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ORIGINAL CONTRIBUTION

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A simple adsorption model for ionic surfactants

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Abstract In the past, few theoretical attempts have been made to describe quantitatively the adsorption of ionic surfactants at liquid interfaces. Well-known adsorption isotherms due to Frumkin or Hill–de Boer cannot respond to the specific electrostatic and geometric properties of the surfactant molecules. Our approach is based on a combination of the Gouy–Chapman theory with a modified Frumkin isotherm. The modification implies that the system is free to choose an optimal head group area and an optimal arrangement of the surfactant molecules in the interface as a function of bulk concentration. Interaction energies between neighbouring adsorbed surfactant molecules and between surfactant and water molecules are taken into consideration. The minimum of the Gibbs free energy of the system is equivalent to a minimal interfacial tension. Thus, the thermodynamically stable isotherm can be obtained as the lower envelope of the family of σ versus $\ln c$ isotherms resulting from different choices of the model parameters, including the area per molecule. According to the Gibbs equation, the Γ versus $\ln c$ adsorption isotherm is obtained as the derivative of this envelope. By variation of the model parameters, the envelope of the calculated adsorption isotherms can be fitted to experimental data of the interfacial tension versus bulk concentration. A computer program is used to calculate the σ versus c and the Γ versus $\ln c$ curves as well as to fit the parameters.

Key words Ionic surfactants · Adsorption · Model · Isotherm · Surface tension

Introduction

Ionic surfactants, often used in everyday life, are of special interest in interface and colloid science. Despite many experimental investigations the physical details of the adsorption process at fluid interfaces are still not very well understood on a molecular basis.

Well-known adsorption isotherms due to Langmuir, Frumkin or Hill–de Boer do not respond to the specific electrostatic and geometric properties of the surfactant molecules. In some cases, this causes large deviations from experimentally determined equilibrium surface tension versus bulk concentration isotherms, especially if long-chain surfactants (large cooperativity) are regarded. In the past, many attempts were made to achieve a proper match of the theoretical isotherm and the measured data without consideration of electrostatics. Some examples of such simple approaches should be mentioned. As a kind of generalized Frumkin isotherm, the so-called power-law cooperativity model [1] allows extended variation of the interaction term between adsorbed surfactant molecules. Another way to model strong cooperativity is to divide the bulk concentration range into two parts, one at low concentrations, representing a gaseous-like surface state and a second, representing a kind of liquid adsorption layer (phasechange model [1]). A similar but more sophisticated approach was presented by Lunkenheimer and coworkers [2, 3]. Here, a Frumkin isotherm is combined with a Henry/Traube equation of state by applying a transition function as a function of the surfactant bulk concentration. In this way a good fit can be achieved to measured data of short-to-medium-chain anionic surfactants [2, 3].

Despite these improvements, there is the problem of fitting parameters (Gibbs standard free energies of adsorption, interaction energies between adsorbed surfactant molecules) used without direct context to the molecular properties of the amphiphiles and to the electrostatic phenomena. Several authors have published models combining a simple adsorption isotherm (or a surface equation of state) with diffusive double layer theory, mostly of the Gouy–Chapman type. A Langmuir isotherm was adopted by Davies and Rideal [4]. Haydon and Taylor [5] used a Volmer isotherm and Borwankar and Wasan [6] a Frumkin isotherm. Kalinin and Radke [7] improved the Borwankar and Wasan type model by introducing a contact-ion pairing of the counterions with the charged head groups (triple layer structure due to Grahame [8]). Eriksson and Ljunggren [9] developed a model taking into account molecular properties of surfactant molecules; hydrophobic and conformational energy contributions were included and electrostatic free energy was again calculated from the Gouy–Chapman theory.

In this article we present a simple adsorption model similar to that in Ref. [6] with the additional feature of a modified Frumkin isotherm allowing the system to choose an optimal head group area and an optimal arrangement of the surfactant molecules in the surface.

Materials and methods

Materials

Three different cationic surfactant salts were used: dodecyl-, tetradecyl- and hexadecylpyridinium chloride. In total, nine different surfactant/KCl/water systems were investigated (three alkylpyridinium chlorides, each in three different KCl concentrations: 0, 0.01 and 0.1 mol l^{-1}). The surfactant solutions were prepared with water from an ultrapure water system using UV photooxidation at 185 nm (Milli-Q_{185}, Millipore, Bedford, USA). Organic contaminants was less than 5 ppb total organic carbon; the surface tension was in the range 71.7–72.0 mN m^{-1} at 25 °C [10, 11]. KCl (purity 99.5%, p.a., Merck, Darmstadt, Germany) was heated to 400 °C for several hours and then stored in an airtight container.

