows monomeric molecules to pass but traps micelles,[37,38] *etc*. are typically applied.

The specificity of the behaviour of mixed solutions of two or more surfactants as compared to solutions of individual surfactants is related to the entropy of mixing (which is observed even for ideal solutions) and non-ideality effects due to differences in the interactions between identical and different molecules. The first models of micellar solutions of surfactant mixtures suggested by Lange [39] and Shinoda [40] postulated that mixed micelles behave as an ideal solution. Within the ideal solution approximation, Clint derived an equation that related the CMC of a surfactant mixture to the relative content of the individual surfactants and their CMC.[41] Mixtures of two surfactants belonging to one type, *i.e*., both ionic [39,40,42,43] or both non-ionic,[41,44] behave in a way similar to that expected for an ideal solution. However, many mixtures demonstrate substantial deviations from ideality with the negative deviations due to synergistic effects. These are manifested in additional reduction of the surface tension, a decrease in the CMC, an increase in the viscosity and some peculiarities of the ternary phase diagrams (*e.g*., extention of the region of a lyotropic liquid-crystalline phase towards lower concentrations of the surfactant, crystallisation of a 1 : 1 compound from surfactant mixtures with a nearly equimolar ratio of components). For instance, synergistic effects are observed in mixtures of an ionic and a non-ionic surfactants due to the fact that polar groups of the latter become incorporated between the similarly charged heads of the former thus reducing their electrostatic repulsion.[45] The most pronounced effects are typical of mixtures of a cationic and an anionic surfactants, which form ionic pairs resembling a zwitter-ionic surfactant with a double tail.[3,9,46] This is accompanied by liberation of formerly bound counterions, which increases the ionic strength of the solution and produces the positive entropy effect. In solutions of such mixtures (commonly referred to as catanionic) at nearly equimolar concentrations, precipitation or segregation often occur at temperatures where solutions of individual surfactants are homogeneous.[47] Such solutions often manifest viscoelasticity. Mixtures of an anionic and a weakly basic surfactants that can be protonated (*e.g*., alkylamine oxides, alkylamines or alkylethoxyamines) reveal strong synergistic effects that are enhanced upon acidification.[48–58] In an acidic medium, such a system becomes similar to a mixture of a cationic and an anionic surfactants and is characterised by very low values of CMC. For instance, CMC of aqueous solutions of sodium dodecyl sulfate and dodecyldimethylamine oxide at 323.2 K are 9.5 mol m^{-3} and 1.6 mol m^{-3}, respectively, whereas their 1 : 1 mixture is characterised by CMC of 0.65 mol m^{-3} and 0.003 mol m^{-3} at normal acidity of the solution and at pH 2, respectively.[58] Among systems manifesting positive deviations from ideality, mixtures of hydrocarbon and perfluorinated surfactants having hydrocarbon similar polar groups are most studied. These surfactants are poorly compatible, their mixing can yield two types of micelles.[59–62]

Micelles with non-classical shapes (*i.e*., other than spherical, globular and spherocylindrical) attract significant attention. In particular, tablet-shaped micelles were found in some catanionic systems using small-angle neutron scattering, although this shape is rarely encountered and sometimes appears to be non-equilibrium.[63] An interesting phenomenon is the network formation by long worm-like micelles. Due to this the solution can become viscoelastic (see Section VI). Vesicles are yet another type of aggregates frequently occurring in surfactant mixtures. These are also observed in solutions of many individual surfactants (*e.g*., phospholipids, other surfactants with two tails or some surfactants with fluorocarbon radicals). The formation of vesicles is particularly typical of mixtures of a cationic and an anionic surfactants,[9,64] which occurs not only in water but in other polar solvents as well.[65] Typical vesicles are characterised by bilayer structures and sizes from *ca*. 100 nm to a few micrometers. In their local properties, vesicles are similar to planar bilayers and thus can serve as convenient models of biological membranes. For a number of surfactant mixtures, it was found that relatively small vesicles (15–40 nm) are formed in dilute solutions, which convert into multilayer onion-like vesicles with an increase in the surfactant concentration.[66] Another type of behaviour has recently been observed in a system sodium oleate–octanol–water: at a high surfactant concentration, small monodisperse bilayer vesicles are assembled into a hard gel that represents a densely packed ordered cubic-like phase.[67] According to studies of mixtures of an ionic and a non-ionic surfactants, an increase in the fraction of the ionic component favours the formation of vesicles, which is in accord with the theoretical predictions indicating the stabilisation of vesicular structures with respect to planar lamellar ones with an increase in the charge density of the bilayers.[68,69] The influence of the ratio of two surfactants, their total concentration, presence of additives and other factors on the transformation of vesicles into micelles and *vice versa* is currently under investigations. The conversion of vesicles into micelles can be promoted by shear stress.[70] For a mixture of tetradecyldimethylamine oxide with dodecylethoxysulfonic acid [$C_{12}H_{25}(CH_2CH_2O)_{2.5}SO_3H$], shear induced the transformation of a lamellar structure into a vesicular one.[71] Evidently, an assesment of the role played by the thermodynamical and kinetic factors in the formation of vesicular systems requires further investigations. Vesicular systems with polymer additives are of special interest. In particular, such additives can stabilise vesicular structures.[72]

The liquid crystal structures and phase boundaries were studied for a number of surfactant mixtures.[2,42,55,73–79] Mixing of different types of surfactants can result in the emergence of new

phases. For instance, upon mixing of tetradecyldimethylamine oxide with sodium dodecyl sulfate, the region of isotropic solutions becomes narrower and an extended region of a nematic phase appears (the total surfactant concentration at the phase boundary is less than 10 mass % at a component ratio of 1 : 1).[55] The available data suggest that the transition of the micellar solution into the liquid-crystalline state can be strongly affected by salts.[2] The phase behaviour in aqueous ethanol solutions of surfactant[80] and mixtures surfactant – water – oil[2,81] have been considered in numerous publications but these systems are beyond the scope of the present review.

III. The critical micelle concentration and the Krafft boundary. The pseudophase model of micellar solutions

The critical micelle concentration and the Krafft boundary are two important characteristics of surfactant solutions. The former defines the tendency of a surfactant towards aggregation and the concentration of monomeric molecules in the aqueous environment of micelles. The latter represents the lower-temperature boundary of stability of homogeneous surfactant solutions, which is determined by the equilibrium between the surfactant solution and the solid phase. The temperature, at which the solid phase starts to precipitate should be sufficiently low for detergents, cosmetics, micellar solutions employed in oil production, *etc*. Therefore, a typical problem of the design of industrial surfactant formulations consists of lowering the Krafft boundary with various additives. At the same time, crystallisation is an efficient means of purification and isolation of individual surfactants from mixtures. In this case, the knowledge of the diagrams of crystallisation is required for optimising the corresponding processes. Thus, the determination of CMC and precipitation temperature for systems containing two or more surfactants based on the respective data for solutions of individual surfactants represents a topical problem. This problem can be solved within a relatively simple model that approximates a homogeneous micellar solution as a combination of two pseudophases, *viz*., an aqueous and a micellar.[82] Although the pseudophase model has limitations[22] it appears quite useful in the description of effects of mixing. Holland and Rubingh derived the following equation for the CMC of a non-ideal mixture of two surfactants based on the pseudophase model:

$$\frac{1}{\mathrm{CMC}} = \frac{y_1}{f_1\mathrm{CMC}_1} + \frac{y_2}{f_2\mathrm{CMC}_2},$$

where $y_i = C_i/(C_1 + C_2)$ is the relative molar fraction, C_i is the molar concentration of the ith surfactant in the solution, f_i is its activity coefficient in a micelle ($f_i = 1$ for a micelle composed of only the ith surfactant); $i = 1, 2$.[83]

Starting from the late 1970's, the concept of a regular solution, which enabled approximate consideration of deviations from ideality in the behaviour of mixed micelles has become widely adopted.[12,83] One of the basic parameters within the regular solution theory is interchange energy, which characterises the difference between the interaction energies of identical and different surfactant molecules. Typically, one uses a dimensionless parameter β defined as the interchange energy divided by kT (k is the Boltzmann constant and T is the temperature). For a binary regular solution, the dependence of the activity coefficients on the mole fractions (x_i) of the components in mixed micelles is symmetrical:

$$f_1 = \exp[\beta(1 - x_1)^2];\ f_2 = \exp[\beta x_1^2].$$

The value of β is estimated based on the CMC values for individual surfactants and at least one solution containing both surfactants. Such estimates have been obtained for many micellar systems.[12,84,85] Calculations of β using the molecular-statistical model of mixed micelles[86,87] are in satisfactory agreement with the respective estimates from the experimental data. In particular, data on CMC and adsorption of aqueous solutions containing dodecylpyridinium bromide and a non-ionic surfactant have been interpreted within the regular solution model and compositions of the micelles and adsorbtion layers were calculated.[88] However, recent investigations have shown that the simple one-parameter regular solution model fails in many cases. Several two- and multiparameter models of non-ideal mixed micelles have been proposed[10,89,90] that allowed the description of non-symmetrical dependences of the activity coefficients on the surfactant ratios. However, the increased number of fitting parameters diminishes the attractiveness of these, virtually empirical, models since they possess only limited predictive power.

