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History of Thermodynamic Models for the Adsorption of Surfactants at Liquid Interfaces

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Abstract

Since the fundamental work of Gibbs, many models have been proposed to describe the interfacial properties of adsorbed surfactant layers. The historical models of von Szyszkowski, Langmuir, and Frumkin are presented here together with their advantages and shortcomings. Only during the last few decades have additional adsorption models been developed by Fainerman and co-workers. These models allow describing particular details of surfactants adsorbed at liquid interfaces. They are derived from the fundamental thermodynamic principle of Braun–Le Châtelier and allow us to assume that surfactant molecules may adsorb in different adsorption states or form small two-dimensional aggregates. The most recently discussed multistate model assumes more than two coexisting adsorption states, which has been shown to be particularly suitable for surfactant molecules capable of undergoing conformational changes upon adsorption. The classical models of Langmuir and Frumkin, as well as the newer multistate models, are all of practical importance for the respective types of surfactants.

1. Introduction

Surfactants are omnipresent in our daily life. In the books by Rosen and Kunjappu [1] and by Fainerman et al. [2], excellent overviews about the characterization of their adsorption layers at liquid interfaces are given. In [2], also an overview is provided of the most frequently used thermodynamic models suitable to describe the adsorption characteristics of surfactants. This includes the starting point of all thermodynamic descriptions, the fundamental adsorption equation derived by Gibbs [3]. This equation allows the determination of the adsorbed amount Γ from the dependence of the interfacial tension γ on the surfactant bulk concentration c. Equation (1), given here in a simplified form, is called the Gibbs fundamental equation of adsorption and is the most important thermodynamic equation for describing the adsorption of surfactants at liquid-fluid interfaces:

$$\Gamma = -\frac{1}{\nu RT}\frac{d\gamma}{d\ln c}. \tag{1}$$

Here, R and T denote the ideal gas constant and the absolute temperature, respectively. The coefficient ν takes the value 1 or 2 for nonionic and ionic surfactants, respectively, or an intermediate value depending on the degree of dissociation of the ionic surfactant molecules [4].

The Gibbs equation is of general character and can be applied to any type of adsorption layers of surfactants, polymers, proteins or their mixtures. However, except that it allows to determine the number of adsorbed molecules Γ per unit surface area, it does not provide specific properties of the adsorbing molecules. Moreover, there is the problem of experimental errors which directly influence the accuracy of any data analysis. This was the reason why people tried to find explicit relations between either Γ as a function of the bulk concentration c (adsorption isotherms), or surface tension γ as a function of the bulk concentration c (surface tension isotherm) or of the adsorbed amount Γ (equation of state). The resulting

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adsorption models of Henry, von Szyszkowski, Langmuir and Frumkin will be presented and discussed in the following sections in detail, while other models proposed for example by Freundlich [5], Volmer [6], Temkin [7] or more recently by Ivanov et al. [8] will not be further analysed and evaluated. However, in the nineties of last century, Fainerman proposed several new adsorption models which took particular properties of surfactant molecules into account. He started from a fundamental law of equilibrium thermodynamics, the so-called principle of Braun-Le Chatelier (for the first time applied by Joos and Serrien [9] to interfacial problems) and derived adsorption models which take into consideration particular specific properties of surfactant molecules in an adsorption layer. These models derived by Fainerman and co-workers represent still the state of the art for a quantitative description of surfactant layers adsorbed at liquid-fluid interfaces.

