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## Role of the counterions on the adsorption of ionic surfactants <sup>☆</sup>

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### Abstract

A theory accounting for the effect of the counterions on the adsorption constant,  $K$ , is proposed. The experimental values of  $K$  were determined by using surface and interfacial tension isotherms measured by us or available in the literature. By accounting for the adsorption energy  $u_0$  of the counterion, a generalization of Gouy equation and a modified expression for the adsorption constant,  $K$ , are derived. The adsorption energy is calculated from the London equation, which involves the polarizabilities  $\alpha_{0i}$  and the ionization potentials  $I_i$  of the respective components and the radius  $R_h$  of the hydrated ion. By careful analysis of the available experimental data for  $\alpha_{0i}$ ,  $I_i$  and  $R_h$ , coupled with some reasonable hypothesis, we succeeded to obtain linear dependences between the calculated values of  $u_0$  and the experimental data for  $\ln K$  with slopes rather close to the theoretical ones. The obtained results for  $u_0$  were used to calculate the disjoining pressure isotherms of foam films stabilized by DTAF, DTACl and DTABr. It turned out that the type of the counterion has significant effect on the disjoining pressure.

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*Keywords:* Surfactant; Adsorbed layer; Counterion; Adsorption constant; Double layer; van der Waals energy

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## 1. Introduction

Almost a century ago Heydweiller [1] discovered that neutral electrolytes raise the surface tension of water. This rather small effect was attributed by Langmuir to negative adsorption of the electrolyte ions, due to their final size. He derived a simple equation based on this concept. Onsager and Samaras [2] attributed the effect to the image potential of the ions, which serves as adsorption potential. Both theories did not account for the ion specificity, which was unknown at that time. The situation changed when Jones and Ray [3,4] found shallow minima (dependent on the nature of the electrolyte) of the surface tension of electrolyte solutions at very low concentrations, below 1 mM. This finding was first dismissed erroneously as an artifact by Langmuir, but the Jones–Ray effect was confirmed by Dole [5].

This effect is similar to the Hofmeister effect [6], which refers to the role of electrolytes on the solubility of proteins. The ranking of the ions according to their efficiency is called Hofmeister series. Simplistically, the protein precipitation can be explained in terms of ion binding to water. The latter is also the explanation of the so-called salting out effect of electrolytes on the solubility  $S$  of a non-ionic solute, for which Setschenow [7] established empirically the following equation:

$$\ln(S(0)/S) = k_s C_{el}$$

where  $S(0)$  is the solubility in pure water,  $C_{el}$  is the electrolyte concentration and the Setschenow constant  $k_s$  depends on the nature of the electrolyte.

The Hofmeister effect is related to many phenomena besides the protein solubility [6,8] and the surface tension of electrolyte solutions [1–5,9,10]: among them are the electrolyte activity [11], pH measurements, zeta potentials, buffers, micellar properties [12,13] and critical micellar concentrations [13], microemulsion structure [14,15] and vesicles [16], enzymatic catalysis [17], lipid monolayers [18], polyelectrolytes [19], nanocrystals [20], DNA aggregation [21], etc. It is of importance also for colloidal stability, including bubble–bubble interaction [9,22–24]. Starov et al. [25] demonstrated the importance of the type of neutral salt for the water transport through membranes. In a special issue of *Current Opinion in Colloid and Interface Science* from 2004 [10] the interested reader can find a collection of papers on most of the subjects mentioned above.

The specific effect of the counterions on adsorbed and spread monolayers of ionic surfactants received attention much later, although the role of the counterions (mainly through their concentration and valence) on the adsorption was well known both from experiments and the theories of Gouy [26] and Davies [27]. In the classical book of Davies and Rideal “Interfacial Phenomena” [28] the only remark on possible specific effect of the counterions is the brief discussion on page 263 of the difference in viscosities of surface monolayers with fluoride, chlorine and bromine counterions, which was attributed to their different sizes.

To the best of our knowledge the first experimental studies of the specific effects of counterions on spread monolayers were published by Schulman and coworkers in 1957 and later [29,30].

The first study of the effect of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  on the dodecyl sulfate adsorption was published in 1966 by Weil [31]. All of them demonstrated considerable specific effect of the ions on the adsorbed and spread monolayers. During the last years this effect received much more attention with the measurements of Warzysynski and coworkers [32–34], Lu et al. [35] and Koelsch and Motschmann [36]. We will use some of these data in our study. Recently Koelsch and Motschmann [37] proposed an ellipsometric method for determination of the effective surface charge, which can be very useful, because it involves also an ion specific parameter, the refractive index increment, and so can provide information on the behavior of the adsorbed counterions.

The first attempts for interpretation of the Hofmeister series and its effect on the interaction between proteins, macromolecules or colloidal particles were qualitative and invoked mainly the ion size, the ion interaction with water and the “hydration force”. The latter was defined by Kunz et al. [38] as “what remains after subtraction of the van der Waals force and the double layer force from the experimentally measured interaction force”. Ninham ([38–41] and the references therein) was probably the first who advocated the role of the van der Waals forces for the interaction between ions in solution for the adsorption of electrolytes, for the interaction between proteins or colloidal particles etc. His suggestion, going against the commonly used assumption that these interactions are dominated by the much stronger electrostatic interactions, is based on the argument, that even moderate electrolyte concentrations can screen the electrostatic interactions without substantially affecting the van der Waals forces. Moreover, since the van der Waals forces increase steeply with decreasing distance (roughly with the sixth power), they may become if not dominant, at least very important for phenomena, occurring at short distances, such as adsorption of ionic species. Ninham and Yaminsky [39] demonstrated the viability of this philosophy in 1997 in their theory of ion binding and ion specificity and their role in Hofmeister series, ion adsorption and colloidal interaction.

Our ambition in this article is to apply Ninham’s ideas to the development of a theory accounting for the effect of the counterions on the adsorption constant,  $K$ , *without using free adjustable parameters* in the framework of the present theory. The reason for this desire is the fact that lately many theories, using several free adjustable parameters, have been published. All of them claim coincidence with the experimental data in spite of the difference in models. In [42] it was shown that very different experimental data could be fitted with correlation coefficient better than 0.999 with equations with three free parameters derived from four different models. It is obvious, that the main reason for the good fits is the large freedom for the fitting procedure to adjust to the data given enough free parameters. This view point is expressed best by two famous scientists: Cauchy, who said “Give me four free parameters and I will fit an elephant” and Landau, according to whom “the experimental data can be always fitted by any not too wild theory, provided that it contains enough undetermined constants”. That is why we believe that a theory, which is at semi-quantitative or even only at qualitative agreement with the experiment, but contains the smallest possible number of free parameters (one, or at most two), gives better

insight on the physical phenomenon and is more useful than a theory fitting perfectly the experimental data but at the expense of four or five free parameters.

The present theory is based to a large extent on the ideas from [42]. The new effect accounted now is the van der Waals interaction energy of the counterions  $u_v$  with the interface. To calculate the distribution of the counterions along the normal coordinate  $z$  from Boltzmann equation,  $u_v(z)$  has to be added to the electrostatic energy  $\pm e_0\psi$ , where  $e_0$  is the unit charge and  $\psi(z)$  the local value of the electrostatic potential. This distribution is used to determine the charge density  $\rho(z)$ , which is inserted into the Poisson–Boltzmann Eq. (4.5) to calculate the potential distribution  $\psi(z)$ . The latter, along with the Gouy Eq. (2.7) for the charge of the diffuse layer,  $Q_{dl}$ , the Henry's adsorption isotherm (2.18) and Boltzmann equation leads to a modified adsorption constant  $K$  (see Eq. (4.16)), which depends on the adsorption energies of the surfactant ion,  $E_a$ , and the counterion,  $u_0$ .

The most difficult problem is the calculation of  $u_0$ . For adsorption from a gas phase on a solid surface  $u_0$  is simply the total interaction energy of the adsorbed molecule with the adsorbent. However, for adsorption from a solution the adsorption energy is the energy needed to interchange the position of the hydrated ion in the bulk of the solution with the same volume of solvent at the surface. The respective energies can be calculated from the simple London Eq. (4.21), which involves the polarizabilities  $\alpha_{oi}$  and the ionization potentials  $I_i$  of the respective components and the radius  $R_h$  of the hydrated ion. The first two parameters can be calculated relatively easily using literature data and some reasonable assumptions, but the ion radius  $R_h$  creates enormous problems. The values of the hydrated radii  $R_h$  quoted in the literature differ very much and in addition, there are indications that upon adsorption the hydration shell may undergo dehydration or deformation. We still succeeded to obtain the theoretical linear dependence between the calculated values of  $u_0$  and the experimental data for  $\ln K$  with slope rather close to the theoretical one (see Fig. 10).