It has been known for a long time that micelle formation in surfactant solutions is affected by the addition of salts. This effect appears as a decrease in the CMC of an ionic surfactant due to shielding of the electrostatic repulsion between the likely charged polar groups of the surfactant molecules. The dependence of CMC of an ionic surfactant on the salt concentration follows approximately the Corrin – Harkins rule, which establishes the linear correlation between the logarithms of CMC and the counterion concentration C:

$$\log \mathrm{CMC} = -k_{\mathrm{CH}} \log C + b_{\mathrm{CH}}\ , \qquad (1)$$

where k_{CH} and b_{CH} are constants specific to the surfactant.[91] This presumes that the surfactant and the salt contain identical ions. If both electrolytes are 1 : 1-charged, then $C = C_{\mathrm{S}} + \mathrm{CMC}$, where C_{S} is the salt concentration; the coefficient k_{CH} is taken equal to the degree of counterion binding by a micelle in the salt-free solution. Equation (1) is valid at relatively low salt concentrations. At higher concentrations, the slope of the function log CMC *vs*. log C is altered, which can be due to the change in the mean activity coefficient of the dissociated surfactant ($f_{\pm}$). Taking into account the activity coefficient, the following expression can be written for a mixture of two 1 : 1-charged surfactants and a salt:

$$\log \mathrm{CMC} + 2\log f_{\pm(\mathrm{CMC})} \approx -\log(C_{\mathrm{S}} + \mathrm{CMC}) + b,$$

where the parameter b is determined by the aggregation number and the micelle formation constant.[92] However, this expression neglects the possibility of an incomplete binding of counterions by the micelles, *i.e*., it assumes that the degree of counterion binding [k_{CH} in (1)] is equal to unity. A similar approximation was elaborated for surfactants and salts with arbitrary stoichiometries.[22,92] Simultaneous treatment of the non-ideality effects (*i.e*., changes in the activity coefficients) and an incomplete binding of ions remains a current challenge. The validity of the Corrin – Harkins rule was discussed[93] on the basis of the Poisson – Boltzmann equation within the approach developed by Evans, Mitchel and Ninham.[94] The dependence of the degree of counterion binding on the ratio of a non-ionic and an anionic surfactants in the solution was analysed in the context of deviations from the linear equation (1).[95,96] Some systems, such as solutions of alkyltrimethylammonium halides with alkali-metal halides as additives, reveal an abrupt change in the slope of the log CMC *vs*. log C lines at a certain salt concentration, which is normally interpreted as the coincidence of two CMC corresponding to the starting point of micelle formation and the transition sphere → cylinder, respectively.

A modification of the ideal pseudophase model, which takes into account the electrostatic contribution into the change in the Gibbs energy upon transfer of a surfactant ion (*e.g*., a dodecyl sulfate anion) from the solution onto the charged surface of a micelle, was proposed to describe CMC of mixtures of anionic surfactants containing different counterions.[97] This approach was applied to calculate CMC of individual surfactants in the absence and in the presence of a salt as well as of mixtures of two anionic surfactants having singly and doubly charged counterions in the absence of a salt. The model was also extended to mixtures of two surfactants and a salt.[98] The calculations show that the depend-

ence of the CMC on the counterion concentration is mainly affected by the charge of the counterions whereas their nature is of low significance, which is in agreement with the experimental data. According to a recently suggested scheme of estimating CMC for a surfactant mixture based on the pseudophase model using the Gibbs–Duhem relation and the Poisson–Boltzmann equation, the synergistic effects upon mixing of an ionic and a non-ionic or of two ionic surfactants are dominated by the entropic contribution.[99] A description of CMC for mixtures of a cationic and an anionic surfactants, where the charge density on the surface of mixed micelles is strongly reduced as compared to that for the respective one-component micelles and synergistic effects are strong (within the regular solution model, the values of the parameter β for such systems lie between -20 and -30), remains a current challenge. The systems manifesting strong pH-dependent changes in CMC are of significant interest.[100]

The majority of published data concerning crystallisation from mixed surfactant solutions dealt with the phase boundaries at constant temperature (*i.e.*, the concentration of an additive as a function of the surfactant concentration in a concentrated solution). The main attention was paid to the effects of additives on the precipitation of anionic surfactants.[101–112] Until recently, data on the precipitation temperature as a function of the relative fraction of one of the surfactants at a constant total surfactant content, which corresponds to the Krafft boundary, were scarce and predominantly related to relatively low total surfactant concentrations, often just slightly above CMC.[47, 113–116] A solid phase that crystallises from a micellar solution typically has constant stoichiometry (*e.g.*, pure surfactant, its hydrate, a complex of two surfactants or ice) whereas solid solutions of surfactants are rarely formed.[117] Therefore, the most common type of the phase diagrams are eutectic diagrams. In the simplest case, such a diagram has two branches corresponding to precipitation of a pure surfactant (or ice) (Fig. 4 *a*). Recently, equilibria of a variety of micellar solutions (aqueous solutions of two non-ionic, two ionic or an ionic and a zwitter-ionic surfactants, solutions of surfactants with addition of salts or alcohols) with solid phases have been elucidated.[29, 44, 58, 118–125] Mixtures of sodium or magnesium dodecyl sulfate [NaDS or $Mg(DS)_2$, respectively], which are anionic surfactants, with alkyldimethylamine oxide (AO), which is a non-ionic surfactant that undergoes protonation and acts as a cationic surfactant in acidic media, were shown to behave anomalously: a strong dependence of the solubility diagrams on pH was observed for the first time (Fig. 4 *b*).[58] In the case of acidic solutions, the diagram precipitation temperature *vs.* mole fraction of AO (for a constant total surfactants content) reveals a maximum corresponding to the composition 1 : 1. According to chemical analysis and X-ray diffraction studies, a 1 : 1 cation-anionic complex (AOH^+DS^-) is crystallised from solutions with nearly equimolar ratios of the two surfactants, while the nature of the cation of dodecyl sulfate is not important. In addition to the 1 : 1 compound, complexes with other stoichiometries are likely formed at higher relative concentrations of AO.

Models allowing prediction of solubility diagrams for ternary systems based on the data for aqueous solutions of individual surfactants (*e.g.*, precipitation temperature at constant concentration of the solution, enthalpy of dissolution) are of great interest, in particular, from the practical viewpoint. The problem can be solved using the pseudophase model of a micellar solution. Equilibrium conditions can be expressed in variables of any of the two pseudophases, *viz.*, aqueous (x_i^{W}) and micellar (x_i^{M}). For ionic surfactants, variables describing the composition of the aqueous pseudophase and a concept of the solubility product are traditionally applied.[101] For instance, the solubility product (K) of the salt $A(DS)_n$ can be written as

$$K = a_{A^{n+}} a_{DS^-}^n ,$$

where a_i is the activity of free ions i in the saturated solution ($i = A^{n+}$, DS^-). However, the application of this approach to compositions far from CMC faces difficulties in estimating the concentrations of free surfactant ions and their counterions. It was established that the applicability of the pseudophase model for predicting the phase behaviour of mixed solutions in the range of relatively high concentrations based on the data for solutions of the individual surfactants can be extended making use of the concentration variables of the micellar pseudophase (this is valid for both non-ionic and ionic surfactants).[29, 118–125] Since the micellar pseudophase is composed of only two surfactants (components 1 and 2) and the water (component 3) content may be neglected, the condition of the equilibrium between the ternary