2. Adsorption model of von Szyszkowski and Langmuir

As mentioned above, there are many adsorption models derived to describe as accurate as possible the adsorption behavior of surfactants. In 1908, von Szyszkowski [10] proposed an empirical equation suitable to describe the change in surface tension γ as a function of the surfactant's bulk concentration c in an aqueous solution:

$$\frac{\gamma_0-\gamma}{\gamma_0} = B\,ln\left(1+\frac{c}{A}\right), \tag{2}$$

here, A and B are empirical constants, and γ_0 is the surface tension in absence of any surfactant. Von Szyszkowski showed that Eq. (2) allows to reproduce his experimental data for aqueous solutions of fatty acids very well. Only few years later it became clear that the empirically proposed Eq. (2) is equivalent to an equation derived by Langmuir [11] for the adsorption of gas molecules at solid surfaces:

$$\Gamma = \Gamma_\infty \frac{bc}{1+bc}. \tag{3}$$

When we combine this adsorption isotherm with the Gibbs fundamental Eq. (1), it leads to an equation equivalent to the relation proposed by von Szyszkowski, now, however, with a physical meaning of each parameter

$$\gamma = \gamma_0 - RT\Gamma_\infty\, ln(1+bc). \tag{4}$$

Moreover, via Eqs. (1) and (4) we can obtain the equation of state of the interfacial layer

$$\gamma = \gamma_0 + RT\Gamma_\infty\, ln\left(1-\frac{\Gamma}{\Gamma_\infty}\right), \tag{5}$$

The physical meaning of the initially empirical constants A and B can be determined by comparing Eqs. (2) and (4).

$$A=1/b \text{ and } B = RT\Gamma_\infty/\gamma_0 \tag{6}$$

The parameter $\Gamma\infty$ represents the maximum adsorbed amount, i.e., the number of molecules adsorbed at a unit interfacial area. For sufficiently small concentrations $c\ b \ll 1$, Eq. (4) simplifies to

$$\Gamma = kc \quad \text{or} \quad \gamma = \gamma_0 \tag{7}$$

which is the linear adsorption model proposed by Henry [12]. Note, the parameter *1/b* is called the adsorption constant and can serve as a very good measure for defining the interfacial activity of a surfactant in a quite broad range of surfactant bulk concentrations [13]. The value of *1/b* is actually the concentration at which the surface layer is covered by 50% when we use the Langmuir adsorption model of Eq. (3).

As an example, the surface tension isotherms of the homologous series of polyethylenglycol oxyethylene ethers (abbreviated by C_nEO_m) are shown in Fig. 1 for four surfactants [14]. Together with the experimental data, also shown are the corresponding Langmuir and reorientation isotherms calculated via best fit of the models adapted to the data. As one can see, the Langmuir model describes the data quite well, however, the reorientation model (presented and discussed in more detail further below) fits the data in a much better way. Chan and Frances [15] in their highly references work used the Langmuir equation successfully for many surfactants of various types to analyse their equilibrium and dynamic interfacial properties, regardless of the fact that maybe other adsorption models might be able to better reflect their interfacial equilibrium properties. This shows the enormous importance of the Langmuir adsorption model.

The isotherms for the four members of the homologous series of the nonionic surfactants C_9EO_8, $C_{10}EO_8$, $C_{11}EO_8$ and $C_{12}EO_8$ are rather accurate shifts to each other, as it is expected from the Traube rule [16]. Thus, the values of the parameter *b* for the corresponding surfactants change in a very regular way because *b* is mainly responsible for the location of the surface tension isotherm along the concentration axis.

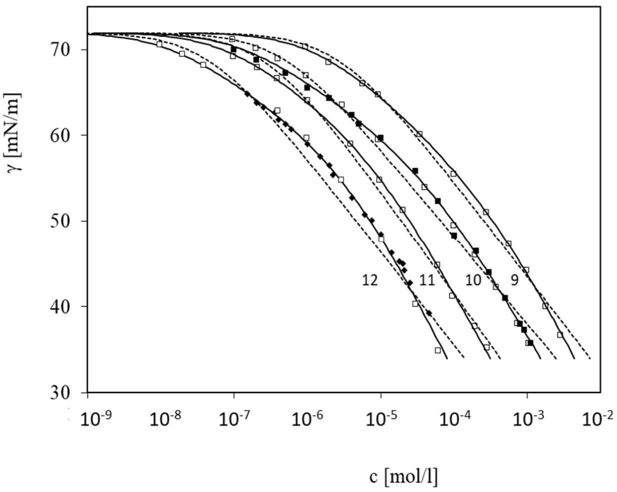

Fig. 1. Surface tension isotherms y(c) for four members of the homologous series of non-ionic surfactants C_nEO_8 with n = 9–12, numbers define the alkyl chain length; solid curves – reorientation model; dashed curves – Langmuir adsorption model; different symbols refer to different literature sources; data taken from [2] and [14].

