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Composition of mixed adsorption layers of non-ionic surfactants on oil/water interfaces

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Abstract

The subject of this work is the adsorption of binary mixtures of non-ionic surfactants whose molecules differ considerably in size. Since the surface layers are known to behave ideally, we investigate the role of the configurational entropy of mixing. We adopt the Gibbs model for the interface and propose a statistical treatment of the Flory–Huggins type for the case of incomplete coverage. Expressions for the surface chemical potentials are derived from the canonic partition function. The solvent–surfactant interactions are also discussed briefly and it is confirmed that for non-ionic surfactants on the oil/water boundary the mixing entropy effects are predominant. The theory allows us to develop a method for obtaining the composition of the adsorption layer using data for the interfacial tension isotherms in mixed systems and for the individual surfactants.

We study xylene–water systems containing Span 20, Tween 20 and their mixtures in proportions of 1:1 and 9:1 (molar ratio). From the equilibrium interfacial tensions we deduce the surface composition in a wide range of concentrations. It turns out that the adsorption layer is always enriched with Tween 20 owing to its higher surface activity. The results can be helpful in connection with emulsion stability.

Key words: Mixed adsorption layers; Non-ionic surfactants; Oil/water interfaces

1. Introduction

Surfactant mixtures are frequently applied to stabilize disperse systems (emulsions) because of the broad possibilities they offer for control over the system behavior. The system, however, is complex enough, with sometimes unexpected synergistic effects. Since the stability of emulsions is generally related to the properties of the interfaces and the thin liquid films between the droplets (rather than to the bulk behavior), the main problem we encounter in the case of mixtures is the determination of the composition of the interfacial adsorption layer which of course differs from the bulk composition. Such investigations are widespread in the literature, with the necessary experimental data coming from interfacial tension isotherms of mixed as well as individual surfactants.

The approach is usually based on the resemblance between mixed surfactant adsorption and the formation of mixed micelles. The latter problem has been solved under the assumption of a regular solution formed by the surfactant molecules in the micelle [1]. For a binary mixture consisting of N molecules the entropy and enthalpy of mixing are

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given by

$$\Delta S_{mix} = -Nk(x_1 \ln x_1 + x_2 \ln x_2) \qquad (1)$$

$$\Delta H_{mix} = \beta x_1 x_2 NkT \qquad (2)$$

where x_1 and x_2 represent the mole fractions of the surfactants 1 and 2 in the micelle, and β is a dimensionless interaction parameter. As usual, k denotes the Boltzmann constant and T is temperature.

It is worth mentioning that this kind of theory, as seen from Eq. (1), does not account for a possible difference in the size of the surfactant molecules, as far as the entropy of mixing is expressed in terms of mole fractions. Under the same assumption and by analogy with the case of micelles, mixed adsorption layers on the solution/air boundary have been treated [2]. Again, a regular solution is adopted as an approximation for the interfacial layer and Eqs. (1) and (2) hold, with x_i being the surfactant mole fractions on the surface ($i = 1, 2$ for binary mixtures). Complete surface coverage is additionally assumed ($x_1 + x_2 \approx 1$). The surface chemical potential is written as [2]

$$\mu_{i,s} = \mu_{i,s}^0(\pi) + kT \ln(f_{i,s} x_i) \qquad (3)$$

where $\mu_{i,s}^0$ is the standard surface chemical potential, π is the surface pressure and $f_{i,s}$ denotes the surface activity coefficient which is representative for the interactions in the adsorption layer (both the solvent–surfactant interactions and those between the surfactant molecules). It is related in a simple way to the parameter β in Eq. (2):

$$f_{i,s} = \exp[\beta(1 - x_i)^2] \qquad i = 1, 2 \qquad (4)$$

(see Ref. 1).

Experimental investigations of various mixed-surfactant systems have been performed [1–3]. The typical values of β given in Ref. 1 for non-ionic surfactants on the water/air boundary are within the range 0.0–(−0.8), i.e. the interaction effects nearly vanish. For mixtures containing charged molecules (anionic–cationic and ionic–non-ionic), large negative β values have been obtained due to the attraction between the polar groups as well as to cohesion between the tails. However, on oil/water interfaces even the ionized

surfactants form almost ideal adsorption layers (the intermolecular interactions are found to be negligible) [4]. The corresponding conclusion drawn in Ref. 4 states that the non-idealities on water/air surfaces arise from the interchain cohesion, which is absent in oil/water systems. The latter case will be considered in this work and that is why we disregard the direct interactions between non-ionic surfactant molecules. A brief discussion is given in Section 4 concerning the possible influence of solvent–surfactant interactions. However, the difference in sizes of the molecules which constitute the adsorption layer should also play a role, and is to be accounted for. It affects the entropy of mixing, Eq. (1).

An attempt has been made to include size effects when treating solution/air interfaces [5]. The theory proposed in Ref. 5 ignores any direct interaction between the surfactant molecules but considers the solvent–surfactant interactions in the surface layer (under the assumption of low solvent adsorption compared with that of the surfactants). The surface chemical potential is written in the Butler form [5]:

$$\mu_{i,s} = \mu_{i,s}^0 + kT \ln(f_{i,s} x_i) + (\sigma_0 - \sigma) a_i \qquad (5)$$

where σ is the interfacial tension and σ_0 is the interfacial tension without additives. This equation holds for each of the surfactants as well as for the solvent. The mixing enthalpy connected with $f_{i,s}$ turns out to be about kT per molecule for various anionic and cationic surfactants [5]. In Eq. (5), $\pi = \sigma_0 - \sigma$ is the surface pressure and a_i denotes the partial molar surface area of the component i.