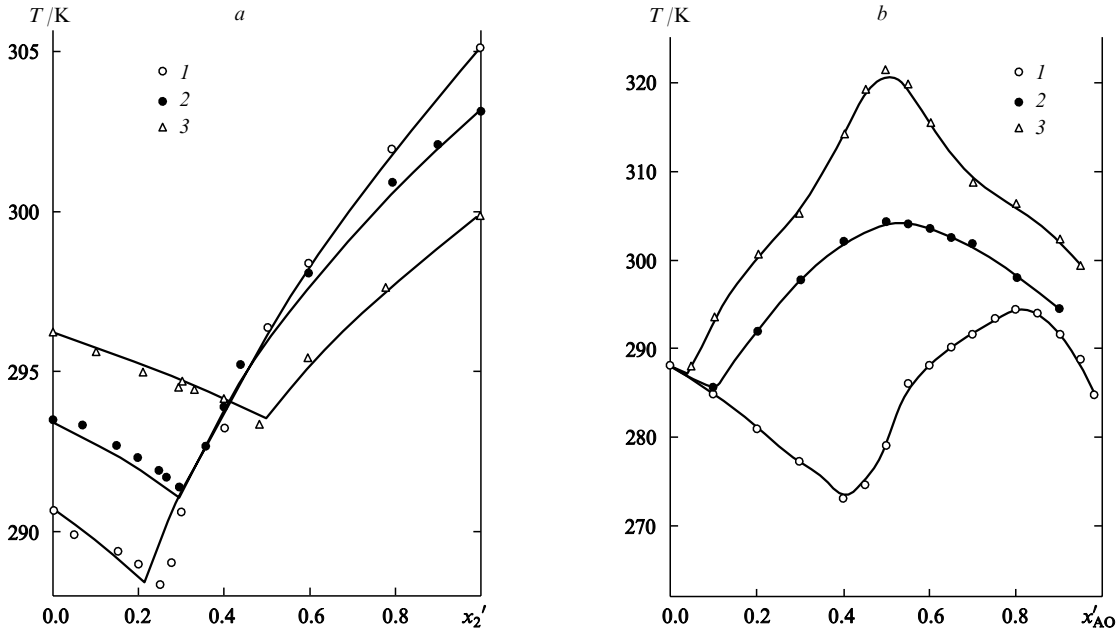


Figure 4. Precipitation temperature as a function of the surfactant relative content.[29]
(*a*) Water–salt solutions of NaDS and $Mg(DS)_2$; $x_2' = x_{Mg_{0.5}DS} / (x_{NaDS} + x_{Mg_{0.5}DS})$; C_{NaCl} /mol litre^{-1}: 0 (*1*); 0.1 (*2*); 0.3 (*3*); (*b*) aqueous solutions of NaDS and dodecyldimethylamine oxide (AO) with variable acidities; $x'_{AO} = x_{AO} / (x_{NaDS} + x_{AO})$; $x'_{HCl} = x_{HCl} / (x_{HCl} + x_{AO})$: 0 (*1*); 0.3 (*2*); 0.6 (*3*).

solution and the solid surfactant can formally be reduced to equations of the biphasic equilibrium for the two-component system 1 – 2. For the line of crystallisation of the surfactant 1:

$$\Delta T = \frac{RTT_0}{\Delta H_1} \ln a_1(x_1^{\mathrm{M}}), \quad (2)$$

where $\Delta T = T - T_0$, T_0 and T are precipitation temperatures of the surfactant from its individual and mixed (at identical total surfactants concentration) aqueous solutions, respectively, R is the gas constant, ΔH_1 is the enthalpy of dissolution, a_1 is the activity in a mixed micelle ($a_1 = 1$ provided that $x_1^{\mathrm{M}} = 1$). If the micellar phase behaves as an ideal solution, then:

$$\Delta T = \frac{RTT_0}{\Delta H_1} \ln x_1^{\mathrm{M}}. \quad (3)$$

Equations (2) and (3) are also valid for surfactant solutions containing additives that do not form micelles on their own (*e.g.*, low-molecular-mass alcohols). These equations suggest that a substantial decrease in the precipitation temperature can be induced by additives that form mixed micelles with the main surfactant, and it is the distribution coefficient of the additive between the micellar and aqueous phases that plays a decisive role. For salt-free solutions of mixtures of two non-ionic or ionic surfactants at concentrations substantially above CMC, the composition of micelles is very close to the composition of the surfactant mixture without taking solvent into account: $x_1^{\mathrm{M}} = x_1/(x_1 + x_2)$, therefore, ΔT depends only on the relative concentrations of the two surfactants but is independent of their total content. The eutectic-type diagrams precipitation temperature – relative concentration of the surfactant for salt-free mixtures of ionic surfactants as well as for mixtures of non-ionic surfactants can be modelled in a similar way. In the case of ionic surfactants, this approach is simpler than that based on the concept of the solubility product. For solutions of ionic surfactants in the presence of salts or low-molecular-mass amphiphilic additives, the ion exchange (for the former) or distribution coefficient (for the latter) between the micelles and the aqueous environment should be taken into account. An account for the non-ideality of mixed micelles and the aqueous pseudophase is a significant aspect of the modelling. For this purpose, approximate models developed for molecular solutions (*e.g.*, the regular solution model, the Flory – Huggins model, *etc.*) are applied.[126] The strong dependence of the solubility diagram for the system sodium dodecyl sulfate – alkylamine oxide – water on pH can be reproduced within a model taking into account protonation of alkylamine oxide and formation of a cation-anionic complex.[29, 58]

In addition to the practical importance, studies of the solubility diagrams represent an efficient means of gaining information on the thermodynamical properties of micellar solutions, the degree of non-ideality in the behaviour of mixed micelles and specific interactions between components of the mixtures. The major difficulties in the calculations of the solubility diagrams for micellar solutions of surfactant mixtures relate to the description of the non-ideality and often to the lack of data on the temperatures and enthalpies of dissolution for individual surfactants. Definitely, the extension of the experimental database is an important task.

IV. Molecular-thermodynamical models of aggregation

Starting from pioneering works by Tenford,[23, 127] Israelachvili, Mitchell and Ninham,[24] Ruckenstein and Nagarajan[128] published in the 1970's, strenuous efforts have been put into development of approximate models establishing relationships between the molecular properties of components and their aggregation behaviour (this is often referred to as the molecular-thermodynamic approach). The formation of a micelle is described as a chemical reaction, the equilibrium concentrations of monomers and aggregates are calculated from the Gibbs energy of the aggregate formation according to the law of mass action. A detailed analysis of the quasichemical approach has been performed by Rusanov.[22] Numerous studies were devoted to estimating different contributions of micelle formation into the Gibbs energy, elucidation of their relationships with the molecular characteristics of the components as well as with the shapes and sizes of the aggregates.[127 – 137] The dependence of the stability of aggregates having specific shapes (spheres, cylinders or planar bilayers) on the packing of the surfactant molecules has been analysed.[24] Each type of the aggregates is characterised by its own range of values of the so-called packing factor $P = v/al$, where a is the surface area of the hydrocarbon core per surfactant molecule in the aggregate, v is the volume of the hydrocarbon radical and l is its length. The packing factor is equal to the mean cross-sectional area of the radical divided by the area occupied by a polar head of the surfactant on the surface of the hydrocarbon core. The packing factor increases in the order spherical micelles → rod-like micelles → planar bilayers ($1/3 \rightarrow 1/2 \rightarrow 1$). The values of the packing factor larger than unity correspond to inverse micelles that form in non-polar media. The packing conditions were generalised to the case of aggregates with concave surfaces and vesicles with a convex and a concave surfaces simultaneously.[138] The effective cross-sectional area of a polar head is affected not only by the structure of the surfactant molecule but by other factors as well. In particular, addition of a salt to a micellar solution of an ionic surfactant gives rise to a decrease in the area of the polar head. This occurs because the degree of counterion binding increases, the electrostatic repulsion between likely charged heads is partially screened and thus they approach closer to each other. As a result, the addition of a salt promotes transition of spherical micelles to rod-like. If the additive forms mixed micelles with the primary surfactant, the packing conditions are mainly affected by the sizes and shapes of polar and non-polar parts of the additive molecule.