Dodecylpyridinium chloride was obtained from Henkel, Dusseldorf, Germany (purity >96%) and hexadecylpyridinium chloride from Fluka, Buchs, Switzerland (purity > 98%). Tetradecylpyridinium chloride was synthesized from pyridinium and 1-bromotetradecane dissolved in absolute ethanol, with subsequent ion exchange in aqueous NaCl (purity 99.5%, p.a., Merck, Darmstadt, Germany) solutions.

All surfactants were highly purified ("surface-chemically pure") at the Max Planck Institute of Colloids and Surfaces, Golm, Germany, by employing the method of Lunkenheimer and coworkers [12, 13]. Details concerning surfactant purification and analysis can be found elsewhere [14].

Methods

Surface tension measurements were performed with a laser tensiometer using the pendant drop technique: LASDA Mk IV (D. & R. Ferstl, Hemau, Germany) [15–17]. For a short description see Ref. [14].

Each measured surface tension isotherm consists of 14–22 single points (surfactant concentrations). Each point is a mean value of 3–5 different drops. A capillary made of high-quality stainless steel of gauge 12 was used. The drop volume was in the range 19–32 μl, depending on surface tension and surfactant concentration. The temperature was kept constant at 25 ± 0.1 °C. The final value of the surface tension was measured after 63 min.

Approach

Model concept

The well-known Frumkin isotherm has three important features: it is simple, includes interaction between adsorbed molecules and is capable of describing phase transitions. Our approach is based on a combination of the Gouy–Chapman theory [18, 19], describing long-range interfacial electrostatics, with a modified Frumkin isotherm. The modification implies that the system is free to choose an optimal head group area and an optimal arrangement of the surfactant molecules in the interface as a function of a given bulk concentration. Interaction energies between neighbouring adsorbed surfactant molecules and between surfactant and water molecules are taken into consideration.

The minimum of the Gibbs free energy of the system is equivalent to a minimal interfacial tension. Thus, with all the other model parameters given, the thermodynamically stable isotherm is obtained as the lower envelope of the σ versus $\ln c$ isotherms resulting from different choices of the area per molecule. According to the Gibbs equation, the corresponding Γ versus $\ln c$ adsorption isotherm is obtained as the derivative of this envelope.

By variation of the model parameters, the envelope of the calculated adsorption isotherms can be fitted to experimental data of the interfacial tension.

In essence, the route is as follows: for a given cross-sectional area the surface coverage is varied in certain steps from 0 to 1. For each value the concentration in the immediate neighbourhood of the interface is calculated from the Frumkin isotherm. Then the bulk concentration is determined numerically by means of the Gouy–Chapman theory. By inserting the values of concentration and surface coverage into the Gibbs adsorption isotherm the surface tension isotherm is obtained (σ versus $\ln c$). Repetition of this procedure for different cross-sectional areas per site, a, results in a set of surface tension isotherms from which the stable isotherm is obtained as described previously.

Basic equations

The electrostatic part of our approach is based on the classical Gouy–Chapman theory [18–20]. We consider a solution containing a symmetrical 1-1 surfactant salt with bulk concentration, c, and a background electrolyte with bulk concentration, c_e. All ions are monovalent. The surfactant is a cationic one. The surfactant concentration in the immediate neighbourhood of the surface is given by

$$c_0 = c \exp[-\Phi_0] \ . \tag{1}$$

The dimensionless surface potential, Φ_0, is equal to $F\varphi_0/RT$. F is the Faraday constant, R the gas constant, T the temperature and φ_0 the surface potential.

The surface charge density, γ_0, is related to the surface potential by

$$\gamma_0 = [8RT\varepsilon(c + c_e)]^{1/2} \sinh\left[\frac{\Phi_0}{2}\right] = F\Gamma_0^+ \ , \tag{2}$$

where Γ_0^+ is surface concentration of the surfactant. The dielectric constant, ε, is assumed to be independent of x, the direction normal to the surface. The fractional coverage of the surfactant in the surface, Θ, is defined by

$$\Theta = \frac{\Gamma_0^+}{\hat{\Gamma}} \ , \tag{3}$$

where $\hat{\Gamma}$ is maximum surface concentration, related to the area per site, a, by $\hat{\Gamma} = (\mathrm{N_A a})^{-1}$. Combination of Eqs. (1)–(3) gives the following expression for Θ

$$\Theta = \frac{(8RT\varepsilon)^{1/2}}{2F\hat{\Gamma}} (c + c_e)^{1/2} \left[\left(\frac{c}{c_0}\right)^{1/2} - \left(\frac{c_0}{c}\right)^{1/2}\right] \ . \tag{4}$$