By setting the surface chemical potential given by Eq. (5) to be equal to the bulk one, it is found that [5]

$$\sigma_0 - \sigma = \frac{kT}{a_1} \left\{ -\ln(1 - \Theta_A - \Theta_B) \right.$$

$$\left. + \ln\left[1 - \Theta_A\left(1 - \frac{1}{v_A}\right) - \Theta_B\left(1 - \frac{1}{v_B}\right)\right] \right\} \qquad (6)$$

The subscripts 1, A and B refer to the solvent, surfactant A and surfactant B respectively. For the

partial molar surface areas we have, by definition,

$$a_A = v_A a_1 \qquad a_B = v_B a_1 \qquad (7)$$

In Eq. (6), θ_i represents the coverage (area fraction) of the component i ($i = 1$, A, B) such that

$$\Theta_1 + \Theta_A + \Theta_B = 1 \qquad (8)$$

The surfactant coverages Θ_A and Θ_B are connected in a simple way with the respective adsorptions Γ_A and Γ_B:

$$\Theta_A = \frac{v_A N_A}{M} = a_A \Gamma_A \qquad \Theta_B = \frac{v_B N_B}{M} = a_B \Gamma_B \qquad (9)$$

where M is the number of sites in the two-dimensional lattice, and N_A and N_B give the number of molecules of the corresponding species present in the interfacial layer, the latter having a total area $A = M a_1$.

A similar type of thermodynamic theory was developed by Huber [6] who examined the case of two surfactants of unequal size. This work, however, as well as the paper by Lucassen–Reynders [5], rests on the Butler equation (Eq. (5)) for the surface chemical potential.

It can be easily proven that Eq. (5) is in agreement with the entropy of mixing given by Eq. (1) (ΔS_{mix} refers to mixing at constant temperature and surface pressure). However, Eq. (1) does not take into account the difference in sizes of the two species. Therefore, although Refs. 5 and 6 have tried to allow for the size effects, their approach is not entirely self-consistent. At least, the results (especially Eq. (6)) should have asymptotic validity, with the sizes of the molecules being approximately equal.

The general theory for mixtures of molecules of different sizes originates from Flory and Huggins (for the particular case of linear polymers) and from Hildebrand and Scatchard [7,8]. According to this theory the chemical potential $\mu_{i,s}$ should contain a more complicated configurational term rather than $\ln x_i$ in Eq. (5).

2. Model of the interfacial layer

In order to be able to obtain the characteristic thermodynamic parameters of the interface, one should represent it as a separate phase. Model considerations are required for that purpose. Here we discuss the two principal model approaches — the Gibbs dividing surface and the so-called monolayer model [9].

For the sake of definiteness, we will confine ourselves to the case of Span and Tween mixtures where the size effects are expected to be essential. A simplified sketch of the interfacial layer between water and oil phases is shown in Fig. 1. (The polar heads of the Tween molecules contain several oxyethylene groups attached to the same sorbitan ring as in Span.)

According to Gibbs, the transition zone is to be replaced by a single mathematical surface to which excess amounts of the chemical components are assigned under the assumption that the bulk phases are homogeneous right up to that surface. Although entirely correct from a mathematical viewpoint, this model makes use of formal excess quantities which in some cases differ substantially from the real amounts of the species present in the interfacial layer. However, for surfactants the bulk concentration is very low compared with that on the surface and consequently, any location of the Gibbs surface within the transition zone would provide an excess close to reality [9,10].

The interfacial composition can be described in a more precise way within the frames of the so-called monolayer model [9]. The surface is regarded as a monomolecular layer of thickness equal to the dimensions of one molecule. This model suffers from the major shortcoming of being in contradiction with the surface thermodynamics
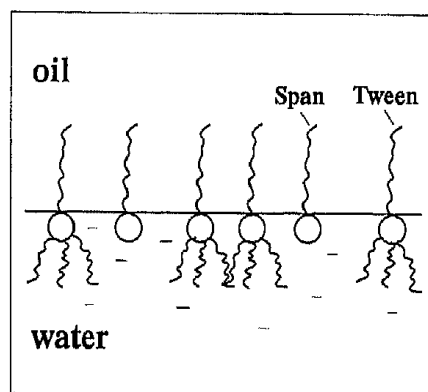

Fig. 1. A sketch of the mixed adsorption layer of Span and Tween on an oil/water interface.

when the interactions between the constituent molecules are to be accounted for (see Ref. 9, p. 178, Eqs. (12.99) and (12.100)). For that reason, several layers of different composition are sometimes introduced to represent the real interfacial zone [9]. In the limiting case of ideal mixing (without any interaction) the monolayer model should be in agreement with the adsorption thermodynamics [9]. There is, however, one more simplification put forward, which is concerned with the configurational entropy of mixing. It states that all kinds of molecules should have one and the same size in a direction perpendicular to the surface (Ref. 9, p. 202). Apparently, this is not the case for Span and Tween mixtures. Indeed, as far as Tween contains oxyethylene groups, its polar head is likely to be more bulky than that of Span (see Fig. 1). Owing to the considerable difference in sizes of water and surfactant molecules, one can hardly regard the interface as a monomolecular layer of uniform thickness. That is why the monolayer model seems to be inappropriate for the Span- and Tween-containing systems. Because of the very complicated formalism of the multilayer model, we prefer to describe the interfacial zone following the Gibbs approach. Adsorptions of the two kinds of surfactant will be sought for. Lattice statistics of the Flory–Huggins type will be applied to attain the configurational mixing terms. The water molecules, which are admittedly present in the surface layer, do not provide a separate contribution to the configurational entropy. Indeed, once the surfactant molecules are located on the lattice, the water has only one choice to dispose (the molecules are indistinguishable). Therefore, from the statistical viewpoint, water is represented as a structureless fluid which just fills up the space left by surfactant molecules. In addition, it will be assumed that water and oil are totally immiscible. Hence, the adsorptions of these solvents on the Gibbs dividing surface will be identically zero. This is a plausible supposition since the thickness of the transition region between oil and water is small even when compared to the dimensions of the surfactant molecules.

The aim of the study is to deduce the interfacial composition in the presence of a binary mixture of surfactants. For that purpose, explicit expressions for the surface chemical potentials $\mu_{i,s}$ are required. Physically, $\mu_{i,s}$ will comprise contributions from (i) the configurational entropy of mixing of surfactant molecules of dissimilar size; (ii) structural entropy coming from the possible alteration in the water structure around the polar heads of the surfactants, and (iii) the enthalpy change due to interactions between the solvent (water) molecules in the surface layer and the surfactant. The last two effects are connected with the hydration of the polar heads of the non-ionic surfactant molecules. It will be shown below that by means of a proper choice of experimental data one can determine the interfacial composition without specifying the explicit form of the structural entropy and enthalpy contributions. Moreover, for the particular case of a mixture of non-ionic surfactants it turns out that the configurational entropy should dominate in the molar surface free energy (as far as the dependence of the latter on the surface coverage is concerned, i.e. up to a constant).