A typical homologous series of surfactants, described very well by the Langmuir adsorption model, is that of the nonionics alkyl dimethyl phosphine oxides, although Lunkenheimer et al. [17] showed that a two-state model even allows a slightly better description. Over a large range of alkyl chain lengths, the quality of data fitting by the simple Langmuir model is excellent. In the book by Fainerman et al. on surfactants [2], the Langmuir model was used for a large number of homologous series of surfactants and compared to other models in order to demonstrate which one is superior. In extensive tables the values of the model parameters, such as maximum adsorbed amount Γ_∞ and adsorption activity coefficient *1/b*, are summarized to show the most suitable model for respective homologous series of surfactants.

The use of the classical Langmuir adsorption model for surfactants with a simple structure and sufficiently large head groups is justified still until today. This model, however, is also often applied for the development of more complex theoretical models just due to the fact that it provides direct relationships between the adsorbed amount Γ, the surface tension y and the surfactant bulk concentration c. For example, to described the adsorption kinetics of surfactants or relaxation processes of interfacial layers generated by external perturbations with the purpose to measure the dilational interfacial viscoelasticity of adsorbed layers, the resulting theoretical models are still obtained as analytical expressions [18].

3. Adsorption model of Frumkin

When comparing his experimental surface tension data for aqueous fatty acids, Frumkin [19] found out that the use of the equation of von Szyszkowski deviated more and more the longer the alkyl chain of the surfactant was. Based on this observation he concluded that there is probably a mutual interaction between the hydrophobic chains of the fatty acid molecules which is the stronger the longer the chains are. Thus, he added a term to the Langmuir adsorption model considering this interaction, i.e., he introduced the empirical constant a into Eq. (4) multiplied by the relative surface coverage $\theta^2 = (\frac{\Gamma}{\Gamma_\infty})^2$:

$$\gamma = \gamma_0 + RT\Gamma_\infty \ln\left(1 - \frac{\Gamma}{\Gamma_\infty}\right) + a\left(\frac{\Gamma}{\Gamma_\infty}\right)^2, \tag{8}$$

Frumkin demonstrated in this historical work published 100 years ago, that positive values for the parameter α describe the surface tension isotherms in a much better way. With increasing chain length from hexanoic to dodecanoic acid, the values for α increase to obtain a better fit of the measured surface tensions.

Combining Eq. (8) with Eq. (1) leads to the adsorption isotherm

$$bc = \frac{\frac{\Gamma}{\Gamma_\infty}}{1-\frac{\Gamma}{\Gamma_\infty}} \exp\left(-2\frac{a}{RT\Gamma_\infty}\frac{\Gamma}{\Gamma_\infty}\right). \tag{9}$$

The parameter α, originally introduced as an empirical term to better describe experimental data, obtained a physical meaning by the later work of Lucassen-Reynders [20]. She demonstrated that α can be derived in a clear thermodynamical way and reflects the heat of mixing, which in other words refers to the mutual interaction between the surfactant molecules adsorbed at the interface.

To obtain values for the model parameters in Eqs. (8) or (9), there are some mathematical problems to be solved, as both equations do not present an analytical relation of the experimental data in form of $y = y$(c). To optimize the parameter values, a special fitting software is needed as it was described by Aksenenko in [21]. This software, which contains many important adsorption models known so far, is available in open access.