The paper is organized as follows: Section 2 is devoted to the discussion of available theories of the Hofmeister effect mainly with proteins and surface tension of simple electrolytes and surfactants. In the final subsection are presented the main results of the theory of adsorption of ionic surfactants [42], which is the basis of the present theory. Section 3 presents experimental results obtained by us and by other authors, which were used in Section 4 to test the theoretical results. Section 4 is devoted to the theory and comparison with the experiment of the effect of the counterions' properties on the adsorption constant  $K$ . In Section 5 the effect of the counterions on the disjoining pressure of foam film is illustrated. Section 6 summarizes the conclusions reached by us.

## 2. Previous theories of the effect of the counterions

### 2.1. Hofmeister effect on the surface tension of simple electrolytes

In a series of papers ([11,15,17,38–41,43–46], see also the references therein) Ninham and coworkers applied and tested Ninham's idea for the role of van der Waals forces on different phenomena. The most difficult test was probably the attempt to

apply the theory for explanation of the adsorption of simple electrolytes. The initial results were encouraging [40], but the subsequent efforts to obtain good quantitative results [43–46] met unexpected difficulties such as the necessity to account for the solvation energy, for the possible dependence of the dielectric permittivity on the electrolyte concentration or for the role of the asymmetry of the solvent profile. Jungwirth and Tobias [47] performed molecular dynamics simulations of a series of sodium halide solutions at air/water interfaces. Although these systems are different from the ones, considered by us, several of their conclusions coincide with our findings. In particular, they found, just as we did (see Section 4 and Table 3), that the larger, more polarizable anions, like  $\text{Cl}^-$  and  $\text{Br}^-$ , are specifically adsorbed at the interface. The smaller anion  $\text{F}^-$  was negatively adsorbed due to image forces in accord with Onsager–Samaras theory [2]. The fact that we found small attractive adsorption energy for  $\text{F}^-$  is probably due to the strong (attractive) electrostatic surface potential, created by the surfactant in our systems, which overwhelms the effect of the (repulsive) image force and leads to closer approach of the ions to the interface.

Although the solution of the problem for surface tension of simple electrolytes is quite different from the subject of the present article, it is worth noting two more attempts for its solution. Karraker and Radke [48] incorporated the energies of van der Waals interaction of the ions into the Poisson–Boltzmann equation and combined its solution with Gibbs adsorption isotherm to calculate the ion adsorptions and the surface tension. They obtained results relatively close to the experimental values and succeeded to reproduce the minimum of the surface tension at 1 mM, found by Jones and Ray [3,4]. However, the decrease of the surface tension in the minimum was only 0.08 mN/m, which is much less than the experimental value. Manciu and Ruckenstein [49] proposed a different approach for calculation of the surface tension of electrolytes, which ignores the van der Waals interaction. Instead, they accounted for the difference in structure making and structure breaking capabilities of the cations and anions. This affects the water profile in the transition region and thus leads to different adsorption of the ions and provokes change of the surface tension.

In another test of the theory Kunz et al. [11] tried to decrease the role of the “well-known uncertainty of radii and polarizabilities of ions on water”. Toward this aim they calculated the osmotic coefficients of electrolyte solutions by accounting for the van der Waals forces. To achieve agreement with the experiment they had to adjust significantly the ionic radii and excess polarizabilities with respect to the literature values. The parameters so obtained were used to calculate the surface tension of the same electrolytes. However, the calculated surface tension increments for most electrolytes were about twice as small as the experimental values.

### 2.2. Hofmeister effect on the interaction between proteins and particles

The problems encountered in the theory of the surface tension of electrolyte solutions demonstrate the enormous difficulties and the extreme care needed to account correctly for

the effects of van der Waals interactions on the behavior of electrolyte solutions. Besides the aforementioned uncertainty in the system parameters, one of the major reasons for the difficulties in the theories of the surface tension of simple electrolytes is that the two ions of the electrolyte usually have similar properties and the outcome of the minor difference between their space distributions, due to the van der Waals interactions, is the reason for the variation of the surface tension. Our goal, which is analysis of the role of the counterions on the adsorption of ionic surfactants, is less demanding, because only one of the ions must be considered. Indeed, the surfactant ion is almost firmly attached to the interface by the large adsorption energy and serves mainly for creating the surface charge and thereby — the surface potential. From this viewpoint the articles on interparticle interactions are closer to our problems, since then the surface charges are supposed to be bound to the interface. Ninham and coworkers published such an article, devoted to the interactions in oxide suspensions [50]. They used the same equations as in [39] for the dispersion energy for an ion at a distance  $z$  from the charged interface:

$$U_i = -B/z^3 \quad (2.1)$$

with

$$B = \frac{1}{4\pi} \int_0^z \frac{\alpha^*(i\xi)\Delta_{12}(i\xi)}{\varepsilon_1(i\xi)} d\xi \quad (2.2)$$

$$\Delta_{12}(i\xi) = \frac{\varepsilon_2(i\xi) - \varepsilon_1(i\xi)}{\varepsilon_1(i\xi) + \varepsilon_2(i\xi)} \quad (2.3)$$

$$\alpha(i\xi) = \frac{\alpha(0)}{1 + (\xi/v_1)^2}; \quad \varepsilon(i\xi) = 1 + \frac{n_D^2 - 1}{1 + (\xi/v_2)^2} \quad (2.4)$$

where  $\varepsilon_k(i\xi)$  is the dielectric function on imaginary frequencies for water ( $k=1$ ) and oxide surface ( $k=2$ ),  $\alpha(0)$  is static polarizability of the ion,  $n_D$  is refractive index of the water and  $\hbar$  is Planck' constant. It is supposed in Eq. (2.4) that there is only one absorption frequency,  $v_1$ , and one ultraviolet frequency,  $v_2$ , which are assumed later equal  $v_1=v_2=v$  and related to the ionization potential  $I \approx \hbar v$ .

The surface charge is determined by pH and by the reactions leading to formation of aluminum hydroxides. That is why the surface potential is not always high and the concentration of coions in the diffuse layer is not negligible. The potential (2.1) was inserted in the Poisson–Boltzmann equation, which was solved numerically. The studied salts were LiCl, NaCl, KCl, CsCl, NaBr and NaI. It was found that the ions of same charge have different local concentrations due to differences in the van der Waals potentials. The obtained ion distributions were used to calculate the electrostatic disjoining pressure. It was strongly dependent on pH, going through a minimum at the isoelectric point. The curves for the different electrolytes did not coincide due to differences in the van der Waals potentials.

Similar study was carried out by Tavares et al. [51] but this time for the interaction of charged proteins. They also used Eqs. (2.1)–

(2.4) to calculate the van der Waals energy of a number of ions. They used literature data for the ion polarizability in water  $\alpha(0)$  and the ionization energy in vacuum  $I$ , and accounted for the effect of the hydration on  $I$  by using a thermodynamic cycle to calculate the hydration free energy of the ion and the electron obtained after the ionization. The authors used for *all ions* the same contact distances: 4 Å for ion–ion and 2 Å for ion–macroion (protein) interaction, i.e. they disregarded the specific effect of the ion size on the interaction energy. The results were used to calculate the purely electrostatic and the van der Waals contribution (without the direct van der Waals interaction, i.e. without the Hamaker force) to the mean force between the macroions and to the respective second virial coefficients. It was found that the van der Waals interaction gives rise to a strong attractive force and decreases the electrostatic repulsion. The effect of the different counterions followed the series  $\text{SO}_4^{2-} > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^-$  and  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$ , which coincides partially with our findings in Section 4. No comparison with experimental data was carried out.

The article of Edwards and Williams [52] deals also with the effect of counterions on the interparticle interaction but only theoretically. They assumed that far away from the interfaces both the electrostatic interaction energy of the ions with the surface and the van der Waals interaction energy between the ions are much smaller than  $k_B T$ . This allowed them to linearize the Poisson–Boltzmann equation and its solution for the considered interactions. The authors assumed that the exponentially decaying electrostatic interaction with the surface is negligible so that at large distance from the interface the ions are strongly coupled to each other via local electrostatic effects. Then the local charge density  $\rho$  is determined only by the difference  $\Delta B = B_+ - B_-$  between the  $B$  constant (see Eq. (2.1)) of the two ions:

$$\rho = e_0(C_+ - C_-) = 6\varepsilon\Delta B/e_0z^5 \quad (2.5)$$

This leads to a new attractive term,  $-16C\Delta B/h^3$ , in the usual expression for the electrostatic disjoining pressure  $\Pi_{el}$  with bulk concentration  $C$  of 1–1 electrolyte between two plates at separation  $h$ . The numerical calculations gave a deep attractive minimum of  $-4000$  Pa at 5 nm in the total electrostatic disjoining pressure  $\Pi_{el}$  for  $B_+ + B_- = 20 \times 10^{-5} \text{ J m}^3$ , surface potential  $\psi_0 = 130$  mV and electrolyte concentration  $C = 0.3$  M.