The concentration c_0 is obtained as a function of Θ from the Frumkin adsorption isotherm

$$c_0 = K \exp\left[\frac{\Delta\tilde{\mu}\Theta}{kT}\right] \frac{\Theta}{1 - \Theta} \ , \tag{5}$$

where $\Delta\tilde{\mu}$ denotes the interaction energy between adsorbed surfactant molecules and K the dissociation constant. This equation allows the calculation of c_0 as a function of Θ. The parameters K and $\Delta\tilde{\mu}$ are discussed later. Then, for a given cross-sectional area, a, c can be easily determined numerically from Eq. (4) by applying root-finding routines.

Surface tension isotherm

The Gibbs equation for a fully dissociated surfactant salt in an ideal solution without additional electrolyte ($c_e = 0$) is given by [21]

$$d\sigma = -2RT\Gamma \, d\ln c \ . \tag{6}$$

If electrolyte is added and $c_e \gg c$, the factor of 2 is replaced by 1 and Eq. (6) becomes formally identical with the Gibbs equation of a nonionic surfactant.

From Poisson–Boltzmann electrostatics it follows that the thermodynamic surface excess concentration, Γ, is related to Γ_0^+ by [22]

$$\Gamma = \Gamma_0^+ \left(\frac{1}{2} + \frac{1}{2}\mathrm{tgh}\left[\frac{F\varphi_0}{4RT}\right]\right) \ . \tag{7}$$

Hence from Eq. (6)

$$d\sigma = -2RT\Theta\hat{\Gamma} \left(\frac{1}{2} + \frac{1}{2}\mathrm{tgh}\left[\frac{\Phi_0}{4}\right]\right) d \ln c \ . \tag{8}$$

From Eq. (1) we deduce

$$\mathrm{tgh}\left[\frac{\Phi_0}{4}\right] = \mathrm{tgh}\left[\frac{1}{4}\ln\left[\frac{c}{c_0}\right]\right] \ . \tag{9}$$

Thus, σ, or $\Delta\sigma = \sigma_0 - \sigma$, where σ_0 is the surface tension of pure water, can be obtained from Eq. (8) as a function of c by numerical integration.

The temperature dependence of σ_0 can be described by [23]

$$\sigma_0(T) = \left(75.668 - 0.1396\left(\frac{T}{K} - 273.15\right) - 0.0002885\left(\frac{T}{K} - 273.15\right)^2\right) 0.001\,\mathrm{N\,m^{-1}} \ . \tag{10}$$

Dissociation constant and interaction term

Let a_c be the geometrical cross-sectional area of a hydrocarbon chain. To incorporate the entropic contribution of the free (unoccupied) surface area $(a - a_c)$ we write K as

$$K = \frac{\tilde{K}}{(a - a_c)/a_c} \ , \tag{11}$$

where $\tilde{K}$ is a constant and is identical with K at $a = 2a_c$.

In our simulations (see later) we use a simple heuristic equation for the maximal interaction energy, $\Delta\tilde{\mu}$; therefore, the outcome of the simulations should not be taken too quantitatively but as a basis for qualitative discussion and qualitative comparison with experimental data. The dependence of $\Delta\tilde{\mu}$ on a is assumed to be of a hyperbolic type and is described by

$$\Delta\tilde{\mu} = \sigma_{ha}\, 3a_s\left(\frac{a}{0.5\, a_s + a} - 1\right) \ , \tag{12}$$

where σ_{ha} is the surface tension of a fluid hydrocarbon (representing surfactant chains) against air and a_s the area of a side face of the alkyl chain. The coefficients of this relation are deduced from the following considerations.

The chain of a surfactant molecule is approximated to be of cuboid shape. The zero of the interaction energy is attributed to an isolated adsorbed surfactant molecule (no interaction with other molecules) lying flat on the water surface with three faces in contact with the vapour ($a \gg a_s$). Therefore, the energy gain of densely packed, upright chains (with $a = a_c, a_c \ll a_s$) approaches a limiting value of $-3\sigma_{ha}a_s$ per chain. The factor of 0.5 in the denominator of Eq. (12) is chosen to get reasonable agreement with experimental data.