The Frumkin model is most suitable for the description of surfactants with small headgroups and long alkyl chains, such as fatty acids and fatty alcohols. Due to the additional interaction parameter, this model is in many cases superior to the Langmuir model.

Purity of surfactants is a great issue in the determination of their adsorption layer characteristics. Already Mysels and Florence [22] emphasized the serious impact of impurities on the quality of results obtained by the comparison of experimental data with those obtained from thermodynamic or any other type of theoretical models. Lunkenheimer and co-workers continued the work of Mysels on impurities in surfactant samples and their effect on interfacial properties, as it was shown for the very classical surfactants fatty acids in [23]. There is even an apparatus designed to purify aqueous surfactant solutions up to a quality called "surface chemically pure" [24]. This grade of purity is required to use experimental data for a further analysis by adsorption models, which was already rigorously requested quite early, for example by Pallas and Pethica [25]. Today, often complicated theoretical models are applied to interpret data of low accuracy for substances of low purity, of even of technical origin, which does not make sense. This statement remains true also for work based on Artificial Intelligence (AI), because it appears rather improbable to extract any correct relationships from a large pool of incorrect and unreliable data.

The classical Frumkin adsorption model is superior for molecules with medium and long alkyl chains and small head groups, as shown already for fatty acids and alcohols in classical works [10, 19]. The better agreement with experimental data is not only due to the fact that the model has one more model parameter for the fitting procedure but also due to the really essential impact of the mutual interaction between adsorbed molecule on the shape of the corresponding equation of state [26].

4. Adsorption models of Fainerman

After the historical work by Frumkin, many more adsorption models were proposed, some derived rigorously on a thermodynamic basis, other with empirical or semi-empirical assumptions, as emphasized further above. However, there are thermodynamic models derived during the last thirty years that continue the strategy of the so-called classical models of Henry, Langmuir and Frumkin, and they extend logically their applicability to a broader system of surface active agents.

There is the reorientation model derived by Fainerman in order to generalize the Frumkin adsorption model [27]. It was found out that the experimental surface tension data for some C_nEO_m cannot be described adequately by the available adsorption models, even not by the Frumkin model with three independent model parameters. As it was shown further above in Fig. 1, the Langmuir isotherm does not describe the data adequately, neither does the Frumkin model (not shown). However, the assumption of two possible adsorption states, coexisting with each other according to the principle of Brown–le Chatelier, i.e., governed by the surface coverage, provide a much better description of the data. Note, the basics of interfacial thermodynamics for deriving adsorption models for surfactant adsorbed at fluid interfaces was presented in detail in [2] and is not repeated here. The resulting equation of state for this reorientation model has the form

$$\frac{\Pi\omega}{RT} = -\ln(1-\Gamma\omega) \tag{10}$$

and the corresponding adsorption isotherm reads

$$bc = \frac{\Gamma_1\omega}{(1-\Gamma\omega)^{\omega_1/\omega}} = \frac{\Gamma_2\omega}{(1-\Gamma\omega)^{\omega_2/\omega}} \quad \text{with} \quad \omega = \frac{\omega_1\Gamma_1+\omega_2\Gamma_2}{\Gamma_1+\Gamma_2} \tag{11}$$

Here, ω_1 and ω_2 are the molar areas for the surfactant molecules adsorbed in the two possible states with the average molar area $\omega = \frac{\omega_1\Gamma_1+\omega_2\Gamma_2}{\Gamma_1+\Gamma_2}$.

Another model, the so-called surface aggregation model, was also proposed by Fainerman et al. [28]. It can be seen as an equivalent to the micellization of surfactants in the solution bulk, but here 2-dimensional aggregates at the interface are assumed to be formed. When a certain critical surface coverage is reached, adsorbed molecules start to form small aggregates, such as dimers or trimers etc. This model should work preferentially for surfactants with small headgroups and long aliphatic chains, the same type of surfactants favourably described by the Frumkin model. However, the impact of the 2D aggregates is different from that expected by the interaction coefficient α. While the interaction coefficient acts at any surface coverage and its impact grows with the coverage squared θ^2, the impact of 2D aggregates starts only above a critical surface coverage.