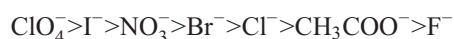
### 2.3. Effect of the counterions on the adsorption of ionic surfactants

The first and the most important breakthrough in the theory of adsorption of ionic surfactants was done by Gouy [26], who derived an equation, relating the potential of the diffuse electrical layer with its charge (see Eq. (2.7) below). Davies [27] used the equation of Gouy to derive an expression for the contribution of the diffuse layer,  $\Delta\sigma_{el}$ , to the equation of state of a monolayer. Lucassen-Reynders [53] proposed an alternative approach for derivation of the adsorption isotherm, based on the Butler equation for the chemical potential, but in her approach the diffuse layer (and thereby the counterions) was not

accounted explicitly. Fainerman and coworkers [54–56] as well as Liggieri et al. [57] extended the theory of Lucassen-Reynders by including the reorientation effect and surface aggregation. Borwankar and Wasan [58] suggested to account for the diffuse layer by using the adsorption isotherms for non-ionic surfactants, but to replace in them the bulk surfactant concentration,  $C_s$ , by the subsurface concentration  $C_{ss}$ .

Kalinin and Radke [59] introduced counterion binding to the adsorbed surfactant ions (the Stern adsorption layer). This process was assumed to be accompanied by dehydration of both ions, which leads, roughly speaking, to the formation of a complex. In principle the binding constant must depend on the nature of the counterion but this effect was not investigated by the authors. These authors also introduced two molecular condensers to account for the different sizes of the dehydrated adsorbed counterions and the freely moving hydrated counterions from the diffuse layer. Kralchevsky et al. [60] investigated the problem regarding the thermodynamic compatibility of the adsorption isotherms for ionic surfactants and counterions, and derived expressions for electrolytes of various valences. Later, they applied the proposed approach to a comparative study of the van der Waals and Frumkin isotherms [61], and to mixtures of ionic–nonionic [62,63] and anionic–zwitterionic [64] surfactants. Mulqueen and Blankshtein [65] simplified the theory by disregarding all other effects besides the molecular condenser (the Stern layer).

Warszynski et al. [32–34] were the first to account explicitly for the specific adsorption of the counterions and to determine the adsorption constants  $K$  ( $=1/\alpha_c$  in their notations) and their sizes. In [32] they investigated the effect of  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$  and  $\text{Cs}^+$  on the adsorption isotherm, whereas [33,34] were devoted to the anions. Following Levine et al. [66] they assumed that the adsorbed counterions are located in the same plane as the ionic heads of the surfactant ions. They accounted also for the difference in sizes between the surfactant ions and the counterions, for the Stern layer and for the electrostatic interaction between the adsorbed ions. Unfortunately, they did not calculate from  $\alpha_c$  the respective adsorption energies,  $u_0$ , of the counterions, which makes the direct comparison with our data in Section 4 impossible. For all alkaline ions they obtained the same values for  $\alpha_c$  (with the exception of  $\text{K}^+$  for which it was slightly different). The alkaline ion sizes, found by them, although different from ours, follow the same trend as our data. Their adsorption constants  $K$  for the anions are increasing in the order



We also found the same sequence for  $\text{Br}^-$ ,  $\text{Cl}^-$  and  $\text{F}^-$  (see Section 4). However, they found that the size of the ion  $\text{F}^-$  is the largest among the halogen ions, whereas our calculations in Section 4 showed that it must be the smallest, although there is little difference with  $\text{Cl}^-$  and  $\text{Br}^-$ .

A relatively simple theory of the adsorbed layers of ionic surfactants was developed and checked experimentally in [42]. However, only a single counterion was considered,  $\text{Na}^+$ , and no van der Waals interaction of this ion with the interface was then

taken into account. The present theory, which is an extension of this from [42], is an attempt to avoid these limitations. Hence, to facilitate the reader, we will present briefly here the main results of [42].

It was assumed in [42] that when the surfactant ions adsorb at the interface air/water (or oil/water) the centers of the ionic heads are at a distance equal to their radius from the interface. The number of molecules per unit area (the surfactant adsorption) is  $\Gamma$  and the minimum possible area per molecule is denoted by  $\alpha=1/\Gamma_\infty$ , where  $\Gamma_\infty$  is the maximum possible adsorption. The charge per unit area of the adsorbed layer is:

$$Q_a = q\Gamma = q\theta/\alpha; \quad \theta = \Gamma/\Gamma_\infty = \alpha\Gamma \quad (2.6)$$

where  $\theta$  is the degree of surface coverage and  $q$  is the charge of the surfactant ion. For an anionic uni-valent surfactant, as SDS,  $q=-e_0$ , where  $e_0$  is the unit charge. For an uni-valent cationic surfactant, as DTAB,  $q=e_0$ . The surface charge is compensated by the charge of the diffuse layer,  $Q_{dl}$  (per unit area), in which the distribution of the counterions was assumed governed solely by the electrostatic potential,  $\psi$ . All counterions were assumed to belong to the diffuse layer. The charge  $Q_{dl}$  is obtained by integrating the Boltzmann distribution for all ions over the entire water volume. The result, found first by Gouy [26], is:

$$Q_{dl} = -\frac{4q}{\kappa_0} \sqrt{C_t} \sinh\left(\frac{\Phi_0^{(0)}}{2}\right); \quad \Phi_0^{(0)} = \frac{q\psi_0}{k_B T} > 0; \quad (2.7)$$

where  $\psi_0$  is surface potential (at  $z=0$ , see Fig. 1),  $C_t=C_s+C_{el}$  is the total electrolyte concentration i.e. the sum of the concentrations of the surfactant,  $C_s$ , and the added electrolyte,  $C_{el}$ , and  $\kappa_0 \approx 1.33 \times 10^{-3} \text{ cm}^{1/2}$  is

$$\kappa_0 = \left(\frac{8\pi q^2}{\epsilon k_B T}\right)^{1/2}$$

where  $\epsilon$  is dielectric permittivity and  $k_B T$  is thermal energy.

Due to the electrostatic potential, the counterions can penetrate into the adsorbed layer. This was assumed also by Levine et al. [66] and Warszynski et al. [32–34] (see Fig. 1). In reality, they can do so freely at small  $\theta$ , but at  $\theta=1$  all counterions must stop at a distance  $z=z_d$  approximately equal to the ion diameter. This effect was accounted for approximately by representing the charge of the diffuse layer as composed of two parts according to the degree of coverage  $\theta$  of the surface.

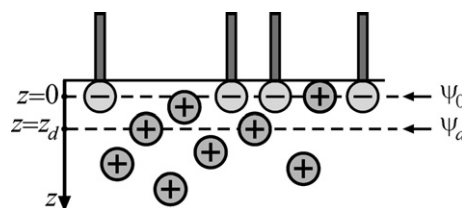


Fig. 1. Model of the adsorbed layer with diffuse layer. Some of the counterions penetrate in the adsorbed layer, beyond  $z=z_d$ .

The result so obtained is:

$$Q_{dl} = (1 - \theta)Q_{dl}^0, \quad (2.8)$$

where the superscript 0 means that the respective diffuse layer charge  $Q_{dl}$  is calculated from the Gouy Eq. (2.7) with  $\psi_0$ .

For typical ionic surfactants the dimensionless potential  $\Phi_0^{(0)}$  is between 4 and 8, so that the approximation  $\sinh(\Phi_0^{(0)}/2) \approx 1/2\exp(\Phi_0^{(0)}/2)$  in Eq. (2.7) is possible.

Then Eq. (2.7) along with (2.8) leads to a modified Gouy equation:

$$\theta = 2a\sqrt{C_1}(1 - \theta)\sinh\left(\frac{\Phi_0^{(0)}}{2}\right) \approx a\sqrt{C_1}(1 - \theta)\exp\left(\frac{\Phi_0^{(0)}}{2}\right) \quad a = \frac{2\alpha}{\kappa_0} \quad (2.9)$$

For low coverage,  $\theta$  in the right hand side can be neglected and we recover the original Gouy equation.