The quasichemical model for a solution of two surfactants A and B considers the process:

$$g_{\mathrm{A}}\,\mathrm{A}_1 + g_{\mathrm{B}}\,\mathrm{B}_1 \longrightarrow \mathrm{A}_{g\mathrm{A}}\mathrm{B}_{g\mathrm{B}},$$

where g_{A} and g_{B} are the numbers of the monomers of A and B within a micelle. The following relation between the mole fractions of aggregates (X_g) and monomers ($X_{1\mathrm{A}}$, $X_{1\mathrm{B}}$) can be obtained from the condition of thermodynamic equilibrium:

$$X_g = X_{1\mathrm{A}}^{g_{\mathrm{A}}} X_{1\mathrm{B}}^{g_{\mathrm{B}}} \exp\left[-\left(\frac{g\Delta\mu_g^\circ}{kT}\right)\right]. \quad (4)$$

Here, $g = g_{\mathrm{A}} + g_{\mathrm{B}}$ is the aggregation number; $\Delta\mu_g^\circ$ is the standard Gibbs energy of micelle formation per molecule. The term $\Delta\mu_g^\circ$ relates to the standard chemical potential of a mixed micelle μ_g° and the standard chemical potentials of the monomeric molecules in the solution $\mu_{1\mathrm{A}}^\circ$ and $\mu_{1\mathrm{B}}^\circ$ in the following way:

$$\frac{g\Delta\mu_g^\circ}{kT} = \frac{\mu_g^\circ - g_{\mathrm{A}}\mu_{1\mathrm{A}}^\circ - g_{\mathrm{B}}\mu_{1\mathrm{B}}^\circ}{kT}. \quad (5)$$

Equation (4) links the concentrations of the monomers and the aggregates having a specific size and composition. The value of $\Delta\mu_g^\circ$ depends on temperature, the aggregation number g, composition and shape of the micelle. If $\Delta\mu_g^\circ$ (T, shape 1, g) < $\Delta\mu_g^\circ$ (T, shape 2, g), then the aggregates with the shape 1 are more stable than those with the shape 2 a d the same aggregation number. Estimating $\Delta\mu_g^\circ$ taking into account the structure of the surfactant molecules and parameters of aggregates (*i.e.*, their sizes and shapes) is the key problem in modelling the aggregation behaviour of the system. Typically, micelles are represented as spheres, globules (ellipsoids) or rod-like aggregates (spherocylinders). The term $\Delta\mu_g^\circ$ is expressed as the sum of several contributions:

$$\Delta\mu_g^\circ = (\Delta\mu_g^\circ)_{\mathrm{tr}} + (\Delta\mu_g^\circ)_{\mathrm{def}} + (\Delta\mu_g^\circ)_{\mathrm{int}} + (\Delta\mu_g^\circ)_{\mathrm{st}} + (\Delta\mu_g^\circ)_{\mathrm{dip}} + \\ + (\Delta\mu_g^\circ)_{\mathrm{ion}} + (\Delta\mu_g^\circ)_{\mathrm{mix}},$$

where $(\Delta\mu_g^\circ)_{tr}$ is the chemical potential of transfer of a hydrocarbon tail from the solution to the aggregate core, which is considered as a structureless liquid hydrocarbon; $(\Delta\mu_g^\circ)_{def}$ is the potential of deformation of the hydrocarbon tail due to configurational confinement of the carbon skeleton imposed by the shape of the aggregate; $(\Delta\mu_g^\circ)_{int}$ is the contribution of the surface tension at the interface between the hydrocarbon core of the micelle and aqueous environment; $(\Delta\mu_g^\circ)_{st}$ is the term describing the steric repulsion of hydrophilic groups of the surfactant molecules located at the surface of the aggregate; $(\Delta\mu_g^\circ)_{dip}$ is the contribution of dipole–dipole interactions between the polar groups; $(\Delta\mu_g^\circ)_{ion}$ is the contribution of electrostatic interactions between charged hydrophilic groups and surrounding solution (for ionogenic surfactants); $(\Delta\mu_g^\circ)_{mix}$ is the contribution due to mixing of A and B within one micelle (applicable only to mixed micelles whereas all other terms apply to both individual and mixed micelles).

The first term from the above list (the transfer potential) does not depend on the size and shape of the aggregate whereas other terms (in particular, the electrostatic contribution) are to a certain extent affected by these parameters. Expressions for the individual terms were obtained based on the theoretical estimates and some experimental data. Two of the most thoroughly developed and widely approved variants are Ruckenstein–Nagarajan [26, 130–132] and Blankschtein [25, 86, 87, 133–137] models. Their advantages include detailed assessment of the methods used to estimate the aforementioned terms, parametrisation of the model for a variety of surfactants, applicability of the models not only to description of properties of various systems but to their prediction as well, in particular, for solutions of surfactant mixtures.

The number of carbon atoms (n_C) is an important parameter characterising a hydrocarbon radical. In addition to $\Delta\mu_{tr}^\circ$, n_C determines geometrical characteristics of the hydrophobic part of the surfactant molecule (*i.e.*, its volume and length), which in turn govern possible sizes of aggregates and, importantly, surface area of the hydrocarbon core per surfactant molecule. Several of the aforementioned contributions into the Gibbs energy of micelle formation are affected by the value of n_C through the geometrical characteristics.

The Gibbs energy of transfer of a hydrophobic tail from the aqueous solution into the hydrocarbon core (which is the major driving force of micelle formation) can be estimated from the experimental data on the solubility of hydrocarbons in water assuming the additivity of contributions from groups constituting the molecule. In the case of n-alkyl radicals:

$$(\Delta\mu_g^\circ)_{tr} = (n_C - 1)(\Delta\mu_g^\circ)_{tr(CH_2)} + (\Delta\mu_g^\circ)_{tr(CH_3)},$$

where $(\Delta\mu_g^\circ)_{tr(CH_2)}$ and $(\Delta\mu_g^\circ)_{tr(CH_3)}$ are contributions of a methylene and a methyl group estimated from solubilities of alkanes in water.[26, 127] Within this homologous series, $(\Delta\mu_g^\circ)_{tr}$ is linearly dependent on n_C. The potential of transfer of a hydrocarbon with one double bond can be written as follows:

$$(\Delta\mu_g^\circ)_{tr} = (n_C - 3)(\Delta\mu_g^\circ)_{tr(CH_2)} + (\Delta\mu_g^\circ)_{tr(CH_3)} + 2(\Delta\mu_g^\circ)_{tr(CH)}.$$

The contribution of a CH group, which is significantly smaller than that of a CH_2 group in absolute value, was estimated from solubilities of saturated and unsaturated hydrocarbons.[139] According to the model estimates, a decrease in the absolute value of the negative transfer potential $(\Delta\mu_g^\circ)_{tr}$ is the primary reason for an increase in CMC upon introduction of multiple bonds in hydrocarbon radicals whereas other contributions change only insignificantly.[140] When estimating the transfer free energies, the above formulas are sometimes modified by reduction of the number of carbon atoms by 1–2 with respect to the actual number to account for partial penetration of water molecules into the hydrocarbon core of micelles.

Within the model, a polar group is characterised by two parameters. The first one is the effective cross-section a_{eff}, which is used in the expression for the steric repulsion of head groups of the surfactant molecules:

$$(\Delta\mu_g^\circ)_{st} = -kT\ln\left(1 - \frac{a_{eff}}{a}\right),$$

where a is the surface area of the hydrocarbon core per surfactant molecule. The second parameter is screening cross-section a_{scr}, which represents the surface area of the micelle core screened by the polar group from contacts with the solution. This parameter influences the term $(\Delta\mu_g^\circ)_{int}$ according to the following relation:

$$(\Delta\mu_g^\circ)_{int} = \sigma_{wc}(a - a_{scr}),$$

where σ_{wc} is the surface tension at the interface between a solution and the hydrocarbon core.