In 2020 Fainerman et al. [29] proposed an improved the reorientation model, which can be also considered for other models, such as the Frumkin equation. They introduced a so-called intrinsic compressibility ε. This coefficient assumes that the molar area of an adsorbed surfactant molecule can change, depending on the surface coverage of surface pressure $\Pi = \gamma_0 - \gamma$:

$$\omega = \omega_0 (1 - \varepsilon\Pi), \qquad (12)$$

Here, $\omega = 1/\Gamma$ and ω_0 is the molar area of an adsorbed surfactant molecule at a given concentration and at extremely low surface coverage θ, respectively. The impact of ε is rather small, except when applied under dynamic conditions, i.e., for example at fast area changes as it is the case for oscillating drops and bubbles at high frequencies used to measure the dilational interfacial viscoelasticity.

The most recent is the multi-state adsorption model [30]. It represents a further generalization of the Frumkin as well as of the reorientation model and allows for n instead of only two adsorption states. The respective equation of state has the following form

$$-\frac{\Pi\omega_1}{RT} = ln(1-\theta) + \theta\left(1 - \frac{\omega_1}{\omega}\right) + a\theta^2, \qquad (13)$$

and the corresponding adsorption isotherm reads

$$b_i \cdot c = \frac{\omega\Gamma_i}{(1-\theta)^{\frac{\omega_i}{\omega}}} exp\left(-2a\frac{\omega_i}{\omega}\theta_i\right), \qquad (14)$$

The surface coverage is now defined by $\theta = \omega\Gamma = \sum_{i=1}^{n}\omega_i\Gamma_i$ and the total adsorption is the sum of molecules in all configurations $\Gamma = \sum_{i=1}^{n}\Gamma_i$. The index i stands for the adsorption state with the molar area ω_i, and the corresponding adsorption activity coefficient b_i. For n = 2 the equations transfer into the reorientation mode while for n = 1, we obtain immediately the original Frumkin model. The second term on the right-hand side of Eq. (13) reflects the non-ideality of entropy of the n adsorption states, which also disappears when there is only one adsorption state.

The multi-state adsorption model as presented in [30] is for sure superior for molecules of the type C_nEO_m, as the headgroups consist of rather flexible ethylene oxide chains. The longer these chains are, the more possible configurations exist and the molecules can adsorb in any of these states, as governed by the principle of Brown-le Chatelier. Of course, the more adsorption states are assumed the more difficult is the reliable determination of the values for the characteristic parameters for this model as shown in [14]. When applying this model for the analysis of experimental data, the obtained parameter values have to be carefully verified with respect to their physical meaning. Before assuming a too large number of possible conformations of surfactant molecules in the adsorption layer, a number of possible experimental shortcomings should be analyzed as discussed in [13].

For the particular description of adsorption layers formed by ionic surfactants, there are several attempts worth to be mentioned here, such as [31, 32, 33]. Note however, a description by the above-mentioned models also describe the behavior of many surfactants adequately. Further progress in a clear understanding of the ionic charge can be expected in the near future when these specific models for ionic surfactants are combined for example with molecular dynamics simulations like [34, 35, 36]. Then, particular characteristics of the surfactant molecules and the structure of the interfacial layer and the adjacent electric double layer can be appreciated in a more detailed way.