The derivation of the equation of state  $\Delta\sigma(I)$  relating the adsorption  $\Gamma$  with the surface pressure  $\Delta\sigma$  ( $\Delta\sigma = \sigma_p - \sigma$ , where  $\sigma_p$  is surface tension of the pure solvent) and the adsorption isotherm  $\Gamma(C_s)$  relating  $\Gamma$  with the surfactant concentration  $C_s$  are based for ionic surfactants on the respective equations for non-ionics. We will quote and analyze only two of them. The van der Waals equation (based on the Volmer model) is:

$$\pi_s = \frac{\theta}{1 - \theta} - \frac{\beta\theta^2}{2} \quad (2.10)$$

where  $\pi_s = \alpha\Delta\sigma/k_B T$  is dimensionless surface pressure and  $\beta$  is a constant accounting for the soft interaction between the adsorbed molecules. The respective adsorption isotherm is obtained by integrating Gibbs equation:

$$\frac{d\pi_s}{d \ln C_s} = \theta \quad (2.11)$$

along with  $\pi_s$  from Eq. (2.10). The result reads:

$$K_s C_s = \frac{\Gamma}{1 - \theta} \exp\left(\frac{\theta}{1 - \theta} - \beta\theta\right); \quad (2.12)$$

$$K_s = \delta_s \exp(E_a/k_B T)$$

where  $K_s$  is the adsorption constant and  $E_a$  the adsorption energy. The effective thickness of the adsorbed layer,  $\delta_s$ , accounts for the fact that due to thermal fluctuations the hydrophobic chain of the

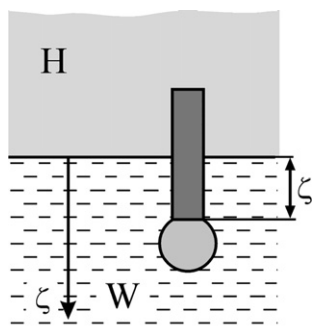


Fig. 2. A surfactant molecule at an interface water/hydrophobic phase (oil or air) partially immersed at depth  $\zeta$ . (W=water, H=hydrophobic phase).

surfactant can be partially immersed in the water phase, so that its energy depends on the immersion depth  $\zeta$  (see Fig. 2). The effective thickness  $\delta_s$  is related to the transfer energy (per unit length),  $w_b$ , of the hydrophobic tail from water to the hydrophobic phase (air or oil) by the relation  $\delta_s = k_B T/w_b$  [42].

Helfand, Frisch and Lebowitz [67], derived an almost exact equation of state for freely moving hard discs of radii  $R_s$  and areas  $\alpha_0 = \pi R_s^2$  on a fluid interface. By analogy with Eq. (2.10) we added to the hard core part of the Helfand, Frisch and Lebowitz equation (HFL for short) a soft interaction term (see [42] for more details), to obtain:

$$\pi_s = \frac{\theta_0}{(1 - \theta_0)^2} - \beta\theta_0^2 \quad (2.13)$$

where  $\theta_0 = \alpha_0 \Gamma$ . Along with Gibbs isotherm (2.11), Eq. (2.13) leads to the respective HFL adsorption isotherm [42]:

$$K_s C_s = \frac{\Gamma}{1 - \theta_0} \exp\left[\frac{\theta_0(3 - 2\theta_0)}{(1 - \theta_0)^2} - \beta\theta_0\right] \quad (2.14)$$

If the equations of state (2.10) and (2.13) are written in dimensional variables and the model independent parts  $\Delta\sigma/\Gamma k_B T$  are put in the left hand side, the remaining expressions must be equal. Neglecting the terms with  $\beta$  one thus obtains the relation:

$$\frac{\Delta\sigma}{\Gamma k_B T} = \frac{1}{1 - \alpha\Gamma} = \frac{1}{(1 - \alpha_0\Gamma)^2} \quad (2.15)$$

which yields the connection between  $\alpha$  and  $\alpha_0$  [42]:

$$\alpha/\alpha_0 = 2 - \alpha_0\Gamma \quad (2.16)$$

Thus we reach the very important conclusion that  $\alpha$  in fact is not a constant but should vary with the adsorption from  $2\alpha_0$  at  $\alpha_0\Gamma < 1$  to  $\alpha_0$  at complete coverage,  $\theta_0 = 1$ . Therefore, one must very carefully interpret the data when the analysis is based on van der Waals Eq. (2.10).

Following Borwankar and Wasan [58] the adsorption isotherms for ionic surfactants were derived by replacing in the adsorption isotherm the surfactant concentration  $C_s$  by the so-called subsurface concentration  $C_{ss}$ , which for this model is the ion concentration due only to electrostatic interaction at potential  $\psi_0$ . It is connected with the bulk concentrations  $C_s$  and the dimensionless potential of the adsorbed layer  $\Phi_0^{(0)}$  by Boltzmann's equation:

$$C_{ss} = C_s e^{-\Phi_0^{(0)}} \quad (2.17)$$

We will not quote the analogs of Eqs. (2.12) and (2.14) for ionic surfactants since they differ from Eqs. (2.12) and (2.14) only by the left hand side [42]. To simplify the presentation we will confine ourselves only with the linear Henry's adsorption isotherm:

$$\Gamma = K_s C_{ss}, \quad (2.18)$$

following from Eq. (2.12) with  $\theta \ll 1$  and  $C_{ss}$  substituted for  $C_s$ . Then in the right hand side of Eq. (2.9) one can set  $\theta = 0$ . The expression so obtained for  $\Phi_0^{(0)}$  is substituted in Eq. (2.17) which,

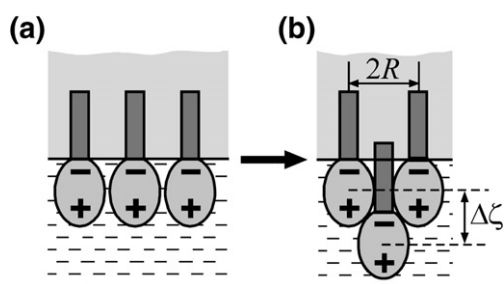


Fig. 3. Expulsion of a surfactant molecule from the adsorbed layer. The combination of surfactant ion and the counterion is modeled as a dipole. In position (a) all dipoles lie in the same plane, which leads to repulsion. To decrease the repulsion, the middle molecule enters deeper into the water phase, as shown in position (b). This is opposed by the adsorption energy, which pulls the molecules up. The result of these opposite effects is that the middle molecule will reach equilibrium at a distance  $\Delta\zeta$  from its initial position.

along with Eq. (2.18) leads to the analog of Henry's isotherm for ionic surfactants:

$$\Gamma = K^{(0)} C^{2/3} \quad (2.19)$$

Here  $K^{(0)}$  is a new adsorption constant for the ionic surfactant, related to the respective constant  $K_s$  for the non-ionic surfactant:

$$K^{(0)} = \left( \frac{4K_s}{\kappa_0^2} \right)^{1/3} \quad (2.20)$$

An important feature of this result is that  $C$  in Eq. (2.19) is in fact an effective concentration:

$$C = \sqrt{C_s C_t}, \quad (2.21)$$

This makes the treatment of solutions with added electrolyte identical to that for systems without added electrolyte. Finally, the isotherm (2.19) reveals that for ionic surfactants the Henry's isotherm depends not on  $C_s$ , as it is for non-ionic surfactants, but on  $C_s^{2/3}$  (or  $C^{2/3}$ ). If one substitutes Eq. (2.19) in Gibbs Eq. (2.11) (written in terms of  $C$  instead of  $C_s$ ) and integrates over  $C$ , one obtains at low coverage a linear dependence of  $\sigma$  on  $C^{2/3}$ , which can be used to determine the adsorption constants  $K$  (they are related to  $K^{(0)}$  and the ion adsorption energy,  $u_0$ , through Eq. (4.16)):

$$\sigma = \text{const} - 3k_B T K C^{2/3} \quad (2.22)$$

The constant in Eq. (2.22) is close to, but not exactly equal to  $\sigma_p$  (see [42]). The dependences  $\Gamma = \Gamma(C^{2/3})$  and  $\sigma = \sigma(C^{2/3})$  have much simpler behavior than  $\Gamma = \Gamma(C)$  or  $\sigma = \sigma(C)$ .

The analysis of the experimental data, based on the derived adsorption isotherms and equations of state revealed, that the area per molecule  $\alpha$  is larger for oil/water interface than for air/water and decreases with increasing the salt concentrations [42]. It was suggested that both effects are related to the lateral electrostatic repulsion between the adsorbed surfactant molecules. They were modeled as dipoles, which repel each other and push some of the molecules deeper in the solution

(see Fig. 3), thus leading to smaller values of  $\alpha$ . Rather crude calculations showed that this effect is larger for larger adsorption,  $\Gamma$ , smaller dipole moment (i.e. larger electrolyte concentrations) and smaller energies of adsorption (which is the case of the interface air/water compared with oil/water).