The deformational contribution relates to the conformational confinement of the hydrocarbon tail with one end connected to the polar group located at the surface of the aggregate, while the distribution of segments inside the core corrresponds to a density of liquid hydrocarbon. The value of $(\Delta\mu_g^\circ)_{def}$ depends on the length of the hydrocarbon chain, the shape of the micelle and its composition (in the case of a surfactant mixture). The estimate of the deformational contribution adopted in the Blankschtein model is based on the conformational characteristics of individual and mixed aggregates with various shapes (*e.g.*, bilayers, spheres and cylinders) analysed within the mean-field approximation.[141, 142] Within such an approach, distribution functions of segments for chains with different lengths in a mixed aggregate were obtained by minimising the free conformational energy of the system. In particular, it was found that longer chains tend to stretch towards the centre of the hydrophobic core with an increase in the fraction of short chains. The conformational entropy of flexible hydrocarbon chains in curved films of surfactants can be related to their elasticity constants.[143] The energy required to bend a film is substantially reduced when short-radical molecules within the film are replaced by longer ones. Nagarajan and Ruckenstein derived expressions for the deformational contribution in the cases of spheres, globules and spherocylinders using the theoretical results obtained by Semenov for microdomains of copolymers.[144]

The difficulties in estimating the electrostatic term, which depends on the sizes and shapes of the aggregates and is strongly affected by the salt background, are due to the fact that no exact analytical solution of the non-linearised Poisson–Boltzmann equation has been obtained for curved charged surfaces in a salt solution. Typically, an approximate solution of the Poisson–Boltzmann equation for spherical and cylindrical surfaces obtained by Evans and Ninham is used in the aggregation models to describe the electrostatic term.[145] The nature of the polar group of the surfactant molecule and counterion is normally taken into account through the parameter δ that characterises the distance from the surface of the hydrophobic core to the centre of a bound counterion. A serious drawback of this approximation is that it fails in the region of low surfactant and salt concentrations (*i.e.*, for large radii of the ionic atmosphere). The influence of curvature on the profile of the electrostatic potential have been considered more stringently by Mitchell and Ninham.[146] However, the necessity of numerical integration impedes applicability of this approximation to calculations of the size and shape distribution of micelles. An approximate analytical solution of the Poisson–Boltzmann equation for spherical colloidal particles in a salt-free solution has been obtained by Ohshima.[147] MacKintosh, Safran and Pincus [148] proposed a method for estimating the electrostatic term, which enabled successful description of the influence of the surfactant and salt concentrations on the growth of rod-like micelles including the region of dilute solutions.[149, 150] Other approximations have also been considered,[137] a search for new solutions [151] and refinement of the existing description of the electrostatic term for mixed micelles composed of an ionic and a non-ionic or a zwitter-ionic surfactants [86] are currently underway. The nature of a counterion is usually taken into account through the hydrated ion radius. This approach gives satisfactory results in many cases, which was demonstrated, in particular, for a number

of mixtures of an ionic and a non-ionic surfactant. However, it neglects a specific binding of counterions, which should also be taken into consideration.[152, 153] The specific binding increases according to the Hoffmeister series (for instance, in the case of cationic surfactants, the specific binding strengthens in the series $AcO^- < NO_3^- < Br^- < ClO_3^- < Sal^- < HNC^-$). An increase in the degree of binding favours growth of micelles. The specificity of ions depends largely on dispersion forces; thus, the dispersion contribution has to be included into the potential of mean force when estimating the Boltzmann distribution of ions around an ionic micelle.[154] Differences in CMC for different pairs surfactant ion – counterion can also be due to polarisation of the boundary between the hydrocarbon core and the polar outer shell of a micelle.[155] However, the aforementioned factors were considered only in a few studies. A number of possible methods to account for the influence of the counterion nature on the transition sphere → cylinder through the electrostatic term have been discussed elsewhere.[156]

The calculations performed within the Nagarajan – Ruckenstein and Blankschtein models for solutions of various types of individual surfactants and mixed systems have been reported.[44, 140, 157] The models adequately describe the influence exerted by the size of the hydrophobic part of the surfactant molecule on CMC and micelle growth. Furthermore, they make it possible to take into account the nature of the polar groups and effects of salt additives, describe solubilisation and reproduce synergistic effects in mixed systems. Model estimates of CMC are more successful than the estimates of concentrations of transitions sphere → cylinder or of mean aggregation numbers in the micelle growth since changes in the sizes and shapes of micelles depend on finer effects than CMC. Determination of model parameters requires experimental data on CMC for a system of the type under study. However, as soon as the model is parametrised, it can be used for predicting properties of systems based on other surfactants with the same polar group. The Nagarajan – Ruckenstein model was applied to systematic studies of relationships between the molecular parameters of surfactants and characteristics of their aggregation (including CMC, mean aggregation number and polydispersity).[140] In particular, factors favouring the micelle growth (elongation of the hydrocarbon radical, addition of a salt, the size of the polar group) were evaluated. A modification of the Nagarajan – Ruckenstein model was used in the development of a colloidal model describing precipitation of asphaltenes from oil.[158–160] Different versions of the molecular-thermodynamic models have been proposed to describe surface tension of solutions of surfactant mixtures and adsorption.[161, 162] Model approaches to the study of stability of vesicles with respect to planar bilayer and micellar structures in catanionic systems have been developed.[163–166]

The interactions between aggregates, which become significant at high surfactant concentrations, can be accounted for using the virial equation of state or more rapidly converging *y*-expansion.[167] The McMillan – Mayer theory and calculations of the potential of mean force were used to describe non-ideal solutions of non-ionic micelles. The repulsive interactions between micelles were estimated through the excluded volume.[168] The electrostatic repulsion between micelles strongly affects deviations of solutions of ionic surfactants from the ideal behaviour. The experimental light scattering and viscosity data for a number of solutions composed of mixtures of an ionic and an anionic surfactants were interpreted with consideration of only the electrostatic contribution calculated according to the Derjaguin – Landau – Verwey – Overbeek theory.[136] A variant of the osmotic equation that takes into account the van der Waals and long-range electrostatic interactions has been proposed to describe micellar solutions, emulsions and microemulsions in a wide range of compositions.[169]

The molecular-thermodynamic approach gives optimal possibilities of using modern theoretical achievements in the search of regularities in relationships between the chemical architecture of surfactants and aggregation behaviour. This approach is mostly suitable for solving applied problems in the field of surfactant systems. In this regard, it can be considered as the optimum theoretical tool. Meanwhile, further developments and improvements of the models are currently needed. In particular, this relates to evaluation of various contributions into the Gibbs energy of micelle formation. The factors complicating correct estimates of the electrostatic term and thus representing a challenge to modern theories have already been mentioned. Furthermore, a correct account of penetration of water molecules into the micelle core (which is typically neglected), the effects of the surface curvature and salt background on the surface tension at the interface between the hydrocarbon core and aqueous environment is highly desirable. A problem of an adequate description of the mixing functions arises in the case of mixed micelles, the systems revealing specific interactions being particularly interesting.

Several issues of interest were considered in the drop and quasidrop models developed by Rusanov *et al.*[170–173] for spherical micelles of individual surfactants. The canonical drop model, which assumes flexibility of the hydrocarbon chains and their complete immersion into the aggregate core, like the Nagarajan – Ruckenstein model, accounts for the surface effects in a more rigorous way. The electrostatic term is estimated according to the model of a spherical capacitor, while the deformational term is calculated using the Semenov formula.[144] The quasidrop model allows partial exit of undistorted hydrocarbon chains from the core. These models were applied to study the dependence of the work of formation of premicellar and micellar aggregates on the aggregation number and concentration of the surfactant monomers in the solution; the analytical approximations were derived.

The lattice theories are often used in studies of micellisation.[174–181] The self-consistent field lattice theory originally developed by Scheutjens and Fleer for polymer adsorption [174, 175] was generalised by Leermakers for the case of surfactant aggregation.[176, 177] In particular, this approach successfully reproduces the diffuse structure of the micellar core – corona boundary. Nevertheless, the Gaussian statistics of chains adopted in the model can give rise to errors in the estimation of the density profiles of micelles for relatively short diphilic molecules.[178] The lattice theories in the single-chain mean-field (SCMF) variant are free of this drawback. A simple model 'a diphilic molecule (a diblock-chain composed of two types of units) – solvent (one unit)' correctly reproduced the dependence of CMC on the length of the hydrocarbon chain and changes in the morphology of aggregates.[180, 181] The molecular structure of aggregates obtained from the theoretical calculations is in qualitative agreement with that found by computer simulations, yet the model represents surfactant molecules in a quite simplified manner.

Studies combining the molecular-thermodynamic modelling and computer simulations for evaluation of certain characteristics of micelles are of special interest.[182–187] This approach was applied to study solutions of cetyltrimethylammonium bromide containing sodium salicylate and describe penetration of salicylate anions inside micelles.[182] The molecular packing, structure and interactions within the corona of a micelle as well as the contribution of the corona to the Gibbs energy of micelle formation were obtained using the Monte Carlo method whereas other contributions were calculated according to the Blankschtein model.[133, 134] The computer experiments (*e.g.*, Monte Carlo and molecular dynamics) can prove extremely useful in parametrisation of model theories based on the molecular structure of surfactants.