5. Peculiarities for water/oil interfaces

The adsorption of surfactants at water/oil interfaces was traditionally described by models derived for water/air interfaces. However, the interfacial tension isotherms of surfactants for these two interfaces show remarkable differences that must be considered in a quantitative way. What is of course identical is the CMC for both interfaces, as one can easily see in Fig. 2 for the cationic surfactant $C_{12}TAB$ as example. This is, however, obvious because the formation of micelles happens in the aqueous bulk phase and not at the interface. The first remarkable difference to be considered is the slope of the isotherms close to the CMC, proportional to the value for Γ_∞. At the water/hexane interface the slope is significantly less, i.e., the molecules obviously require more area at this interface. Moreover, the total decrease in surface/interfacial tension amounts to 35 mN/m for the W/A, and 47 mN/m for the W/H interface. Thus, the structure at the W/H interface must be much tighter packed, which sounds like a contradiction to the larger molar area for each surfactant molecules in the adsorption layer. And there is the most striking difference at very low surfactant bulk concentrations. While the change in surface tension for the W/A interface starts at a concentration about three orders of magnitude below the CMC, for the W/H interface, even at concentrations more than seven orders of magnitude below the CMC, the interfacial tension of the solution has not yet reached the value corresponding to the surfactant-free system.

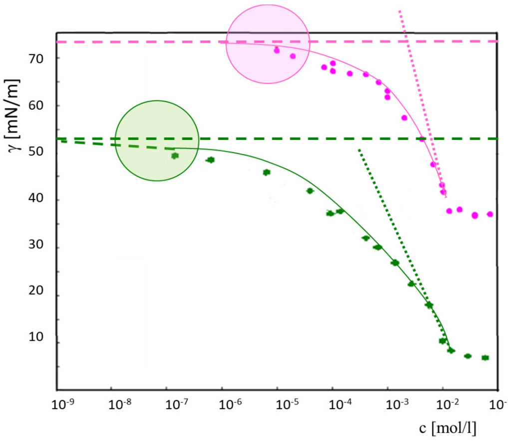

Fig. 2. Remarkable differences in the surface/interfacial tension isotherms for C_{12}TAB at the water/hexane as compared to the water/air interface.

The given peculiarities for the surfactant adsorption at the W/H interface, and in general at W/O interfaces, can be interpreted by a scheme presented in [29]. This physical picture is based on the formation of a mixed adsorption layer comprised of surfactant and oil molecules. At very low surfactant bulk concentrations, first adsorbing surfactant molecules are attracted by the oil phase. The oil molecules, in turn, start to form an interfacial structure and attract further surfactant molecules to adsorb. This cooperative effect continues until both types of molecules fill the interfacial layer and start to compete with each other. From this bulk concentration on, the adsorption process proceeds in a way similar to the W/A interface. The only but significant difference is, however, that oil molecules remain at the interface although getting less and less. These remaining oil molecules lead to a less steep slope of the interfacial tension isotherm, mimicking as if a larger area is requested by each single surfactant molecule. A cartoon is presented in [29] showing the change in composition of the interfacial layer as a function of the surfactant bulk concentration, and also showing the transition from a cooperative to a competitive adsorption of the two components.

To describe the mixed interfacial layer at W/O interfaces, Fainerman et al. proposed a model which was originally developed for binary surfactant mixtures [37]. Defining the surfactant and the oil molecules as the two compounds that form the interfacial layer, it was possible for the first time to describe adequately the particular structure at W/O interfaces. The equation of state for mixed interfacial layers reads

$$-\frac{\Pi\omega_0^*}{RT} = ln(1-\theta_1-\theta_2)+a_1\theta_1^2+a_2\theta_2^2+a_{12}\theta_1\theta_2. \tag{15}$$

where θ_1 and θ_2 are the relative surface coverages by the two components, oil and surfactant, α_1 and α_2 are the respective mutual interaction parameters, and α_{12} is the parameter for the interaction between the two different adsorbing molecules. The mean molar area ω_0* in Eq. (15) can be defined as the coverage-weighted average of the two individual molar areas ω_{10} and ω_{20}, respectively:

$$\omega_0^* = \frac{\omega_{10}\theta_1+\omega_{20}\theta_2}{\theta_1+\theta_2}. \tag{16}$$