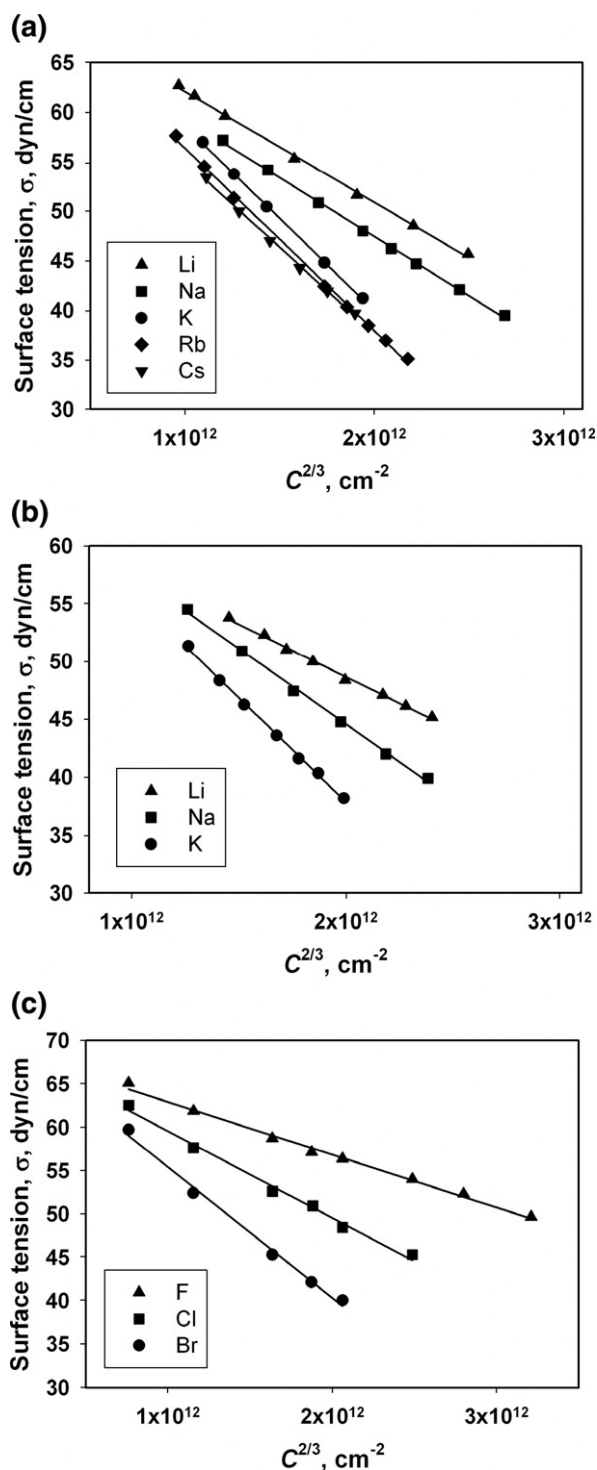


Fig. 4. Plots of the surface tension,  $\sigma$ , vs.  $C^{2/3}$  for: (a) salts of dodecyl sulfate at 33 °C [35], (b) salts of dodecyl sulfate at 25 °C [31], and (c) 1-dodecyl-4-dimethylaminopyridinium bromide in the presence of 100 mM KF, KCl or KBr [36].



### 3. Experimental data

In this section we present and process surface tension data obtained by other authors and by ourselves, demonstrating the effects of the concentration and/or the type of electrolyte. From them we calculate the experimental values of the adsorption constant  $K$ . Most of the results will be used in Section 4 for experimental check up of the theories presented there.

The adsorption constant,  $K$ , can be determined from the fit of the experimental data by a given adsorption isotherm, but the analysis in [42] revealed that more reliable data are obtained from the slope of the initial part of the equation of state (2.22), corresponding to Henry's Eq. (2.19). The use of the effective concentration  $C$  (defined by Eq. (2.21)) allows treating together and comparing results obtained at constant electrolyte concentration and varying surfactant concentration and *vice versa*.

We processed and compared the experimental data of several authors: Lu et al. [35], Weil [31], and Koelsch and Motschmann [36] who have measured surface tension isotherms of ionic surfactants in the presence of different counterions. They are presented in Fig. 4 in coordinates  $\sigma$  vs.  $C^{2/3}$ . We did not use the data of Warszynski et al. [32–34] since almost all of them were obtained with surfactants with chain different from  $C_{12}$  and cannot be compared directly with our data. The data in Fig. 4 have been obtained by varying the surfactant concentration at zero or constant additional electrolyte concentration. The initial portions of the curves  $\sigma(C^{2/3})$  are linear although this dependence is not always so good. That is why we performed in addition ourselves experiments with ionic surfactants but we varied the concentration of the counterions at constant surfactant concentration (see below). These data were also processed and analyzed (see Fig. 5). One of the reasons to perform such measurements was the fact that when the electrolyte concentration is varied the data are less scattered and the linear portion of the surface tension extends to higher concentration. Possible reasons for this are (i) smaller contribution of non-ionic impurities at higher electrolyte concentration [62] and (ii) smaller error of the approximate Eq. (4.16) at higher electrolyte concentration (see Appendix A). To demonstrate only the effect of the salt concentration, i.e. of the ionic strength, for the same counterion,  $\text{Na}^+$ , the data by Gurkov et al. [68], Haydon and Taylor [69,70], and Rehfeld [71] were used. Finally, we checked the theory by measuring the dependence of the  $\zeta$ -potential of emulsion droplets on the concentration of sodium dodecyl sulfate (SDS) in the presence of 10 mM NaCl and comparing the obtained dependence with the one predicted by the model (Eq. (4.18) in Section 4).

#### 3.1. Materials and methods

For our measurements we used constant concentration 0.5 mM of the anionic surfactant sodium dodecyl sulfate (SDS, product of Acros, USA) and of the cationic surfactant dodecyl trimethyl ammonium bromide (DTAB, from Sigma). The surfactants were used as received. The solutions were prepared with deionized water from a Milli-Q purification system (Millipore, USA). All measurements presented in Fig. 5 were performed with excess electrolyte with concentration 11 to

110 times larger than that of the surfactant, i.e. 5.5 to 55 mM. Alkali chloride salts LiCl (Sigma), NaCl (Merck), KCl (Sigma), RbCl (Aldrich) and CsCl (Aldrich) were added to the SDS solutions. Sodium halogen salts NaF (Sigma), NaCl (Merck) and NaBr (Sigma) were added to the DTAB solutions. The used inorganic salts were preliminarily roasted in oven for 4 h at temperature, which was 100–150 °C lower than the melting temperature for each salt.

The surface tension,  $\sigma$ , of the used aqueous solutions was measured by applying Drop Shape Analysis (DSA) on pendant bubbles in the surfactant solutions. The measurements were performed by means of a Drop Shape Analysis System DSA 10 (Krüss GmbH, Hamburg, Germany) at  $23.3 \pm 0.3$  °C. The bubbles were formed by using a U-shaped metal needle attached to a syringe and dipped into the cuvette with the surfactant solution. The outer phase was loaded in a glass cuvette with plane-parallel optical front and back windows. The kinetics of the surface tension relaxation, after a pendant bubble has been formed in the solution, was followed during at least for 20 min. The equilibrium value of  $\sigma$  was determined from the intercept

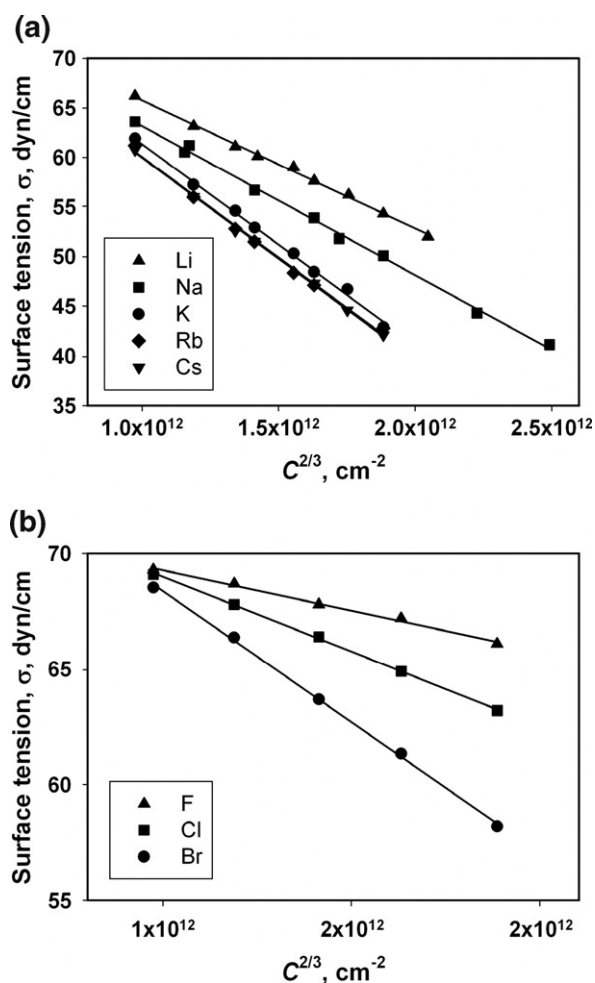


Fig. 5. Surface tension vs.  $C^{2/3}$  for: (a) 0.5 mM SDS in the presence of LiCl, NaCl, KCl, RbCl, CsCl, and (b) 0.5 mM DTAB in the presence of NaF, NaCl, NaBr. All salts are with varying concentration,  $C_{e1}$  to adjust  $C = C_s + C_{e1}$  (present work).

of the plot  $\sigma$  vs.  $t^{-1/2}$  [72], where  $t$  is the time after the bubble formation.