The temperature dependence of σ_{ha} is described by the following relation [24]

$$\sigma_{ha}(T) = \left[35.0 - 325M^{-2/3} - 0.098\left(\frac{T}{K} - 298\right)\right] \text{mN m}^{-1} \ . \tag{13}$$

The relative molecular mass, M, of a surfactant chain is approximated by

$$M = (n_c - 1.5)\,14.027 \ , \tag{14}$$

where n_c denotes the number of carbon atoms of the alkyl chain. The reduction by 1.5 takes into account that, as a mean, roughly 1.5 CH_2 segments of an adsorbed surfactant molecule are still within the water phase, as found in NMR measurements [25] on micelles and in small-angle neutron scattering investigations on adsorbed surfactants [26, 27].

With the length, l_c, and the volume, v_c, of a surfactant chain, the area, a_s, is

$$a_s = (v_c\,l_c)^{1/2} \ . \tag{15}$$

According to Tanford [28], l_c and v_c are given by

$$l_c = (n_c - 1.5)\,12.65 \times 10^{-11}\,\text{m} + 15.0 \times 10^{-11}\,\text{m} \tag{16}$$

$$v_c = (n_c - 1.5)\left[26.9 + 0.014\left(\frac{T}{K} - 298\right)\right] \times 10^{-30}\,\text{m}^3 + \left[54.6 + 0.124\left(\frac{T}{K} - 298\right)\right] \times 10^{-30}\,\text{m}^3 \ , \tag{17}$$

where the second term is an additional contribution of the CH_3 end group.

Results and discussion

Simulations

The following results were obtained from a computer program calculating c, c_0, Γ, σ and σ_{ha} as a function of Θ for given values of a, c_e and l_c (see model concept earlier).

For every envelope 19 single surface tension isotherms (for 19 different cross-sectional areas) were determined. Figures 1–9 show dependencies on different parameters: chain length ($C_{10}, C_{12}, C_{14}, C_{16}, C_{18}$), dissociation constant, $\tilde{K}$, ($1 \times 10^{-4}, 1 \times 10^{-6}, 1 \times 10^{-8}$ mol l^{-1}) and background electrolyte concentration (0.0, 0.1, 1.0 mol l^{-1}) at 298.15 K.

Except for the calculations of Fig. 5, $\tilde{K}$ was set to 4.0×10^{-8} mol l^{-1}. The normalization concentration, c_n, is 1.0 mol l^{-1} and the critical cross-sectional area, a_c, is 0.21 nm^2 [28]. It is somewhat bigger than the geometrical cross-sectional area of an all-trans crystal alkyl chain (0.19 nm^2).

Isotherms including a phase transition (loop in surface tension isotherm, S-shaped branch in adsorption isotherm) are drawn in a corrected form and unstable regions are omitted. Therefore, a phase transition is simply shown by a kink (surface tension isotherm) or a vertical jump (adsorption isotherm).

Some theoretical curves are not quite smooth. This is due to the discreteness of the calculated points. No smoothing between these points was performed.

The features of the simple adsorption model are demonstrated in Figs. 1–6. The general modeling route is

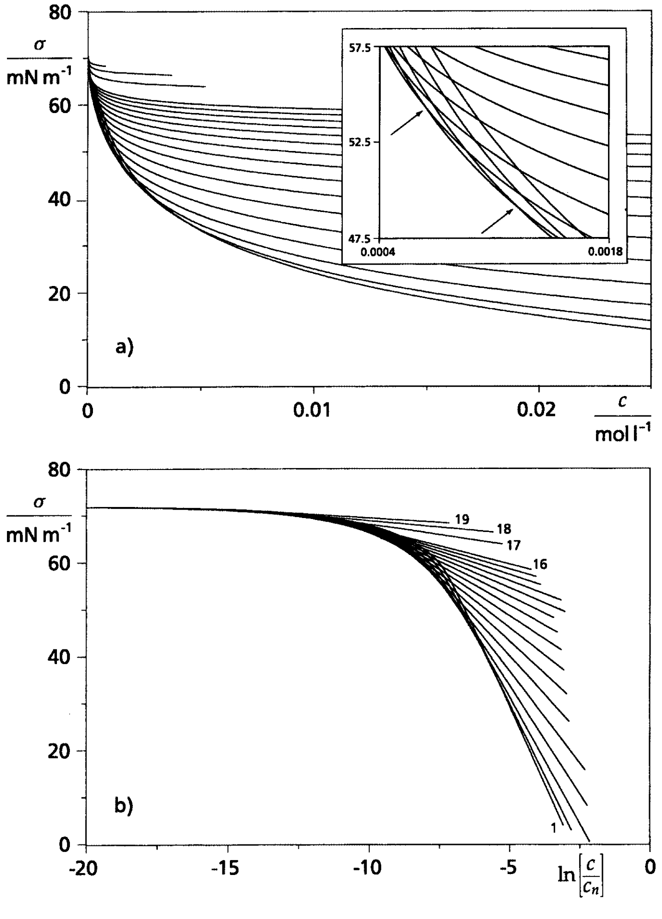

Fig. 1a, b Surface tension isotherms for an ionic surfactant with chain length 12, $c_e = 0.1$ mol l^{-1}. **a** Linear plot, **b** logarithmic plot