3. Lattice statistics of mixed surface layers

Let us now consider two homogeneous bulk phases (water and oil) separated by a surface of zero thickness. The Gibbs adsorptions of water (w) and oil (o) supposedly vanish, $\Gamma_o = \Gamma_w = 0$. Excesses of two different surfactants of types A and B are assigned to the dividing surface. The surfactant molecules will be regarded as hard disks having an area per molecule of a_A and a_B respectively. We represent the surface phase as a two-dimensional lattice which consists of M sites of area a_0 each (Fig. 2). A molecule of type A (or B) occupies ν_A (or ν_B) sites

$$a_A = \nu_A a_0 \qquad a_B = \nu_B a_0 \qquad (10)$$

where N_A and N_B are the respective numbers of molecules attached to the surface of total area

$$A = M a_0 \qquad (11)$$

We define the coverages Θ_A, Θ_B by means of Eqs. (9); Γ_A and Γ_B denote the adsorptions (number of molecules per unit area). It is noteworthy that the total area fraction filled up with surfactant is less than unity, i.e. $\Theta_A + \Theta_B < 1$.
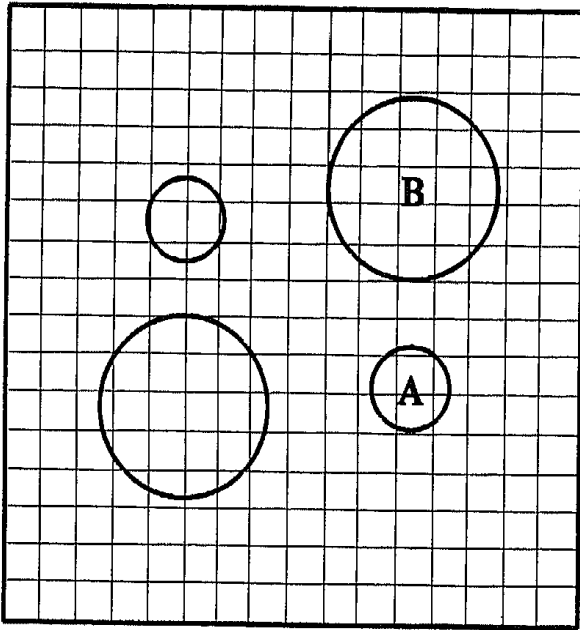
Fig. 2. Two-dimensional lattice containing two kinds of molecules of dissimilar size.

We apply Flory–Huggins type statistics to count the number of possible configurations of the two types of molecules mixed on the lattice. The procedure consists of placing the molecules successively one after another onto the free sites. Since the results are symmetric with respect to A and B, it does not matter which kind of molecule is to be allocated first. For the first molecule A there are M possible positions (as usual, we neglect the edge effects). The placing of the second molecule A (with the first one already fixed) corresponds to

$$(M - v_A)\left(1 - \frac{v_A}{M}\right)^{v_A - 1} = M\left(1 - \frac{v_A}{M}\right)^{v_A}$$

possibilities. For the third molecule we have

$$(M - 2v_A)\left(1 - \frac{2v_A}{M}\right)^{v_A - 1} = M\left(1 - \frac{2v_A}{M}\right)^{v_A}$$

and so on to the N_Ath.

Since one particle occupies v_A sites, we account for the probability that v_A single positions will be simultaneously empty in order to accommodate one molecule. In the same manner the number of configurations of the N_B molecules of type B can be found. For the ith particle B, with all molecules

A and $(i - 1)$ of type B already disposed, we have

$$[M - N_A v_A - (i - 1)v_B]\left[1 - \Theta_A - \frac{(i - 1)v_B}{M}\right]^{v_B - 1}$$

$$= M\left[1 - \Theta_A - \frac{(i - 1)v_B}{M}\right]^{v_B}$$

possibilities. Therefore the configurational part of the canonic partition function (Q^c) acquires the form

$$Q^c = \frac{M^{N_A + N_B}}{N_A! N_B!}\left\{\prod_{k=0}^{N_A - 1}\left(1 - \frac{kv_A}{M}\right)\right\}^{v_A}$$

$$\times \left\{\prod_{k=0}^{N_B - 1}\left(1 - \Theta_A - \frac{kv_B}{M}\right)\right\}^{v_B} \tag{12}$$

We take the logarithm and replace the sums by integrals to find

$$\ln Q^c = (N_A + N_B)\ln M - \ln(N_A! N_B!)$$
$$- M[\Theta_A + \Theta_B + (1 - \Theta_A - \Theta_B)$$
$$\times \ln(1 - \Theta_A - \Theta_B)] \tag{13}$$

The corresponding entropy change can be obtained from the relationship

$$\Delta S_{mix}/k = \ln Q^c - \ln Q_A^c - \ln Q_B^c \tag{14}$$

where Q_A^c denotes the partition function of N_A molecules located on $v_A N_A$ elementary sites of the lattice before mixing, and the meaning of Q_B^c is analogous. To derive an expression for $\ln Q_A^c$ we put $M = v_A N_A$, $\Theta_A = 1$, $N_B = 0$ and $\Theta_B = 0$ in Eq. (13) and thus

$$\ln Q_A^c = N_A \ln v_A - N_A(v_A - 1) \tag{15}$$

Similarly

$$\ln Q_B^c = N_B \ln v_B - N_B(v_B - 1) \tag{16}$$

From Eqs. (13)–(16) it follows that

$$\Delta S_{mix}/k = -N_A \ln \Theta_A - N_B \ln \Theta_B$$
$$- (M - v_A N_A - v_B N_B)\ln(1 - \Theta_A - \Theta_B) \tag{17}$$

This result can be discussed in view of the theories of Flory–Huggins and Hildebrand–Scatchard [7,8]. The approach adopted here

holds for incomplete surface coverage, i.e. for $\Theta_A + \Theta_B < 1$. In contrast, the existing theories refer to the case where all sites of the lattice are occupied by molecules ($\Theta_A + \Theta_B = 1$). As seen from Eq. (17), the space free from surfactant molecules can be considered as an imaginary chemical component (the third term in the right-hand side). The single site of size a_0 represents a "particle" of this imaginary component. It should be noted that a_0 cannot be determined within the frame of the statistical model. It stands as a free parameter which can only come from independent experimental data. Owing to the complicated structure of the real interfacial layer (Fig. 1), a_0 does not coincide with the size of a solvent molecule.