For the  $\zeta$ -potential measurements we used SDS solutions containing 10 mM NaCl. Hexadecane (purchased from Merck, and purified by passing through a column with adsorbent Florisil) was used as oil phase. Emulsions were prepared by stirring 0.2 mL oil in 40 mL SDS solution by means of a rotor-stator homogenizer (Ultra Turrax T25, Janke & Kunkel GmbH & Co., IKA Labortechnik) operating at 8500 rpm for 3 min. Zeta-potential of emulsions of hexadecane in SDS solutions was measured by using a Zetasizer IIC (Malvern Instruments, UK). At least three independent measurements were made at each surfactant concentration and the results were averaged.

### 3.2. Data processing

From the slopes of the straight lines on Figs. 4 and 5) by using Eq. (2.22) we determined the adsorption constants,  $K$ . The experimental values of  $K$ , obtained by processing all sets of available data, are shown in Table 1. As it is evident from the table the adsorption constants for all surfactants clearly increase as the mass of the counterion increases.

The three sets of data for dodecyl sulfate have values of  $K$  which differ by e.g.  $\pm 15\%$  for the same counterion although all of them follow qualitatively the same trend. This difference is probably due to the different temperature of measurement (23.5 °C in this work, 25 °C used by Weil [31] and 33 °C in the measurements of Lu et al. [35]). The used cationic surfactants, DTAB and 1-dodecyl-4-dimethyl aminopyridinium bromide [36], differ considerably in structure which is the reason for the difference in the values of  $K$  for the same counterion.

Note that the obtained values of the adsorption constant of dodecyl sulfate in the presence of  $\text{Rb}^+$  and  $\text{Cs}^+$  as counterions are almost the same as those in the presence of  $\text{K}^+$ . This is so both for the data of Lu et al. (Fig. 4a and [35]) and for our data (Fig. 5a). We believe that most probably the salts of the sodium dodecyl ion with  $\text{Rb}^+$  or  $\text{Cs}^+$  were not fully dissociated. In favor of this hypothesis speaks the fact that Lu et al. [35] worked at 33 °C to avoid precipitation in the solutions with Cs and Rb. Hence, we did not use the data obtained with  $\text{Rb}^+$  and  $\text{Cs}^+$  as counterions in any further calculations or analysis.

The effect of the counterion concentration on the adsorption constant for air/water and oil/water interfaces obtained with

Table 1  
Adsorption constants,  $K$ , determined from the slopes of the linear portions of  $\sigma(C^{2/3})$  in Figs. 4 and 5

| Author, surfactant  | Counterion    |               |              |               |               |
|---|---------------|---------------|--------------|---------------|---------------|
|   | $\text{Li}^+$ | $\text{Na}^+$ | $\text{K}^+$ | $\text{Rb}^+$ | $\text{Cs}^+$ |
| This work, sodium dodecyl sulfate, 23.3 °C                                | 105           | 123           | 166          | 165           | 166           |
| Lu et al. [35], dodecyl sulfate, 33 °C                                    | 94            | 101           | 151          | 154           | 150           |
| Weil [31], dodecyl sulfate, 25 °C   | 76            | 111           | 152          | –             | –             |
|   |               |               | $\text{F}^-$ | $\text{Cl}^-$ | $\text{Br}^-$ |
| This work, trimethyl ammonium bromide, 23.3 °C                            |               |               | 29           | 53            | 93            |
| Koelsch and Motschmann [36], 1-dodecyl-4-dimethyl aminopyridinium bromide |               |               | 48           | 81            | 119           |

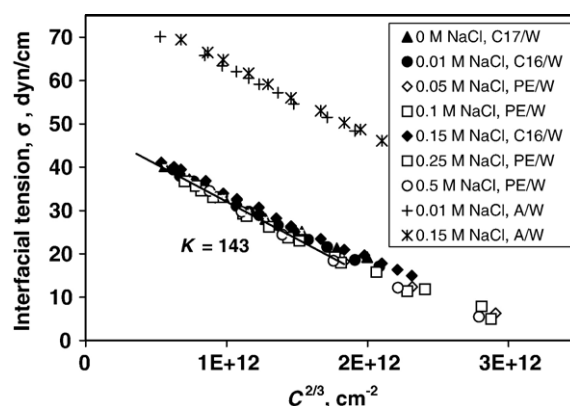


Fig. 6. Plots of the interfacial tension,  $\sigma$ , vs.  $C^{2/3}$  for sodium dodecyl sulfate with different concentrations of NaCl. Data from Haydon and Taylor (for petroleum ether=PE [69,70]), Rehfeld (for heptadecane=C17 [71]), and Gurkov et al. (for hexadecane=C16 and air=A [68]) were used. The straight line is a fit through all data of Haydon and Taylor at low concentration ( $C < 1.5 \times 10^{12} \text{ cm}^{-2}$ ) according to Eq. (2.22).

sodium dodecyl sulfate at various concentrations of NaCl is illustrated in Fig. 6. From the linear dependences of  $\sigma$  at low surfactant concentration in Fig. 6 we determined the adsorption constants,  $K$ . The values of  $K$  are shown in Table 2. The determined adsorption constants were almost the same for all electrolyte concentrations.

## 4. Specific effects of the counterions on the adsorption constant of ionic surfactants

### 4.1. Generalized Gouy equation

The Gouy Eq. (2.7) gives the total charge of the electrical double layer,  $Q_{dl}$ , which must be equal by absolute value and have an opposite sign to the surface charge, which is proportional to the adsorption,  $\Gamma$ . We consider throughout this paper  $\Gamma$  as surface concentration, i.e. as number of adsorbed molecules per unit area, since it is used in this sense in the adsorption isotherms. The difference between the surface concentration  $\Gamma$  and the Gibbs surface excess  $\bar{\Gamma}$  becomes significant only at very low concentrations (below  $10^{-4}$  M in the absence of added electrolyte and at even lower concentrations with electrolyte) [68].

We will use the model of the surface layer, formulated in [42] (see Fig. 1) and presented briefly in Section 2.3. We will assume that the counterions can reach the surface  $z=0$ . But then a problem appears: whether the counterions situated in the space  $0 < z < z_d$  are part of the adsorbed layer or still belong to the diffuse layer? We will show later that they must be considered as part of the diffuse layer even when they are in the plane  $z=0$ .

We will derive now a generalized form of the Gouy equation, accounting also for the van der Waals interaction of the counterions with the interface. We will represent the respective energy  $u_v(z)$  by the simple equation.

$$u_v(z) = u_0 \frac{R^3}{(R+z)^3} \quad (4.1)$$

Table 2

Adsorption constants  $K$  (from the slope of the linear portions of the curves  $\sigma(C^{2/3})$  in Figs. 4 and 5); (W = water, A = air, C16 = hexadecane, C17 = heptadecane, PE = petroleum ether)

| Author, interface            | NaCl, M | $K$ , from $\sigma(C^{2/3})$ |
|------------------------------|---------|------------------------------|
| Rehfeld [71], C17/W          | 0       | 137                          |
| Gurkov et al. [68], C16/W    | 0.01    | 140                          |
| Haydon and Taylor [69], PE/W | 0.05    | 143                          |
| Haydon and Taylor [69], PE/W | 0.1     | 143                          |
| Gurkov et al. [68], C16/W    | 0.15    | 136                          |
| Haydon and Taylor [69], PE/W | 0.25    | 138                          |
| Haydon and Taylor [69], PE/W | 0.5     | 147                          |

where  $R$  is the ionic radius (of the bare or of the hydrated ion,  $R_i$  or  $R_h$  respectively) and  $u_0$  is the (negative) van der Waals energy when the ion is in the plane  $z=0$  (for simplicity we will ignore the difference between the radii of the surfactant ionic head and the counterion). This equation is in fact the same as Eq. (2.1) with somewhat different notations:  $-u_0R^3$  stands for  $B$  and the zero of the coordinate system is in the center of the ion as in Fig. 1, whereas in Eq. (2.1) it is at the interface. In fact, Eq. (4.1) can be obtained in a similar way as Eq. (4.25) is derived below — by integration over the volume of the water phase the London Eq. (4.21) for an ion of radius  $R$  with coordinate of the center  $z$ .

The energy  $u_v(z)$  must be added to the electrostatic energy to obtain the total energy, which gives the ion distribution,  $C_k(z)$ , of the  $k$ -th component through the Boltzmann equation:

$$C_k(z) = C_k \exp\left(-\frac{u_k}{k_B T}\right) \quad (4.2)$$

where  $C_k$  and  $u_k$  are the bulk concentration and the total energy of the component  $k$ , respectively. We have neglected in Eq. (4.2) the energy of image interaction, which is very small [48].