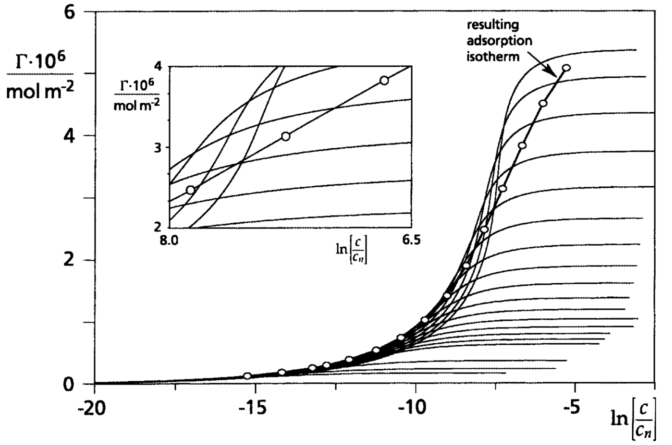

Fig. 2 Adsorption isotherm (Γ versus ln c) of the system described in Fig. 1

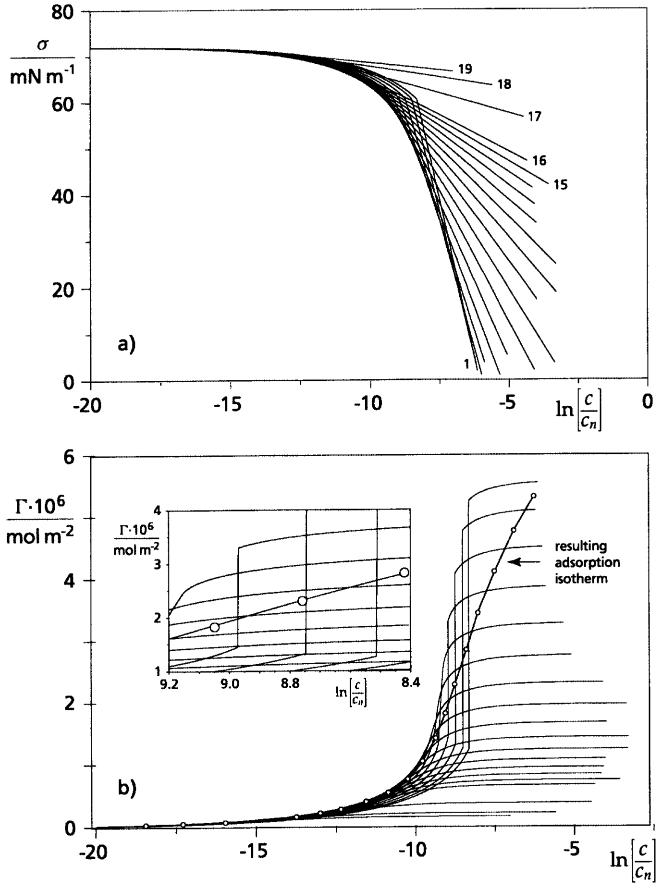

Fig. 3a, b Ionic surfactant with chain length 16, $c_e = 1$ mol l^{-1}. **a** Surface tension isotherms, logarithmic plot. **b** Adsorption isotherm Γ versus ln c

shown in Figs. 1–3 and the effect of parameter variation is illustrated in Figs. 4–6. Comparison with measured isotherms is presented in the following section.