The incomplete surface coverage leads to one more difference from the Flory–Huggins theory, connected with the number of independent variables. Indeed, when $\Theta_A + \Theta_B < 1$, the number of surfactant molecules N_A, N_B and the total area $A = a_0 M$ will be independent. (If $\Theta_A + \Theta_B = 1$, only two of these three quantities vary independently.) The kinetic surface pressure due to the presence of surfactant can be expressed by means of the partition function Q^c:

$$\sigma_0 - \sigma = \frac{kT}{a_0}\left(\frac{\partial \ln Q^c}{\partial M}\right)_{T,N_A,N_B} \qquad (18)$$

σ_0 denotes the interfacial tension without any additives. After performing the calculations we obtain from Eq. (13)

$$\sigma_0 - \sigma = \frac{kT}{a_0}\left\{-\ln(1-\Theta_A-\Theta_B) - \Theta_A\left(1-\frac{1}{v_A}\right) \right.$$
$$\left. -\Theta_B\left(1-\frac{1}{v_B}\right)\right\} \qquad (19)$$

It is worthwhile to compare this result with the relationship given by Lucassen–Reynders [5] — Eq. (6). As pointed out above, the latter can only have asymptotic validity, with the size of the two kinds of surfactant molecules nearly equal. Indeed, after expanding Eq. (6) in a series at $v_A \to 1$, $v_B \to 1$ we obtain Eq. (19). Therefore the Lucassen–Reynders expression can be considered as a particular case of the more general Eq. (19) which holds for any difference in molecular size.

4. Composition of the interfacial layer

Our goal here will be to find the surface coverages Θ_A, Θ_B, by using the interfacial tension isotherms in oil–water systems. For this purpose, we need to know the surface chemical potentials of the species A and B. From the statistical theory of the canonic ensemble [7] we have

$$\mu_{A,s} = -kT\left(\frac{\partial \ln Q}{\partial N_A}\right)_{T,M,N_B}$$

$$\mu_{B,s} = -kT\left(\frac{\partial \ln Q}{\partial N_B}\right)_{T,M,N_A} \qquad (20)$$

where Q represents the total partition function for the mixed layer. Generally, we can write [7]

$$Q = Q^c q_A^{N_A} q_B^{N_B} \exp\left(-\frac{\Delta H_{mix}}{kT}\right) \qquad (21)$$

where Q^c is given by Eq. (12), and q_A and q_B (functions of T and M) denote the partition functions of the single molecules. Now, we use Eq. (2) for ΔH_{mix} and carry out straightforward calculations inserting Eqs. (12) and (21) into Eq. (20) to obtain

$$\mu_{A,s} = \mu_{A,s}^0 + kT \ln \frac{\Theta_A}{v_A(1-\Theta_A-\Theta_B)^{v_A}}$$
$$+ \beta kT x_B^2 \qquad (22)$$

Here $x_B = N_B/(N_A + N_B)$. As usual, the standard chemical potential is introduced by

$$\mu_{A,s}^0 = -kT \ln q_A \qquad (23)$$

It is clear from Eq. (22) that if the interaction term is written in the form $kT \ln f_{A,s}$ we recover Eq. (4). In our further considerations we will neglect this term on the basis of a numerical assessment given below in this section. Therefore we apply the following expressions for the surface chemical potentials:

$$\mu_{A,s} = \mu_{A,s}^0 + kT \ln \frac{\Theta_A}{v_A(1-\Theta_A-\Theta_B)^{v_A}}$$

$$\mu_{B,s} = \mu_{B,s}^0 + kT \ln \frac{\Theta_B}{v_B(1-\Theta_A-\Theta_B)^{v_B}} \qquad (24)$$

where $\mu_{i,s}$ refers to a mixed adsorption layer formed in a system where each surfactant A or B is dissolved either in one of the two bulk phases or in both of them.

Let us now consider a solution of pure surfactant A (or B) with the same concentration as it has in the mixture. In other words, we merely remove the second surfactant from the mixed system. This state will be denoted by (0). The interface will contain only component A (or B) and then the usual statistical theory of adsorption [7] can be used. In such a case the unit site of the lattice is chosen to coincide in size with an adsorbed molecule [7] (there are no particles of different size). Equation (19), with $a_0 = a_A$ (or $a_0 = a_B$), acquires the form

$$\sigma_0 - \sigma_A(0) = -\frac{kT}{a_A}\ln[1 - \Theta_A(0)]$$

$$\sigma_0 - \sigma_B(0) = -\frac{kT}{a_B}\ln[1 - \Theta_B(0)] \qquad (25)$$

where $\sigma_A(0)$ and $\sigma_B(0)$ represent the interfacial tension in a system where the surfactant A or B alone is present in the same concentration as in the mixture, the latter having an interfacial tension σ according to Eq. (19). For the chemical potentials in the state (0) we obtain the corresponding expressions from Eq. (24), also putting $\nu_A = 1$ and $\nu_B = 1$:

$$\mu_{A,s}(0) = \mu_{A,s}^{\circ} + kT\ln\frac{\Theta_A(0)}{1 - \Theta_A(0)}$$

$$\mu_{B,s}(0) = \mu_{B,s}^{\circ} + kT\ln\frac{\Theta_B(0)}{1 - \Theta_B(0)} \qquad (26)$$

Thus we recover the Langmuir adsorption, as is expected for a single surfactant in the absence of lateral interactions.