In principle, one should use different constants  $u_0$  and  $R$  in Eq. (4.1) for the surfactant ions in the diffuse layer, for the coions and the counterions. The situation is additionally complicated when the added salt produces counterions different from those of the surfactant. Fortunately, in our experiments the added electrolyte has usually concentration at least one order of magnitude larger than the surfactant, which means that the diffuse layer in the vicinity of the surface will contain predominantly one type of counterions: either the counterions of the surfactant in the absence of added electrolyte or the counterions stemming from the added electrolyte even when they are different from the counterions of the surfactant. On the other hand, since for practically all ionic surfactants the electrostatic energy is much larger than the thermal one, one can assume that close to the surface the diffuse layer contains only counterions while the concentrations of surfactant ions and coions in the diffuse layer is zero. These considerations allow us to use only the expression (4.1) for the van der Waals energy for all ions. This involves a little error, because in the expression, derived below, we will neglect the terms, referring to all ions having charge of the same sign as the surfactant ions.

The relation between the potential  $\psi(z)$  in the diffuse layer and the charge density  $\rho(z)$  is given by Poisson equation:

$$\frac{d^2\psi}{dz^2} = -\frac{4\pi}{\varepsilon} \rho(z) \quad (4.3)$$

where  $\varepsilon$  is the dielectric constant of the solution. According to the assumptions, made above, and to Eq. (4.2), one has

$$\rho(z) = -2q(C_s + C_{el}) \sinh \Phi \exp\left(-\frac{u_v}{k_B T}\right) \quad (4.4)$$

Thus one obtains the following form of the Poisson–Boltzmann equation:

$$\frac{d^2\Phi}{dz^2} = \kappa^2 \sinh \Phi \exp\left(-\frac{u_v}{k_B T}\right) \quad (4.5)$$

where

$$\kappa = \left(\frac{8\pi q^2 C_t}{\varepsilon k_B T}\right)^{1/2} = \kappa_0 C_t^{1/2} \quad (4.6)$$

is the Debye screening parameter. Multiplying Eq. (4.5) with  $2d\Phi/dz$  and integrating the obtained result with respect to  $z$  from 0 to infinity one obtains (with the boundary condition at infinity  $d\Phi/dz=0$ ):

$$\left(\frac{d\Phi}{dz}\right)_{z=0}^2 = -2\kappa^2 \int_0^\infty \exp\left(-\frac{u_v}{k_B T}\right) \sinh \Phi \frac{d\Phi}{dz} dz \quad (4.7)$$

This result can be put in the form:

$$\left(\frac{d\Phi}{dz}\right)_{z=0} = -\kappa \exp\left(-\frac{u_0}{2k_B T}\right) \left[-2 \int_0^\infty \exp\left(\frac{u_0 - u_v}{k_B T}\right) \sinh \Phi \frac{d\Phi}{dz} dz\right]^{1/2} \quad (4.8)$$

If  $u_v=0$  (i.e. if the counterions are not specifically adsorbed), Eq. (4.5) can be integrated in the same way as we did to arrive at Eq. (4.7). In this case the integral over  $\Phi$  in the right hand side can be taken and by using the boundary condition at  $z \rightarrow \infty$  (where  $\Phi=0$  and  $d\Phi/dz=0$ ) after some algebra one obtains:

$$\frac{d\Phi^{(0)}}{dz} = -2\kappa \sinh\left(\frac{\Phi^{(0)}}{2}\right) \quad (4.9a)$$

Integrating one more time on  $z$  and using the condition  $\Phi^{(0)}=\Phi_0^{(0)}$  at  $z=0$  one finds the dependence of  $\Phi^{(0)}$  on  $z$ :

$$\tanh\left(\frac{\Phi^{(0)}}{4}\right) = \tanh\left(\frac{\Phi_0^{(0)}}{4}\right) \exp(-\kappa z) \quad (4.9b)$$

In the equations above the superscript (0) means that the respective quantity refers to a system without specific adsorption of the counterions and the subscript “0” indicate value at  $z=0$ .

Direct numerical integration of Eq. (4.5) showed that the potential  $\Phi(z)$  is close to the potential  $\Phi^{(0)}(z)$  corresponding

Table 3

Physical parameters of the counterions: ion radii, bare,  $R_i$ , and hydrated,  $R_h$ ; hydration number,  $n_w$ ; polarizability in water,  $\alpha_{0hi}$ ; hydration energy,  $\Delta G_{\text{hyd}}^0$ ; ionization potential,  $I_i$ , in vacuum and in water

| Counterion      | $R_i$ , Å | $n_w$<br>[76] | $n_w$<br>[74] | $R_h$ , Å<br>[76] | $R_h$ , Å<br>[74] | $\alpha_{0hi}$ Å <sup>3</sup><br>[52] | $\Delta G_{\text{hyd}}^0$<br>10 <sup>12</sup> erg [52] | $I_i$ in vacuum,<br>10 <sup>12</sup> erg [52] | $I_i$ in water, 10 <sup>12</sup> erg,<br>Eq. (4.32), Eq. (4.33) | $-u_0/k_B T$<br>( $I_i$ in vacuum) | $-u_0/k_B T$<br>( $I_i$ in water) | $1-f_u$ ,<br>Eq. (4.11) |
|-----------------|-----------|---------------|---------------|-------------------|-------------------|---------------------------------------|--|---|---|------------------------------------|-----------------------------------|-------------------------|
| Li <sup>+</sup> | 0.69      | 5 (5.2)       | 2.3           | 2.4               | 2.6               | 0.0285                                | -7.99  | 121.2   | 97.23   | 0.09                               | 0.09                              | 0.82–0.92               |
| Na <sup>+</sup> | 1.02      | 3 (3.2)       | 0.7           | 2.18              | 1.8               | 0.1485                                | -6.23  | 75.76   | 57.07   | 0.31                               | 0.32                              | 0.81–0.94               |
| K <sup>+</sup>  | 1.38      | 3 (2.6)       | 0.4           | 2.13              | 1.8               | 0.7912                                | -5.05  | 50.68   | 35.53   | 0.58                               | 0.83                              | 0.83–0.91               |
| F <sup>-</sup>  | 1.33      | -(2.7)        | -             | (2.11)            | -                 | 1.304                                 | -7.84  | 5.449   | 13.29   | 0.70                               | 0.22                              | 0.84–0.73               |
| Cl <sup>-</sup> | 1.81      | -(2)          | 0.5           | (2.22)            | 2.1               | 3.764                                 | -5.76  | 5.788   | 11.55   | 1.24                               | 0.35                              | 0.85–0.72               |
| Br <sup>-</sup> | 1.96      | 2 (1.8)       | 0.7           | 2.33              | 2.3               | 5.068                                 | -5.33  | 5.389   | 10.72   | 2.14                               | 0.60                              | 0.88–0.75               |

The radius of the surfactant ionic head  $-\text{SO}_4^-$ , calculated according to the theory in [76] is 2.5 Å. The adsorption energy,  $-u_0/k_B T$ , is calculated with Eq. (4.26) for K<sup>+</sup> and Br<sup>-</sup> and with Eq. (4.27) for the other ions. For water:  $I_w=2.02 \times 10^{-11}$  erg,  $\alpha_w=1.48$  Å<sup>3</sup>. Two values of the correction multiplier  $(1-f_u)$ , see Eqs. (4.10) and (4.11), are given in the last column, corresponding to the smallest (first number) and to the highest (last number) concentrations in Fig. 5.

to a system without van der Waals interaction (see Appendix A). Hence, it seems legitimate to use an iterational procedure for the calculation of the integral in Eq. (4.8) by replacing in the integral the exact dependence  $\Phi(z)$  by  $\Phi^{(0)}(z)$ . Using the expressions (4.9a) (written for  $z=0$  where  $\Phi^{(0)}=\Phi_0^{(0)}$ ) and (4.9b), Eq. (4.8) can be presented as:

$$-\frac{1}{2\kappa \sinh(\Phi_0^{(0)}/2)} \left( \frac{d\Phi}{dz} \right)_0 = \exp \left[ -\frac{u_0}{2k_B T} (1-f_u) \right] \quad (4.10)$$

where we have introduced the correction term  $f_u$ :

$$f_u \equiv \frac{k_B T}{u_0} \ln \left[ -\frac{1}{2 \sinh^2(\Phi_0^{(0)}/2)} \int_0^\infty \exp \left( \frac{u_0 - u_v}{k_B T} \right) \sinh \Phi^{(0)} \frac{d\Phi^{(0)}}{dz} dz \right] \quad (4.11)$$

The dependence of  $f_u$  on  $\Phi_0^{(0)}$ ,  $C_{\text{el}}$  and  $u_0$  is illustrated in Appendix A. The values of  $1-f_u$  for the systems under consideration are presented in Table 3: the term  $f_u$  turned out to be small enough to be disregarded.