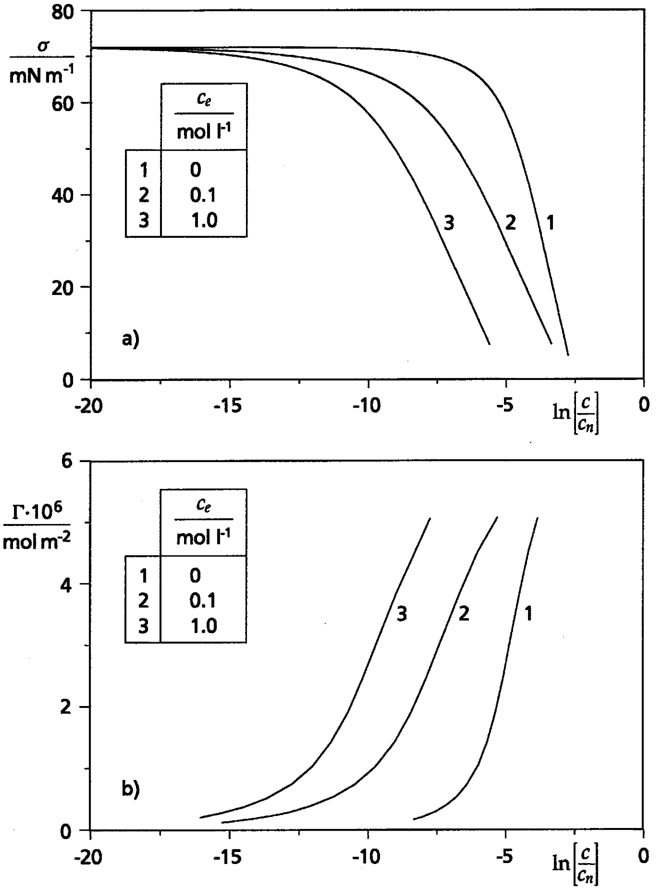

Fig. 4 **a** Resulting stable surface tension isotherms and **b** resulting adsorption isotherms as a function of background electrolyte concentration. All parameters according to Fig. 1. The maximum value of $\hat{\Gamma}$ is 5.37×10^{-6} mol m^{-2} (corresponding to $a = 0.309$ nm^2 as largest area). *Curves 2* can also be seen in Figs. 1 and 2

The surface tension isotherms for different cross-sectional areas are shown in Fig. 1. Curve 1 is for the smallest area (0.309 nm^2) and curve 19 is for the largest one (10.0 nm^2). The corresponding interaction energies vary from -6.4 to $-0.4\,kT$ and the values for K vary from 5.2×10^{-8} to 7.7×10^{-10} mol l^{-1}. The areas increase linearly, except for the three largest areas which were chosen to be quite large (4.5, 7, and 10 nm^2) in order to include the range of very low bulk concentrations (which is needed for comparison with experimental data).

As discussed, the stable isotherm is given by the lower envelope. The arrows in Fig. 1a indicate the transitions between the single isotherms forming this envelope.

Figures 2 and 3b show how the resulting adsorption isotherm is obtained. As pointed out, the transition concentrations can be easily read from the surface tension isotherms. The corresponding value of Γ is taken as the mean value obtained from the respective adsorption isotherms. The resulting adsorption isotherms in

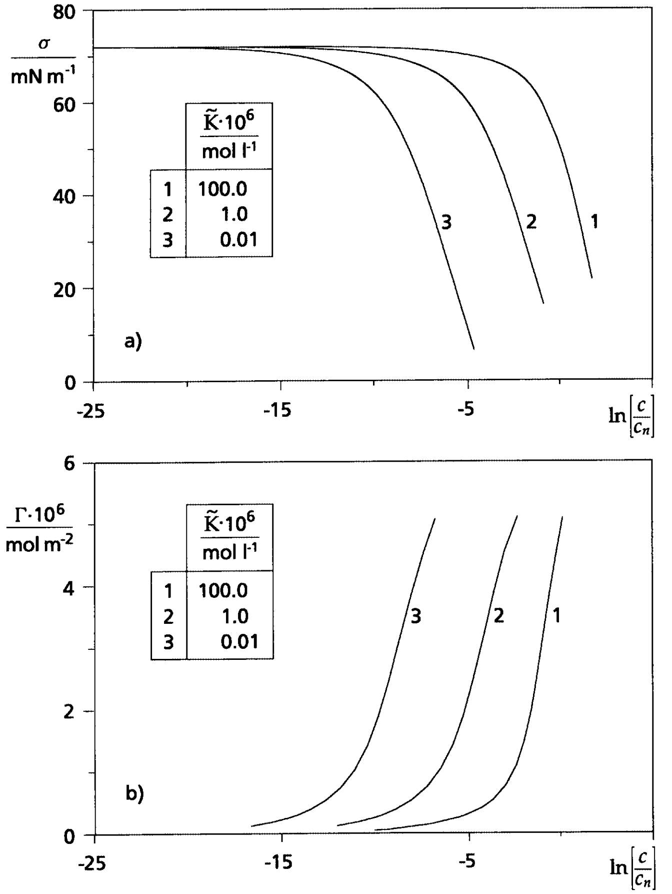

Fig. 5 **a** Resulting surface tension isotherms and **b** resulting adsorption isotherms as a function of $\tilde{K}$. All parameters, except $\tilde{K}$, according to Fig. 1, $c_e = 0.1$ mol l^{-1}