Since by definition the bulk concentrations of the species A and B are one and the same in the state (0) and in the mixture, the surface chemical potentials should be equal too:

$$\mu_{A,s} = \mu_{A,s}(0) \qquad \mu_{B,s} = \mu_{B,s}(0) \qquad (27)$$

We recall that in thermodynamic equilibrium $\mu_{i,s}$ ($i = $ A, B) is equal to the bulk chemical potential and the latter coincides in the state (0) and in the

mixture for each of the surfactants. Hence, using Eqs. (27), (26) and (24) we derive that

$$\frac{\Theta_A(0)}{1 - \Theta_A(0)} = \frac{\Theta_A}{\nu_A(1 - \Theta_A - \Theta_B)^{\nu_A}}$$

$$\frac{\Theta_B(0)}{1 - \Theta_B(0)} = \frac{\Theta_B}{\nu_B(1 - \Theta_A - \Theta_B)^{\nu_B}} \qquad (28)$$

Equations (28) and (19) represent a set of non-linear equations from which the surface coverages Θ_A, Θ_B along with a_0 (a model parameter) can be found numerically; $\Theta_A(0)$ and $\Theta_B(0)$ are easily obtained through Eqs. (25). The quantities known from experimental data are σ_0, σ, $\sigma_A(0)$, $\sigma_B(0)$, a_A and a_B. The determination of the last two is explained in the next section.

There is one more point concerning $\mu_{i,s}$ which deserves special attention. The standard chemical potentials (Eqs. (24)), which are independent of the surface coverage, are related to the closest environment of the surfactant molecules in the interfacial layer (see Eq. (23)), that is, the standard potentials are representative for the structure and interactions in the hydration shell which covers the polar heads of the surfactant. Our consideration is restricted to the case of Span and Tween. The polar groups of these molecules contain a sorbitan ring (Span) with bonded polyoxyethylene chains (Tween). Hence, the head can be regarded as being composed of oxyethylene fragments ($-CH_2-CH_2-O-$). This allows us to estimate qualitatively the free energy of hydration. From thermodynamic data (see Ref. 11, p. 17) it follows that the change in the standard chemical potential on hydration of one $-CH_2-CH_2-O-$ group amounts to -1800 cal mol^{-1} (about $3kT$ at $25\,^{\circ}$C). Therefore the process of hydration is thermodynamically favorable enough and the water shell around the polar head of a surfactant molecule is not affected by the thermal motion. In other words, the water molecules are affixed to the polar groups.

It is essential to point out that the standard chemical potentials concerned with the hydration are the same regardless of whether the surfactant molecule belongs to a mixed adsorption layer or to a layer consisting of pure surfactant. For that reason, Eqs. (24) (mixed system) and Eqs. (26) (individual surfactant) contain identical constant

terms for A and B respectively. On equating the chemical potentials via Eq. (27) the constants cancel. Therefore, the final relations (Eqs. (28)) are not influenced by the hydration free energy and $\mu_{i,s}^{\circ}$.

As a matter of fact, one more complication may arise from possible long-range effects concerned with hydration. As two surfactant molecules come closer towards each other, their hydration layers can interfere, being mutually disturbed. This leads to entropy and enthalpy changes which do depend upon the amount of surfactant present, i.e. upon the surface coverage. The effect is usually attributed to an activity coefficient in the surface chemical potential, Eq. (22), referring to the solvent–surfactant interaction. The contribution of this kind of non-ideality to the free energy of mixing was studied in Ref. 5 for ionic surfactants. The enthalpy change for mixing of the surfactant molecules with water in the surface layer was written in the form of Eq. (2). For anionics and cationics (fatty acids, their salts and quaternary ammonium salts) β was found to be about 1.2–1.5. In the case of non-ionic surfactants the effect should be less pronounced because the solvent–surfactant interactions are described in terms of dipole–dipole interactions instead of ion–dipole interactions. Moreover, β is multiplied by the mole fractions, which are always less than 1 (Eq. (2)). Therefore the enthalpy of mixing of non-ionic surfactant with water should always be considerably lower than kT per molecule. In the next section we will see that the free energy change due to the mere configurational entropy of mixing of Span and Tween is about kT per molecule. We come to the conclusion that the contribution of non-ideality concerned with the long-range solvent–surfactant interaction can be safely neglected with respect to the entropy of mixing.

5. Experiments and numerical results

Xylene (p.a. grade) and water purified by a Milli-Q system (Millipore) were used as bulk phases. The surfactants Tween 20 (polyoxyethyl-ene(20) sorbitan monolaurate) and Span 20 (sorbitan monolaurate) were I.C.I. products. The interfacial tension was measured versus time using

the du Nouy platinum ring method. Prior to the measurement, the xylene and water phases were pre-equilibrated for 24 h. Tween is soluble in both water and oil (preferably in water), whereas Span is only oil soluble. The equilibrium interfacial tension was obtained by extrapolation of the relaxation of σ to infinite time (with the last point being taken 5 h after the loading of the bulk phases in the vessel).

Let us first determine the area occupied by one molecule of Span and Tween. The interfacial tension curves for oil–water systems in which pure Span 20 or Tween 20 is dissolved are shown in Figs. 3 and 4. It is obvious from the shape of the σ curves that Tween 20 forms micelles in the water phase at a total concentration of about 10^{-5} mol l^{-1} whereas no micelles of Span 20 exist in the oil.

We make use of the data in the region of the maximum slope of the function $\sigma(\ln c)$. According to the Gibbs isotherm, this corresponds to an adsorption close to the saturated one:

$$\frac{d\sigma_i}{d \ln c_i} = -kT\Gamma_i = -kT\frac{\Theta_i}{a_i} \tag{29}$$

where $i = A$ (Span 20) or B (Tween 20). The bulk concentration c_i is expressed in moles per unit volume of the whole system (1:1 water to oil). It is denoted by c_{total} in Figs. 3–6.

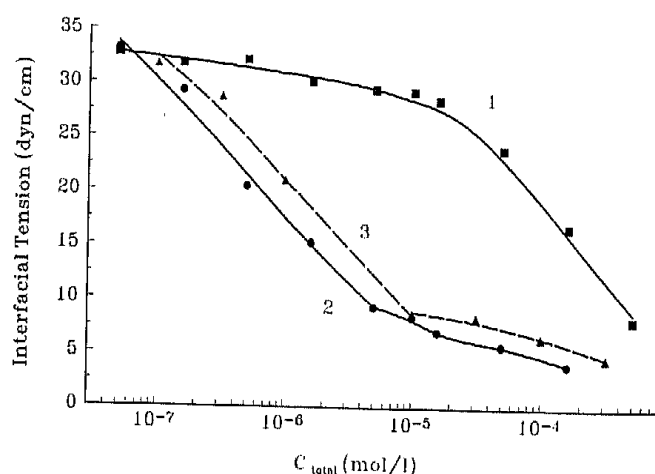Along with Eqs. (29), we apply, for pure Span

Fig. 3. Interfacial tension isotherms vs. the total surfactant concentration c_{total} in the two-phase system xylene–water (volume ratio, 1:1): curve 1, pure Span 20; curve 2, pure Tween 20; curve 3, mixture of Span 20 and Tween 20 in the proportion of 1:1 (molar).