V. Computer simulations of surfactant solutions

Results of computer simulations of surfactant solutions have recently been surveyed.[27, 28, 188] Computer simulations of biological lipid membranes are especially numerous, but these studies represent a special field. The structure and interactions between the particles constituting a surfactant solution can be described at different levels, depending on the purpose of the study. All atoms

or ions constituting the system and interactions between them are explicitly taken into account in the atomistic models, although several atoms can be combined into one pseudoatom, such as methyl group. In the so-called coarse grain models, atoms are grouped into larger species, *i.e.*, represented more roughly. Furthermore, the electrostatic and torsion potentials are normally neglected, in contrast to the atomistic approach. Simulations commonly referred to as mesoscopic are undertaken using various methods including dissipative particle dynamics, calculations within the lattice gas model and dynamic mean-field density functional approach. The time scales of different events occurring in solutions of aggregated surfactants are estimated as follows: 10^{-10} s for shape fluctuations, 10^{-6} s for exchange of surfactant molecules between micelles and the surrounding solution, hundreds seconds or longer for such macroscopic events as shear-induced changes. The typical time and spatial scales for the atomistic calculations are 1 ns and 1 nm, respectively. So far, simulations of the equilibrium structures of ordered surfactant solutions are impossible at this level, but still computer experiments can yield detailed information on the local structure and some kinetic aspects of the self-assembly process. In the majority of cases, it is the premicellar surfactant aggregates that are the subject of the studies, and the conformations and arrangement of the molecules at a distance scale on the order of 1 nm are obtained as outcome. As a rule, solutions of individual surfactants are studied.[27, 28, 183, 189–193]

Extended molecular dynamics (MD) calculations at the atomistic level have been performed for aqueous solutions of nonyltrimethylammonium chloride and erucylbis(2-hydroxyethyl)methylammonium (50 surfactant molecules and 3000 water molecules);[191] the mechanism and kinetics of micelle formation were studied for time scales up to 3 ns and the effects of sodium salicylate addition were simulated (the salicylate anions can incorporate into micelles between the polar groups of the cationic surfactant and thus promote growth of rod-like aggregates). Among other systems, for which atomistic calculations have been accomplished, mixtures of surfactants with lipids are worth noting.[194] Computer simulations of inverse micelles,[195] hexagonal and lamellar phases and interface layers in surfactant-containing systems have been performed. MD-simulations of bilayers of cationic surfactants in water using the software package GROMACS[196, 197] were reported. The simulations included 242 and $\sim$4000 surfactant and water molecules, respectively. The radial distribution functions, density profiles, surface areas per surfactant molecule and diffusion coefficients were estimated; it was revealed that water molecules and counterions penetrate into the hydrophobic core to a significant extent,[198] which was not observed for anionic surfactants.[199]

The coarse grain models enable calculations in wider time and spatial ranges as compared to the atomistic approach, which makes it possible to investigate equilibrium sizes of aggregates, growth of rod-like micelles, formation of vesicles, kinetics of the aggregation processes, solubilisation, phase transitions in two- and three-component systems and adsorption. However, these calculations take into account the chemical nature of the system under study only qualitatively, and their main goal consists of establishing general regularities in the aggregation and phase behaviour (in particular, for systems surfactant–water–oil)[200, 201] and verification of the results of approximate analytical theories, such as the mean-field theory.[202] The models can be formulated in the lattice and non-lattice versions.[203] Implementation of the latter is usually based on the methods proposed by da Gama, Gubbins and Smit *et al.*[204, 205] A model proposed by Larson[206, 207] is a prototype for many lattice models. Within the lattice approach, the Monte Carlo method was applied to study films of diphilic compounds[208, 209] and simulate conformational transitions in a three-component mixture solvent–diphilic compound–polymer.[210] Capabilities of the theoretical description of the self-assembly processes in surfactant solutions and prediction of the phase diagrams and dynamical properties can be extended by utilisation of mesoscopic simulations using the dissipative particle dynamics method[211, 212] and the lattice gas model[213, 214] as well as dynamic mean-field density functional approach.[215] Many aspects of the behaviour of real systems and specific influence of the molecular structure on the macroscopic parameters have been successfully reproduced by relatively simple models at the coarse grain and mesoscopic levels. However, only qualitative matching has been reached so far and further developments of the models are required to adequately reflect the chemical identity of the components constituting the system under study. Bridging the gaps between the models of different levels, including atomistic, is a current challenge.

VI. Viscoelastic surfactant solutions

Surfactant solutions manifest diverse rheological properties owing to the self-assembly of diphilic molecules in aqueous solutions and formation of various mesoscopic structures. The viscosities of many solutions even at high concentrations is only slightly larger than that of water so that they behave as ordinary Newtonian liquids. On the other hand, some solutions reveal viscoelastic properties at low surfactant concentrations.[51, 53, 216–222]

Dilute solutions where micelles are independent of each other are characterised by small changes in viscosity as a function of the surfactant concentration. In the case of spherical micelles, this dependence is represented by the Einstein formula:

$$\eta = \eta_0 (1 + 2.5\varphi), \quad (6)$$

where η_0 and η are viscosities of the pure solvent and the solution with a volume fraction of micelles φ (calculated with account of hydration of the surfactant molecules), respectively. The nearly linear correlation (with a slightly different coefficient) is also held for dilute solutions of monodisperse ellipsoids of revolution. The contribution of the intermicellar interactions into the viscosity of dilute solutions is proportional to the concentration squared and is relatively small. Even in the case of strong hydration of micelles (which can give rise to an increase in their apparent volume fraction by a factor of 2–3), the viscosity of a 10% solution will not exceed that of pure solvent more than twice, according to (6). This however is valid only provided the dilute solution approximation remains applicable. There are many systems manifesting a dramatic change in the viscosity *vs.* composition and a transition into the viscoelastic state, at a certain (sometimes low) concentration. As a rule, the reason for such a transition is the emergence of long worm-like micelles forming a network. In a sense, worm-like micelles are analogous to polymer macromolecules, although the size distribution of the latter is constant for a specific sample whereas the micelles are dynamic entities of a changing size and shape. These structural parameters of micelles strongly depend on the surfactant concentration, nature of counterions, presence of electrolytes and temperature. Growth of micelles can result in their branching under certain conditions. Long micelles can easily break down or coalesce with each other. These properties of micellar systems determine their more complex behaviour as compared to polymeric systems and make additional difficulties in the interpretation of the experimental data.[223, 224] Viscoelastic systems can be prepared by mixing two ordinary dilute micellar solutions (say, of a cationic and an anionic surfactants) or a micellar and a salt solutions with viscosities close to that of water, whereas the resultant solution resembles a gel. Solutions of some non-ionic and zwitter-ionic surfactants also manifest the viscoelastic behaviour. An increase in viscosity can be caused by addition of salts, especially with hydrophobic counterions capable of incorporating between the polar groups of the surfactant.[53, 222, 225–228] For instance, this is typical of mixtures of cetyltrimethylammonium bromide (CTAB) and sodium salicylate, the maximum effect is observed upon mixing of equal volumes of CTAB and the salicylate with concentrations of 0.05 mol litre^{-1} and 0.03 mol litre^{-1}, respectively (see Ref. 51).

Solutions of some cationic surfactants with unsaturated hydrocarbon tails manifest the viscoelastic properties (even at high temperatures) in the presence of salts.[218] An intense search for new surfactants and mixed systems forming viscoelastic solutions is currently underway. These studies are to a large extent stimulated by strong practical demand, since viscoelastic surfactant solutions are widely employed in the production of cosmetics and detergents, in some oil production technologies, as thickening agents and lubricants. It is often desirable to have viscoelastic behaviour appearing already at low surfactant concentrations and persisting over a wide temperature range. Numerous recent publications and reviews [219–221] devoted to viscoelastic surfactant solutions clearly demonstrate an increasing interest of researchers in this field.