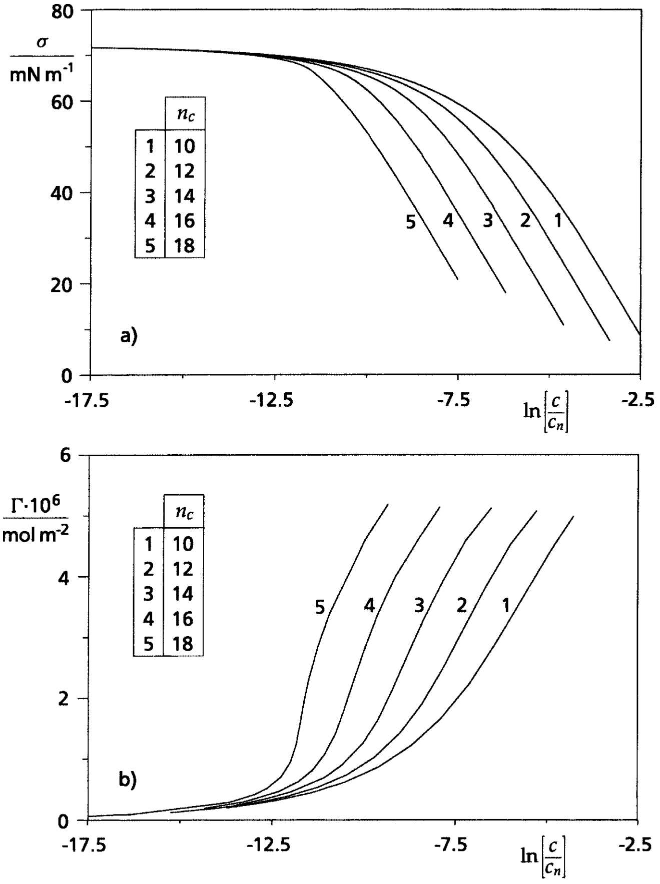

Fig. 6 **a** Resulting surface tension isotherms and **b** resulting adsorption isotherms as a function of chain length. All parameters according to Fig. 1

Figs. 2 and 3b do not show a phase transition. Phase transitions in the resulting isotherm require much higher interaction energies, which, in the present model, would be obtained for very long chain lengths, far beyond 25 carbon atoms. The effect of increasing background electrolyte concentration is demonstrated in Fig. 4. As expected, the isotherms shift towards lower concentrations. The same effect is achieved by decreasing the dissociation constant, K, (Fig. 5) or increasing the chain length (Fig. 6). In the latter case there is a drastic drop in the maximum interaction energies between C_{18} and C_{10} from -11.7 to $-3.6\,kT$. This leads to decreasing cooperativity between adsorbed molecules.

Comparison with experimental data

As mentioned, we investigated nine different surfactant/KCl/water systems. The surface tension isotherms of the three alkylpyridinium chlorides, each in three different KCl concentrations (0, 0.01 and 0.1 mol l^{-1}) were determined.

Fitting of the theoretical curves to the adsorption data (variation of parameter $\tilde{K}$) was done by eye.

As is obvious, deviations between model and experimental data grow with increasing chain length. This may be due to oversimplifications in the expression for the interaction energy (Eq. 12). On the other hand, these deviations might reflect dynamic limitations of the pendant drop technique. This issue is discussed in Ref. [14]. It is shown there that thermodynamic limitations become most severe in cases of long-chain surfactants with high amounts of added salt (Figs. 8, 9); therefore, we disclaimed a calculation of the theoretical curves for these cases.

It should be mentioned that in the C_{12} system with 0.01 M salt added (Fig. 7), the requirement $c_e \gg c$ is not met in the whole concentration range.

Conclusions

As can be seen from Figs. 7–9, our concept of combining the Gouy–Chapman theory with a modified Frumkin