Fig. 4. Interfacial tension isotherms vs. the total surfactant concentration c_{total} in the two-phase system xylene–water (volume ratio, 1:1): curve 1, pure Span 20; curve 2, pure Tween 20; curve 3, mixture of Span 20 and Tween 20 in the proportion of 9:1 (molar).
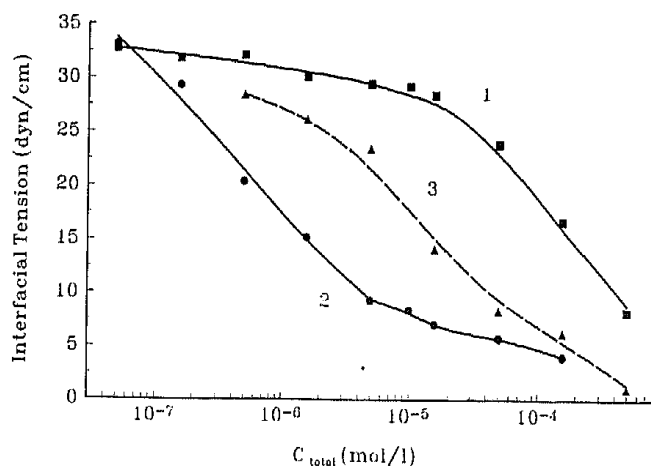
and Tween adsorption layers, equations analogous to Eqs. (25):

$$\sigma_0 - \sigma_i = -\frac{kT}{a_i}\ln(1 - \Theta_i) \qquad (30)$$

The combination of Eqs. (29) and (30) allows us to determine Θ_i and a_i from the numerical values of σ_i and $(d\sigma_i/d\ln c_i)$ taken from Fig. 3. Thus we obtain

$$a_A = 53.2 \text{ Å}^2 \text{ for Span 20}$$

$$a_B = 81.2 \text{ Å}^2 \text{ for Tween 20} \qquad (31)$$

Besides, we have $\Theta_A = 0.942$ and $\Theta_B = 0.987$, which indicates that the adsorption layers of pure surfactants are quite closely packed.

Further, we use the interfacial tension isotherms in mixed systems: (i) a 1:1 molar ratio of Span 20 to Tween 20 (Fig. 3); (ii) a 9:1 molar ratio (Fig. 4). From the curves we extract numerical values for σ, $\sigma_A(0)$ and $\sigma_B(0)$. For example, if we take from Fig. 4 the interfacial tension σ at 1×10^{-5} mol l^{-1} total surfactant concentration (mixture 9:1), then $\sigma_A(0)$ will refer to 9×10^{-6} mol l^{-1} on the curve for pure Span 20, and $\sigma_B(0)$ will correspond to 1×10^{-6} mol l^{-1} on the curve for pure Tween 20. We put σ, $\sigma_A(0)$ and $\sigma_B(0)$ into Eqs. (25) and find $\Theta_A(0)$ and $\Theta_B(0)$. All these parameters are then inserted into Eqs. (28) and (19) and the latter are solved numerically with respect to the unknown

variables Θ_A, Θ_B and a_0. The results for the surface coverages are presented in Fig. 5 for a 1:1 Span to Tween molar ratio and in Fig. 6 for a 9:1 molar ratio.

It is evident from these data that Tween 20 always dominates in the surface layer, even if the bulk composition of the mixed solute is 9:1 in
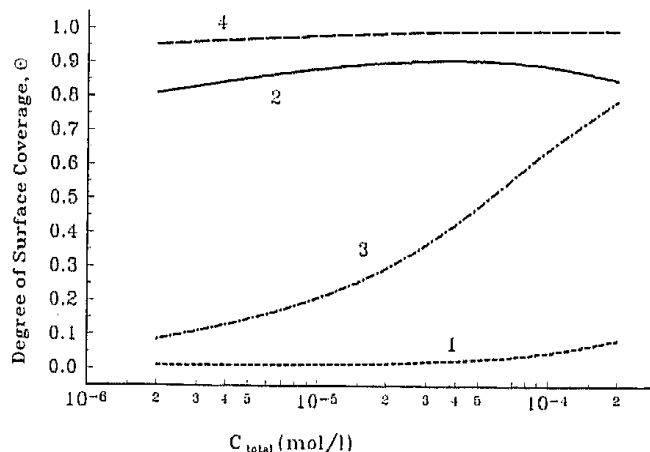

Fig. 5. Coverage of the xylene–water surface vs. the total surfactant concentration of the mixed system containing Span 20 and Tween 20 in the proportion of 1:1 (molar): curve 1, Span 20 in the mixed layer; curve 2, Tween 20 in the mixed layer; curve 3, coverage of Span 20 when Tween 20 is removed from the mixture whose concentration is shown on the abscissa; curve 4, coverage of Tween 20 when Span 20 is removed from the mixture.