According to the experimental results, the viscosities of surfactant solutions beyond the point of viscoelastic transition (at concentration c^*) change with concentration (c) obeying a power law $\eta \propto (c/c^*)^x$ with $x = 1.5-8.5$; higher values of x are typical of systems containing charged non-shielded micelles whereas lower values are observed for shielded or non-ionic micellar systems near the liquid-crystalline region. The power law usually holds in a wide composition range. In some systems the viscosity passes through maximum and then starts to decrease with increasing surfactant concentration or upon salt addition. For instance, such a behaviour is observed for solutions of cetylpyridinium chloride upon an increase in the concentration of sodium salicylate.[53] The non-monotonic dependence of viscosity on composition can be due to a decrease in the contour length of linear micelles or formation of branched aggregates.[224, 229–231] Theoretical approaches to the description of viscoelastic micellar solutions postulate two basic mechanisms ensuring flexibility of rod-like aggregates, *viz*., reptation [232–234] and scission–recombination.[223, 229] Probably, both mechanisms can operate simultaneously. Exponents in the scaling correlation viscosity *vs*. volume fraction of the surfactant (ϕ) for the two mechanisms are different: $\eta \propto \phi^{5.25}$ if the reptation prevails and $\eta \propto \phi^{3.5}$ if the scission–recombination plays the dominant role (see Ref. 223).

In the analysis of factors favouring the micelle growth, the molecular-thermodynamical models described in Section IV are useful as well as alternative approaches, which allows estimation of the concentration of a transition sphere → cylinder (the second CMC), growth of rod-like micelles and dependence of the mean aggregation number on composition. According to the general equations (4) and (5), long rod-like micelles can form spontaneously only if the decrease in the combinatorial entropy corresponding to the process is exceeded by the decrease in the Gibbs energy associated with the transfer of a surfactant molecule from the spherical cap to the cylindrical part of the micelle. The tendency of micelles to transform from spheres to spherocylinders is quantified by the parameter K, which is defined as:

$$\ln K = g_{\mathrm{cap}} \left(\frac{\Delta\mu^{\circ}_{\mathrm{cap}} - \Delta\mu^{\circ}_{\mathrm{cyl}}}{kT} \right). \qquad (7)$$

Here, g_{cap} is the number of surfactant molecules in the terminal spherical caps of a rod-like micelle, $\Delta\mu^{\circ}_{\mathrm{cap}}$ and $\Delta\mu^{\circ}_{\mathrm{cyl}}$ are the Gibbs energy of micelle formation per surfactant molecule in the spherical cap and infinite cylinder, respectively. The right part of Eqn (7) can be defined as a dimensionless free energy (expressed in kT units) of scission of a rod-like micelle. The values of the parameter K have been estimated experimentally for a number of systems,[156, 235, 236] their dependences on temperature and salt content have been measured (K increases with an increase in the salt concentration). Typical values of K for systems that form rod-like micelles lie in the range of 10^8-10^{12}. If long micelles are abundant and the solution concentration significantly exceeds CMC, the dependence of the number-average (g_{n}) and weight-average (g_{w}) aggregation numbers on the total mole fraction of the surfactant in the solution (X) are given as:

$$g_{\mathrm{n}} \approx K^{1/2} X^{1/2}; \; g_{\mathrm{w}} \approx 2 K^{1/2} X^{1/2}.$$

The size distribution of rod-like micelles is broad in contrast to that of spherical aggregates. In the case of non-ionic surfactants or strongly screened ionic micelles (*i.e*., at high salt concentrations), the dependence of K on the solution composition can be neglected. Therefore, the dependence of the average aggregation number (and, respectively, the average micelle length) on the surfactant concentration under conditions of growth of rod-like micelles obeys a power law. Two other distinct modes are possible for ionic surfactants at low salt concentrations, *viz*., the dilute mode where the micelle growth is insignificant and the semidilute mode, which is characterised by a rapid growth. Only with a further increase in concentration, the growth starts to obey the power law typical of strongly screened micelles.[148, 149]

According to the formula (7), the parameter K characterising the transition sphere → cylinder is determined by the difference in the Gibbs energy between the two parts of a micelle having different geometries. The difference is substantially smaller than the energies themselves since it is caused by relatively weak effects.[152] Thus the results of modelling of the micelle growth are substantially more sensitive to errors in $\Delta\mu^{\circ}_{\mathrm{cap}}$ and $\Delta\mu^{\circ}_{\mathrm{cyl}}$ determination than estimates of CMC. Although the values of K calculated within theoretical aggregation models differ from the experimentally measured ones,[26] the model calculations make it possible to follow the effects of the chemical structure of the surfactant and the composition of the solution on the micelle growth. A model proposed for worm-like polymer molecules in solutions [237–239] adopted to long micelles in a combination with a micelle formation model. Calculations fairly reproduced viscosities of dilute solutions of hexaethylene glycol n-dodecyl ether (a non-ionic surfactant) and afforded an estimate for the concentration of the transition to semidilute solutions where long micelles start to form a network.[240] However, recent calculations for solutions of ionic surfactants accomplished within a similar model were only in qualitative agreement with the experiment.[241] The major difficulties associated with the simulations relate to the adequate description of the size distribution of worm-like micelles and to estimates of their flexibility.

VII. Self-assembly phenomena in solutions of amphiphilic polymers and of their mixtures with low-molecular-mass surfactants

The self-assembly phenomena giving rise to mesostructures of various morphologies occur in many polymeric solutions and melts and strongly affect the behaviour of these systems. Properties of many polymeric materials and nanocomposites are determined by the structures of the intrinsic microheterogeneities.[242] Investigations into self-assembled polymeric structures represent a huge independent field and thus we mention here only a few relevant directions.

Self-assembly processes in solutions of low-molecular-mass surfactants bear a remarkable resemblance to those of amphiphilic polymers. A prerequisite to self-assembly of macromolecules (as well as of low-molecular-mass surfactants) is the presence of chemically different groups. A simple example is a diblock-copolymer AB composed of a sequence of monomer units A covalently bound to a sequence of units B. There are diverse more complex systems, such as linear triblock copolymers of the types ABA or ABC, multiblock copolymers $(AB)_n$, comb-like polymers (in which side chains B are grafted to the backbone chain A), star-like polymers and various mixed structures. Polymeric melts or solutions composed of poorly compatible copolymer blocks can undergo microphase segregation resulting in the formation of nanosized areas having various morphologies and containing predominantly blocks of only one type. However, the self-assembly of low-molecular-mass surfactants is only possible if the molecules have a non-polar and a polar (or charged) groups simultaneously, whereas the self-assembly of a macromolecular system can occur even at small differences in the polarity of

blocks. In particular, copolymers of two low-polar organic blocks (*e.g.*, copolymers of styrene and butadiene) form micelles in organic solvents. A difference between micelles formed by high- and low-molecular-mass compounds consists of the larger size of the former. The radius of a micelle often increases with the length of the block that forms the micelle. Flexibility of long chains imparts a number of features (which are, in particular, manifested in dilute solutions) to micelles formed by macromolecules.

Nanostructures that can be formed by amphiphilic polymers in solutions and melts are diverse, they include spherical, cylindrical and disk-shaped micelles, vesicles, several types of liquid-crystalline microphases and complex bicontinuous structures.[1,243] Many amphiphilic block copolymers form micelles in dilute aqueous solutions with cores composed of non-polar blocks and polar coronas.[244–246] Other structures (*e.g.*, cylinders or disks) can be formed, depending on the polymer concentration, solvent nature and presence of additives. Comb-like copolymer macromolecules with strongly self-attracting side chains can form associated networks above a certain concentration and collapse in dilute solutions.[247,248] Mixtures of a hydrophobically modified polymer and a low-molecular-mass surfactant tend to form mixed micelles, like mixtures of two surfactants. With an increase in the solution concentration, a spatial network (*i.e.*, a micellar gel) can form due to binding of one polymeric chain to many micelles simultaneously. A similar phenomenon, which leads to an abrupt increase in the viscosity, is observed upon mixing of a polyelectrolyte solution with an oppositely charged ionic surfactant. The addition of a non-ionic surfactant yields a significantly smaller increase in viscosity whereas the addition of a similarly charged ionic surfactant does not virtually affect the viscosity. This can be illustrated with experimental data on the addition of cationic, non-ionic and anionic surfactants to hydrophobically modified polyacrylate.[249] Copolymers containing ionic hydrophilic blocks bind the oppositely charged low-molecular-mass surfactant and assemble into small vesicles with a neutralised polyion surrounded by the hydrophilic blocks of the copolymer.[250–255] In micellar solutions of copolymers with additives solubilisation can occur. The experimental data on the solubilisation capacity of micelles formed by different copolymers have recently been surveyed.[256]