This model is based on Frumkin's adsorption equation and can be seen as the generalized Frumkin model for mixed adsorption layers. The particular aspect for its application to W/O interfaces is that the co-adsorption of the adsorbing oil molecules is also considered, leading to mixed layers of oil and surfactant molecules. While in the past, effects of the oil phase were discussed just as a penetration of oil molecules into the surfactant layer, this new physical picture really assumes mixed layers, at low surface coverage based on cooperativity and at larger surface coverage on competition between the two compounds. Recent molecular dynamics simulations were made to support this idea about the molecular structure of adsorbed layers at W/O interfaces. The success of these first simulations confirms the proposed physical picture [34].

The analysis of the adsorption behavior of surfactants at water/oil interfaces has to be reconsidered in the near future after it was clearly shown that the molecules of the oil phase are part of the interfacial layer structure. This will include specific experiments with neutrons or X-rays [36] or with non-linear optical methods [38] as well as dedicated molecular dynamics simulations and their combinations of all these methods [34].

6. Summary and outlook

In this work, we describe the most important adsorption models, restricting ourselves to those derived from a clear thermodynamic basis. Naturally, many other models exist—some proposed as empirical relations, others derived in a semi-thermodynamic manner. Several of them, such as the Freundlich [5], Volmer [6], or Temkin [7] models, are frequently used, to mention only a few of the many available approaches. These equations are sometimes applied to describe surfactant adsorption at interfaces; however, in our view, they are of minor relevance compared to the thermodynamically grounded models discussed here. It is worth noting that the adsorption models proposed by Henry [12], Langmuir [11], Frumkin [19], and, more recently, by Fainerman [27, 30] are closely related: each more complex model is built upon the preceding, simpler ones. Conversely, through appropriate simplifications, each model can be reduced to a lower-complexity form, as illustrated in Flowchart 1 below.

Flowchart 1: Hierarchical scheme of available surfactant adsorption models

Henry model Eq. (7) [12]	
↓ surfactant molecules adsorb in localized adsorption layera with a minimum surface area required by each adsorbed surfactant molecule	↑ the adsorbed molecules do not require a limited adsorption area
Model of Langmuir and von Szyszkowski Eq. (4) [11]	
↓ there is additional mutual interaction between adsorbed molecules	↑ there is no interaction between adsorbed molecules
Frumkin model Eq. (8) [19]	
↓ there are two possible adsorption states	↑ there is only one possible conformation of adsorbed molecules
Fainerman's reorientation model Eqs. (10) and (11) [27]	
↓ there are more than 2 possible adsorption states	↑ there are only 2 instead of n possible adsorption states
Fainerman's multi-state model Eqs. (13) and (14) [30]	

Note also that the surface aggregation model proposed by Fainerman et al. [28] represents a generalization of the Frumkin model. When the formation of aggregates within the adsorption layer is neglected, this model immediately simplifies and reduces to Eq. (8).

The set of equations presented and discussed here are a solid basis of thermodynamic models suitable to describe quantitatively the adsorption layers of various types of surfactants at W/A and W/O interfaces. While simply structured molecules like fatty acids and alcohols, or alkyl dimethyl phosphine oxides follow quite well the behavior described by the Langmuir or better Frumkin model, surfactants with a more complex structure like C_nEOm, having a very flexible hydrophilic headgroup, are much better described by the reorientation or multi-state model. A deeper insight into the real structure of the discussed interfacial layers can be expected from a combination of several experimental methods and additional insights gained by molecular dynamics simulations.

The selection of the most suitable model to describe the adsorption of surfactants in an optimum way is still an issue. The application of more complex models, for example the Frumkin or reorientation models requires quite a bit of mathematical expertise, which was for example provided in [21] as a free software. With the help of machine learning algorithms and AI, the search for the most suitable adsorption model will become easier. Moreover, as demonstrated in [39], combining complementary experimental methods, together with molecular dynamics simulations [34], will further support this endeavor.

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