Fig. 6. Coverage of the xylene–water surface vs. the total surfactant concentration of the mixed system containing Span 20 and Tween 20 in the proportion of 9:1 (molar): curve 1, Span 20 in the mixed layer; curve 2, Tween 20 in the mixed layer; curve 3, coverage of Span 20 when Tween 20 is removed from the mixture whose concentration is shown on the abscissa; curve 4, coverage of Tween 20 when Span 20 is removed from the mixture.
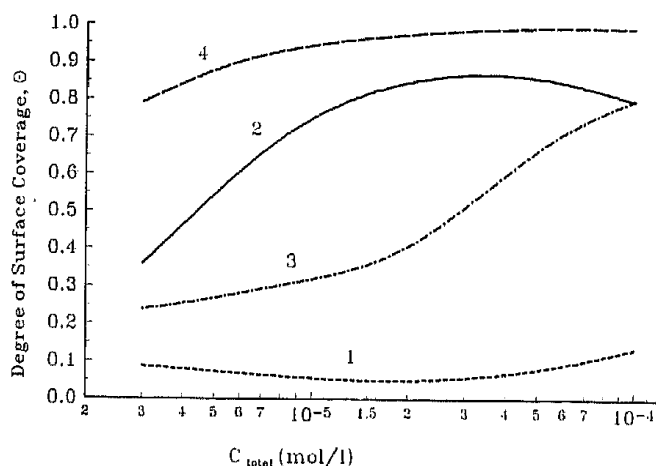
favor of Span 20. Of course, this fact is attributed to the much higher surface activity of Tween (compare with Figs. 3 or 4). If the total surfactant concentration is high enough (above $1 \times 10^{-4}\,\mathrm{mol\,l^{-1}}$) the adsorption of Tween tends to decrease and that of Span increases. This finding is explained in view of the competition between the two surfactants — the surface activity of Span rises sharply in this region (Fig. 3). In the case of the 9:1 molar ratio of Span to Tween, the adsorption of Tween descends very steeply below a $1 \times 10^{-5}\,\mathrm{mol\,l^{-1}}$ total solute concentration (Fig. 6). Undoubtedly, the low bulk concentration of Tween causes the adsorption ability to be weak. For the sake of clarity we have also drawn in Figs. 5 and 6 curves showing what the surface coverage would have been if Span and Tween had been present alone, at the same bulk concentration as in the mixture.

These data also confirm the low surface activity of Span and its substantial increase with concentration. The theory should be used with caution when mixed micellization is likely to occur. Indeed, formation of mixed micelles can influence the bulk chemical potentials (and therefore the surface ones). As a consequence, Eqs. (28) could be violated.

It is worthwhile noting that a_0, the model parameter in Eq. (19), ranges between 20 and 40 Å^2 for different points in Figs. 5 and 6. In other words, the single site of the two-dimensional lattice does not coincide in size with the solvent (water) molecules (see the discussion in Sections 2 and 3 above).

The configurational entropy of mixing of Span and Tween in the surface layer can be readily estimated from Eq. (17) by means of typical values for Θ_A, Θ_B and a_0. With $\Theta_A = 0.1$, $\Theta_B = 0.8$ and $a_0 = 30$ Å^2, we find that $T\Delta S_{mix} \approx 1.2kT$. This figure is to be compared with the free energy, which comes from the structure and enthalpy contributions due to hydration, i.e. due to the solvent–surfactant interactions. The latter can be decomposed into two parts. The first does not depend on the surface coverage and is related to the closest environment (hydration shell) of the surfactant molecules. Although much greater than kT (see the previous section), this contribution is included in the standard surface chemical potential and can be eliminated by a proper choice of experimental data. The standard potentials cancel in Eqs. (28). The second part of the excess free energy corresponds to activity coefficients which depend on the surface coverage (Eq. (22)). These terms are connected with the long-range solvent–surfactant interactions. For the case of non-ionic surfactants the respective free energy contribution turns out to be much smaller than $T\Delta S_{mix}$ (the configurational mixing entropy). Therefore we can draw the conclusion that the presence of solvent (water) in the interfacial layer is not relevant for the determination of the surface composition. Thus we support the assumption put forward in Section 2.

6. Discussion

Here we apply the theory described in Sections 3 and 4 in order to treat literature experimental data for the surface tension at the solution/air boundary [2]. Of course, our model is not particularly restricted to oil–water systems (nor to Span–Tween mixtures) and can be used provided the equilibrium between the bulk and the surface is established. The system studied in Ref. 2 was composed of a mixture of two non-ionic surfactants, $C_{12}H_{25}(OC_2H_4)_8OH$ (component 1, $C_{12}EO_8$) and $C_{12}H_{25}(OC_2H_4)_3OH$ (component 2, $C_{12}EO_3$). The isotherms (at 25 °C) for the surface tension versus surfactant concentration are presented in Figs. 1 and 2 of Ref. 2. The surface areas of the two components, a_1 and a_2, are to be determined from our Eqs. (29) and (30). For pure $C_{12}EO_8$ (curve 1 in Fig. 2, Ref. 2) the slope is $\mathrm{d}\sigma_1/\mathrm{d}\ln c_1 = -7.23\,\mathrm{dyn\,cm^{-1}}$ in the region just below the CMC, i.e. at $\sigma_1 = 36\,\mathrm{dyn\,cm^{-1}}$. Then elimination of Θ_1 from Eqs. (29) and (30) with $\sigma_0 = 72\,\mathrm{dyn\,cm^{-1}}$ [2] yields $a_1 = 56.5$ Å^2. Similarly, for pure $C_{12}EO_3$ (curve 1 in Fig. 1, Ref. 2) we have $\mathrm{d}\sigma_2/\mathrm{d}\ln c_2 = -10.41\,\mathrm{dyn\,cm^{-1}}$ at $\sigma_2 = 42\,\mathrm{dyn\,cm^{-1}}$ (the experimental points around the CMC are somewhat scattered, so we prefer to take the slope at $\sigma_2 = 42\,\mathrm{dyn\,cm^{-1}}$). Thus $a_2 = 36.8$ Å^2. Further, we make use of the data for different mixtures given in Table I of Ref. 2. The calculation procedure is the same as in Section 5 and the results are shown in our Table 1.

Table 1

Results of calculations for the surface coverage in the system $C_{12}EO_8$–$C_{12}EO_3$; experimental data are taken from Ref. 2