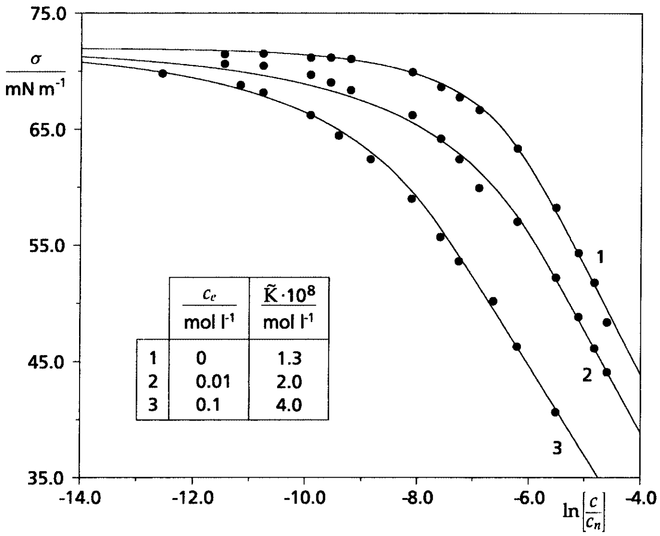

Fig. 7 Comparison between the measured surface tension isotherm (*points*) of dodecylpyridinium chloride in different electrolyte solutions and the calculated isotherm (*line*)

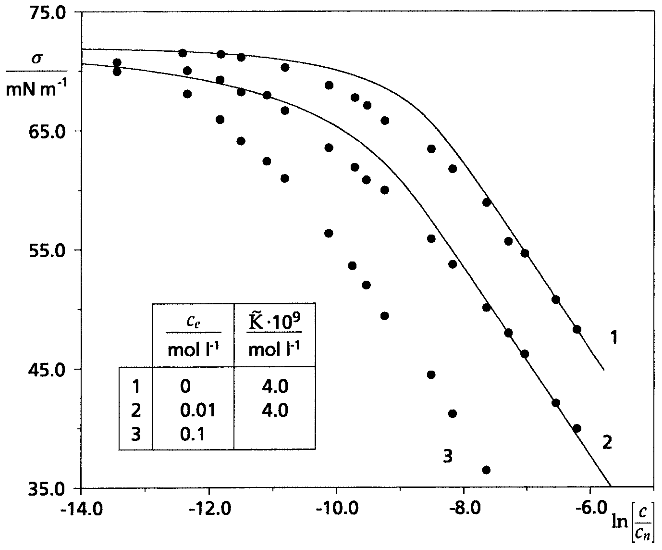

Fig. 8 Comparison between the measured surface tension isotherm (*points*) of tetradecylpyridinium chloride in different electrolyte solutions and the calculated isotherm (*line*)

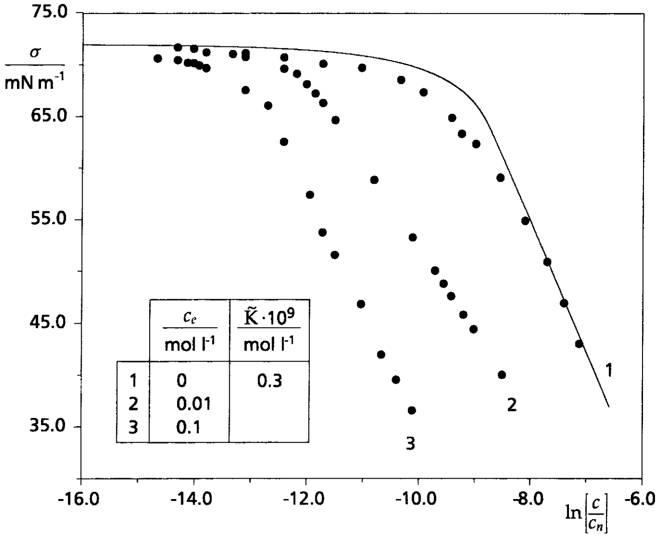

Fig. 9 Comparison between the measured surface tension isotherm (*points*) of hexadecylpyridinium chloride in different electrolyte solutions and the calculated isotherm (*line*)

isotherm leads to a qualitatively reasonable description of adsorption and surface tension isotherms of ionic surfactants.

The rough treatment of the interaction energy will be refined by statistical methods in a molecular theory. Improvements concerning the electrostatic contribution can be achieved by replacing the Gouy–Chapman theory. A more elaborated electrostatic theory has been developed by Woelki and Kohler.

As pointed out earlier, the final isotherms obtained from our theoretical calculations are smooth curves for all the systems calculated. In other words, despite strong attractive interactions between the alkyl chains, there are no phase transitions in the interfacial plane. The lack of phase transitions is a direct consequence of the variability of the area per site which is admitted in our approach.

As can be seen from Eqs. (5) and (11), changes in $\tilde{K}$ cause a shift along the concentration axis (as long as $c_e \gg c$). The values of $\tilde{K}$ obtained by curve-fitting in Figs. 7–9 (insets) are in agreement with qualitative considerations: the value of $\tilde{K}$ decreases with growing chain length and with increasing electrolyte concentration, c_e. The latter effect could reflect a decrease in the activity coefficient of surfactant and counterions in solution.

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