In theoretical studies of the self-assembly phenomena in solutions of polymers the dominant role is played by the self-consistent mean-field theories [144,242,257–277] and the phenomenological scaling approach.[278,279] The driving force of the microphase segregation is a difference in the interaction energies of identical and different blocks ε_{ij} (i, j = A, B), which is quantified by the Flory–Huggins parameter:

$$\chi_{AB} = \frac{z}{kT}\frac{\varepsilon_{AB} - (\varepsilon_{AA} + \varepsilon_{BB})}{2}.$$

The parameter χ_{AB} (expressed in the kT units) determines the change in the free energy upon formation of z mixed contacts A–B between the monomeric units instead of identical contacts A–A and B–B; z is the number of the nearest monomer neighbours in the configurational cell of the copolymer. Positive values of χ_{AB} suggest the tendency of the blocks A and B to segregate, whereas negative values indicate their tendency to mix with each other. Systems revealing no specific interactions are typically characterised by small (significantly smaller than unity) positive values of χ_{AB} (for instance, $\chi \approx 0.1$ for a pair styrene–isoprene). The degree of segregation (weak or strong) is characterised by the product $\chi_{AB}N$, where $N = N_A + N_B$ is the total number of units in the polymeric chain. Since the blocks within a copolymer are bound by covalent bonds, a copolymer melt with a negative value of χ_{AB} can undergo only microphase rather than macrophase segregation. The tendency of the blocks A and B to segregate is opposed by the entropy factor since the formation of microphases imposes restrictions on possible configurations of the polymer chains with concomitant decrease in entropy. The changes in entropy due to configurational restrictions are associated with the elasticity of polymeric chains and networks. Within an approximation that the elasticity is of the purely entropic origin, it can be calculated from the configurational statistics of independent Gaussian chains.[280,281] The balance between the energetic and entropic factors (*i.e.*, between the interface tension and the entropy expenses to straightening of polymeric coils) determines the equilibrium sizes and geometries of the microdomains. In the case of a copolymer AB with similar volume fractions of blocks A and B, the microphase segregation gives rise to a lamellar structure formed by straightened polymer chains. According to estimates made within the mean-field theory, the transition from a completely disordered structure to the lamellar one occurs for a copolymer containing N units at $\chi_{AB}N \approx 10.4–10.5$ (see Ref. 242). In the case of a diblock copolymer with the compositional asymmetry (*e.g.*, due to different degrees of polymerisation of the two components), the interface tends to bend thus giving rise to different morphologies of the microphases. A transition of a diblock copolymer from the lamellar structure to hexagonal or cubic structures depending on the composition was predicted in early analytical mean-field theories developed by Semenov [144] within the strong segregation limit ($\chi_{AB}N \to \infty$) and by Leibler [258] within the weak segregation limit ($\chi_{AB}N$ slightly exceeds the threshold for the order–disorder transition). A spectral method for the numerical solution of equations of the self-consistent mean-field theory developed later [260–269] made it possible to describe microphases with quite complex structures and demonstrate the diversity of possible patterns of the phase behaviour in the intermediate segregation regime. For instance, a change in the fraction of the units A in the diblock copolymer AB from 0.5 to 0 or 1 at $\chi_{AB}N = 20$ gave rise to the following sequence of microphases: lamellar L, bicontinuous G (gyroid), hexagonal C (hexagonally packed cylinders), cubic S (spheres packed into a body-centred cubic lattice). According to the calculations, a perforated lamellar phase (PL), in which layers composed of the blocks present in the copolymer in a lower concentration are perforated with hexagonally arranged channels, becomes nearly stable in the proximity of the phase boundary L–G, which is supported by the experimental results. The enhanced segregation between blocks of a diblock copolymer gives rise to a change in the shape of the micellar structures formed from spherical to cylindrical and disk-like.[271,272] The stable gyroid phase of block copolymers was successfully described within the self-consistent field theory corrected for fluctuations either in the weak [270,273] or strong [274] segregation limit. A theory of the microphase segregation in mixtures of block copolymers and homopolymers was developed;[275,276] another theory predicting formation of secondary-domain structures in disordered multiblock copolymers was proposed.[277]

Birschtein *et al.* [282] performed extensive theoretical investigations into the so-called polymeric brushes (*i.e.*, grafted polymeric monolayers). A numerical self-consistency procedure for the mean-field equations originally proposed by Scheutjens and Fleer [175] and developed in further studies [174,283] proved to perform well for various systems. The scaling method was used to elucidate the influence of the solvent selectivity on the morphology of microphases and sizes of domains.[282,284–286] In particular, bicontinuous structures were considered. The self-consistent field theory was applied to concentrated solutions of copolymers in low-molecular-mass solvents,[287,288] although concentrated solutions remain less explored as compared to dilute ones. A model for the analytical description of swelling of a bicontinuous gel in a selective solution was formulated based on the mean-field theory in the strong segregation limit.[289] A theory of gelation of associating polymers was developed.[290,291]

Important regularities of the influence exerted by the structures of macromolecules, their lengths and rigidities, the character of the segment–segment and segment–solvent interactions and component concentrations on the self-assembly processes were

established within the framework of the mean-field theories and scaling approach. Nevertheless, these approaches afford a qualitative picture rather than quantitative description of the behaviour of specific systems taking into account the chemical structures of components and potentials of the interparticle interactions. A description at the microscopic level is required to solve the problems. This level of detalisation is approached in the theory of associating polyelectrolytes developed by Khokhlov *et al.*[292,293] for macromolecules composed of a hydrophilic backbone and hydrophobic side chains that are distributed along the backbone and can aggregate with each other in polar solvents. Within this theory viewing various contributions into the free energy of association such phenomena as stabilisation of finite-size aggregates, abnormal gelation upon a decrease in the number of associating groups, microphase segregation in semidilute solutions, shear-induced thickening of solutions, adsorption of polyelectrolytes on oppositely charged surfaces, *etc*. can be described.

The method of integral equations opens wide prospects in explicit accounting for structural features of specific macromolecules and intermolecular interactions. The integral equation RISM (Reference Interaction Site Model) proposed by Chandler and Andersen as a generalisation of the Ornstein–Zernike equation for systems with multi-site interactions[294] was applied to various self-assembling polymer-containing systems (the RISM equation applied to polymers is referred to as PRISM). Systems containing macromolecules and disperse particles,[295–297] charged copolymers with different types of distribution of monomeric units over a macromolecule (protein-like and statistical copolymers composed of two types of monomeric units, *viz*., associating neutral hydrophobic and charged ones),[298,299] self-assembling comb-like polymers, polyelectrolytes in bad solvents, *etc*. were studied.

Substantial progress has been achieved in computer simulations of the aggregation in polymeric systems using the Monte Carlo, molecular dynamics and Brownian dynamics methods.[234,300–305] Simplified models of molecules are often used in numerical simulations of polymeric systems. An amphiphilic polymer can be represented as a sequence of two types of beads (hydrophilic and hydrophobic ones). Specific arrangements of the beads mimic a block copolymer or a comb-like copolymer. Using such a model, it has been shown that a collapse of comb-like macromolecules with associating side chains is accompanied by the microphase segregation.[306] The side chains then form spherical micelles and the backbone is located at the surface of these micelles twining between them. A combination of the Brownian dynamics (*i.e*., a variant of the mesoscopic approach) and self-consistent mean-field algorithms applicable to polymeric brushes was developed.[307,308] Simulations of the microphase segregation in the brushes capable of liquid-crystalline ordering[300] confirmed the major conclusions of the analytical study accomplished earlier.[282] The results of calculations of the thermodynamic parameters for a simple model system, *viz*., a rigid-chain polymer, obtained using the integral equations RISM and the Monte Carlo method were systematically compared. A self-consistent hybrid approach combining the atomistic Monte Carlo method and the numerical solution of the integral equation RISM was elaborated and adopted to the description of polymer chains in the presence of colloidal particles.[309]

* * *

There is no doubt that investigations into the solutions of surfactant mixtures will develop intensely and converge with studies devoted to the self-assembly processes in other soft-matter systems. A substantial progress in the field might be anticipated owing to combined application of the theoretical studies, physical and computer experiments.

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