Sample no.	Bulk concentration (mol l^{-1})		$\Theta_1(0)$	$\Theta_2(0)$	$\sigma_0 - \sigma$ [2] (dyn cm^{-1})	Degree of surface coverage			Mole fraction of $C_{12}EO_3$ in the surface $N_2/(N_1 + N_2)$	
	$C_{12}EO_8$	$C_{12}EO_3$				Θ_1	Θ_2	$\Theta_1 + \Theta_2$	This work	Ref. 2
1	2.13×10^{-5}	8.91×10^{-6}	0.9748	0.8978	32.1	0.5403	0.4122	0.9525	0.54	0.53
2	1.30×10^{-5}	3.16×10^{-6}	0.9630	0.7774	27.0	0.6945	0.2434	0.9379	0.35	0.33–0.36
3	1.30×10^{-5}	4.47×10^{-6}	0.9630	0.8204	27.8	0.6280	0.3053	0.9333	0.43	0.43
4	1.30×10^{-5}	1.26×10^{-5}	0.9630	0.9239	32.3	0.3224	0.5889	0.9113	0.74	0.70–0.72
5	1.30×10^{-5}	8.91×10^{-6}	0.9630	0.8978	30.4	0.4122	0.4942	0.9064	0.65	0.60–0.62
6	4.34×10^{-6}	1.26×10^{-5}	0.9144	0.9239	30.1	0.1447	0.6970	0.8417	0.88	0.84–0.89
7	4.34×10^{-6}	4.47×10^{-6}	0.9144	0.8204	23.8	0.3384	0.4536	0.7920	0.67	0.60–0.63
8	4.34×10^{-6}	6.31×10^{-6}	0.9144	0.8651	25.4	0.2461	0.5385	0.7846	0.77	0.67–0.74
9	4.34×10^{-6}	3.16×10^{-6}	0.9144	0.7774	22.3	0.3741	0.3837	0.7578	0.61	0.47–0.53

For example, let us take the system consisting of 4.34×10^{-6} mol l^{-1} $C_{12}EO_8$ and 1.26×10^{-5} mol l^{-1} $C_{12}EO_3$ (line 6 in Table 1). Here, $\sigma_1(0)$ for the pure component 1 is found on curve 1, Fig. 2, Ref. 2, at a concentration equal to 4.34×10^{-6} mol l^{-1}. Thus, $\sigma_1(0) = 54.1$ dyn cm^{-1}. Having the value for a_1, one then obtains from Eq. (25), $\Theta_1(0) = 0.9144$ (the third column in Table 1). Similarly, for the pure component 2 we obtain $\sigma_2(0) = 43.2$ dyn cm^{-1} from curve 1, Fig. 1, Ref. 2, at a concentration of 1.26×10^{-5} mol l^{-1}. Hence, Eq. (25) gives $\Theta_2(0) = 0.9239$ (the fourth column in Table 1). The surface tension for the mixture is taken from Table I of Ref. 2, i.e. $\sigma_0 - \sigma = 30.1$ dyn cm^{-1}. Now, having $\Theta_1(0)$, $\Theta_2(0)$, $\sigma_0 - \sigma$, a_1 and a_2, the set of Eqs. (19) and (28) is solved numerically for a_0 and for the surfactant coverages in the mixed layer, Θ_1 and Θ_2 ($a_0 = 19.39$ Å^2, not shown in Table 1). The results in Table 1 are aligned in order of descending values of $\Theta_1 + \Theta_2$.

Reference 2 presents also data for the mole fraction of $C_{12}EO_3$ in the surface. Those data were calculated by means of two different methods [2] — the Hutchinson method and the regular solution theory (discussed in Section 1). The corresponding results obtained in Ref. 2 are shown in the last column of Table 1, with the second numbers referring to the regular solution treatment. We determine the surface mole fraction of $C_{12}EO_3$ using our values for the coverages Θ_1 and Θ_2 for the same mixtures

$$x_2 = \frac{N_2}{N_1 + N_2} = \frac{\Theta_2 a_1}{\Theta_1 a_2 + \Theta_2 a_1}$$

One can compare x_2 values in the last two columns of Table 1. In general, for high surfactant concentrations and high degrees of total coverage ($\Theta_1 + \Theta_2$ close to unity 1) the agreement between our theory and the results of Ref. 2 is very good. At lower concentrations, $\Theta_1 + \Theta_2$ decreases substantially. Under these conditions, the mole fraction of the component 2 determined in Ref. 2 becomes lower than ours. The effect is particularly evident in line 9 of Table 1. For this mixture, almost one-fourth of the surface remains uncovered by surfactant. The regular solution theory [2] predicts a considerably lower amount of component 2 compared with that for the theory proposed here.

It has to be mentioned that the difference in sizes of the two kinds of molecules, $C_{12}EO_8$ and $C_{12}EO_3$, is not very large. As explained in Section 3, the regular solution theory based on the Butler equation is expected to give results close to ours in this case. That is probably why we find a good coincidence with the data of Ref. 2 at high coverages. Still, for incomplete surfactant coverage the size effects do not seem to be properly accounted for by the more simplified theories [2]

which underestimate the content of the smaller-sized component in the surface (the regular solution treatment is better than the Hutchinson method).

7. Conclusions

We propose a Flory–Huggins type theory for mixed adsorption layers of surfactant molecules of dissimilar size at an oil/water interface. The theory accounts for the configurational mixing effects and discards the interactions in the surface layer since they are negligible for non-ionic surfactants. We consider the case of incomplete surface coverage in the frame of the Gibbs model. The free space in the two-dimensional lattice is occupied by the solvent which is considered to be a structureless fluid. The contribution of the solvent–surfactant interactions in the free energy of mixing is estimated and is shown to be much smaller than the configurational contribution. The size of the single site of the lattice, which is a model parameter, is determined numerically from experimental data. Owing to the complex structure of the surface layer, the site dimensions do not coincide with those of the solvent molecules.

A method is proposed for calculating the composition of the adsorption layer on the oil/water (or the solution/air) boundary from the interfacial tension isotherms of the mixed and the individual surfactants. We apply the expression for the surface chemical potentials derived from the canonic partition function. Other workers' experimental data for the water/air surface tension in the mixed system $C_{12}EO_8$–$C_{12}EO_3$ are discussed in view of our theory. It is found that at high total surfactant coverage, our results for the interfacial composition coincide with those obtained by means of other more simplified considerations available in the literature. The latter, however, underestimate the

content of the smaller-sized component when compared with our results at lower total coverage.

The xylene–water system containing Span 20, Tween 20, and their mixtures in proportions of 1:1 and 9:1 (molar) is investigated. Since Tween 20 has considerably higher surface activity than Span 20, the interface is enriched with Tween for all experimental conditions studied, namely, for total surfactant concentrations falling within the range 2×10^{-6}–2×10^{-4} mol l^{-1} at the 1:1 molar ratio as well as at the 9:1 Span–Tween molar ratio. The results can be helpful with respect to emulsion stability. The two kinds of surfactants are connected with different mechanisms of stabilization and the slender balance could be crucial.

8. Acknowledgment

9. References

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