By integrating Eq. (4.3) over  $z$  from  $\infty$  to 0 one finds

$$\left( \frac{d\Phi}{dz} \right)_{z=0} = -\frac{\kappa^2 \Gamma}{2C_t} \quad (4.12)$$

where we have used the relation

$$\int_\infty^0 \rho(z) dz = Q_{\text{dl}} = -q\Gamma \quad (4.13)$$

From Eqs. (4.10) (with  $f_u=0$ ) and (4.12) we obtain a generalized form of Gouy equation:

$$\Gamma = \frac{4\sqrt{C_t}}{\kappa_0} \sinh \frac{\Phi_0^{(0)}}{2} \exp \left( -\frac{u_0}{2k_B T} \right) \quad (4.14)$$

If  $u_0=0$ , at the same total electrolyte concentration  $C_t$  the adsorption will be  $\Gamma^{(0)} \neq \Gamma$ . Thus Eq. (4.14) yields:

$$\Gamma = \Gamma^{(0)} \exp \left( -\frac{u_0}{2k_B T} \right) = K C^{2/3} \quad (4.15)$$

where we have substituted  $\Gamma^{(0)}$  from Eq. (2.19) and have introduced a new adsorption constant:

$$K = K^{(0)} \exp \left( -\frac{u_0}{2k_B T} \right) \quad (4.16)$$

accounting for the adsorption energy  $u_0$  of the counterion.

On the other hand, the adsorption  $\Gamma$  can be expressed also through Boltzmann's and Henry's Eqs. (2.17) and (2.18), which yield (with  $\Phi_0$  instead of  $\Phi_0^{(0)}$ ):

$$\Gamma = K_s C_{\text{ss}} = K_s C_s \exp(-\Phi_0) \quad (4.17)$$

Inserting this expression for  $\Gamma$  into Eq. (4.14) and using (2.20) one obtains a useful expression for  $\Phi_0$ , which we will present only for  $\Phi_0 \gg 1$ :

$$\exp(\Phi_0) = \left( \frac{C_s^2}{C_t} \right)^{1/3} \left( \frac{K\kappa_0}{2} \right)^2 \exp \left( \frac{3u_0}{2k_B T} \right) \quad (4.18)$$

Eq. (4.18) is based on the linear isotherm (2.18) and will be valid therefore only for small concentrations. The relation between  $\Phi_0^{(0)}$  and  $\Phi_0$  can be found from the expression (4.17) and the analogous equation:

$$\Gamma^{(0)} = K_s C_s \exp(-\Phi_0^{(0)}) \quad (4.19)$$

By using Eqs. (4.17) and (4.19) and the relation (4.16) between  $K$  and  $K^{(0)}$  one obtains:

$$\Phi_0 = \Phi_0^{(0)} + \frac{u_0}{2k_B T} \quad (4.20)$$

When deriving the adsorption isotherm (4.15), we tacitly assumed that the surface charges is created only by the surfactant ions (i.e. that it is  $\Gamma q$ ) in spite of the fact that part of the counterions are also located at the surface  $z=0$  with potential  $\Phi_0$ . This is justified by the fact that when calculating the double layer charge  $Q_{\text{dl}}$  we integrated from  $z=0$ . If the counterions at  $z=0$  were considered also as part of the adsorbed layer, several changes should have been made: (i) one should account for the counterion adsorption,  $\Gamma_c$ , which means that in the left-hand sides of Eq. (4.14) one should have  $\Gamma - \Gamma_c$  rather than only  $\Gamma$ ; (ii) when

calculating  $Q_{dl}$  one should integrate from  $z=z_d$  rather than from  $z=0$ ; (iii) one must use also an adsorption isotherm for the counterions. But our calculations (not published) showed that the latter approach, even when it is based on Henry's adsorption isotherm, will not lead to the linear dependence of  $\Gamma$  on  $C^{2/3}$  exhibited by all experimental data for low concentrations (see Figs. 4 and 5). Therefore, our approach is consistent with the experimental results.

#### 4.2. Adsorption energies of the counterions

The calculation of the non-electrostatic adsorption energy of the counterions from electrolyte solutions  $u_0=u_v(0)$  is the most difficult problem of the present theory. The parameters of the intermolecular interaction, namely the polarizabilities  $\alpha_{0i}$ , the ionization potentials  $I_i$  and the hydrated ionic radii  $R_{hi}$  are not always available and even when they are, they are not very reliable. The most difficult problem is related to the radii of the hydrated ions,  $R_{hi}$ . The number of hydrating molecules and thereby the radii of the hydrated ions usually varies widely (sometimes by a factor of 2 or 3) from one literature source to another. Besides, there is a possibility that some ions dehydrate totally or partially upon adsorption. The adsorption energy depends on the third power of the ionic radius (see Eq. (4.27)), so that sometimes it can vary by orders of magnitude depending of the used value of the ionic radius.

We gathered all data we could find for the interaction parameters and tried to compare and analyze them critically, based on theoretical concepts as sound as possible. When we could not choose one from several possibilities, we performed calculations with all found data and used as final criterion our theory and the surface tension data, namely the experimental values of the adsorption constants,  $K$ , and the theoretical finding that their logarithm must be linear function of the negative adsorption energies,  $-u_0/k_B T$ , with slope 1/2 (see Eq. (4.16)). This philosophy is similar to the approach used by Kunz et al. [11], who selected what seemed to be the most reliable literature data for the system parameters but in order to fit the experimental results for the osmotic coefficients of electrolyte they had to adjust, sometimes considerably, the interaction parameters.

##### 4.2.1. Derivation of the equation for the adsorption potential

We will base our calculations on the simple London expression [73] for the intermolecular potential  $u_{ij}$  between molecules  $i$  and  $j$  at a distance  $r_{ij}$ :

$$u_{ij} = -\frac{L_{ij}}{r_{ij}^6} \quad (4.21)$$

where the London constant is

$$L_{ij} = \frac{3}{2} \alpha_{0i} \alpha_{0j} \frac{I_i I_j}{I_i + I_j} \quad (4.22)$$

Having in mind the aforementioned problems with the system parameters, we do not think it is worthwhile using more precise but complicated expressions.

The adsorbed counterion displaces an ensemble of several water molecules having total volume equal to the volume of the

immersed part of the ion (see Fig. 7). In the initial state 1, before adsorption, the ion is in the bulk and has energy  $u_i^b$  and the ensemble of water molecules (called "surface water" in Fig. 7) is at the surface and has energy  $u_w^s$ . In state 2, the ion and the water molecules exchange positions and their energies become  $u_i^s$  and  $u_w^b$  respectively. The change of energy when the ion and the respective water molecules exchange positions is the adsorption energy  $u_0$ :

$$\begin{aligned} u_0 &= u_{(2)} - u_{(1)} = (u_i^s + u_w^b) - (u_i^b + u_w^s) \\ &= \Delta u_i - \Delta u_w \end{aligned} \quad (4.23)$$

Although each water molecule has its own energy due to its interaction with the other water molecules, we will model this ensemble as a single large molecule, having the same geometry as the ion with which it interchanges position. However, its polarizability is equal to  $N_w \alpha_{ow}$ , where  $N_w$  is the number of water molecules, occupying the same volume as the ion and  $\alpha_{ow}$  is the polarizability of the water molecule (for details see below).

Robinson and Stokes argued (see Chapter 9 in [74]) that the hydration layer of the cations has some compressibility (or freedom of lateral motion of the hydrating molecules) so that upon their collision with the anions (which they assumed non-hydrated) the latter can penetrate around 0.7 Å inside the cation hydration layer. We will show later that such effect is probable also with some of the adsorbing hydrated ions — the hydrating molecules are pushed away by the interface, so that the bare ion of radius  $R_i$  can touch it (Fig. 8). Although this situation is realized only in some special cases, we will base our derivation of the adsorption energy on such more complicated model since the adsorption energy for the more common case of spherical hydration shell with radius  $R_h$  can be obtained by simply replacing in the final Eq. (4.26)  $R_i$  by  $R_h$ .

The interaction energy of the adsorbed ion with a cylindrical ring in the water phase with radius  $r$ , width  $dr$  and thickness  $dz$ , situated at a distance  $z$  from the center of the ion (see Fig. 9) is

$$du_i = -\rho_w L_{iw} \frac{2\pi r}{(r^2 + z^2)^3} dr dz \quad (4.24)$$

where  $\rho_w$  is the number density of the water. The energy  $du_i$  is integrated over  $z$  from  $-R_i$  to  $R_h$  and from  $R_h$  to  $\infty$ . In the first

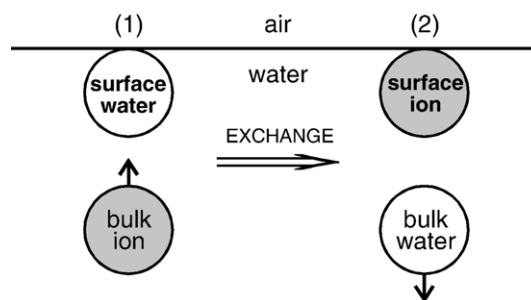


Fig. 7. Schematic presentation of the process of adsorption of an ion: (1) ion in the bulk; (2) ion at the surface.

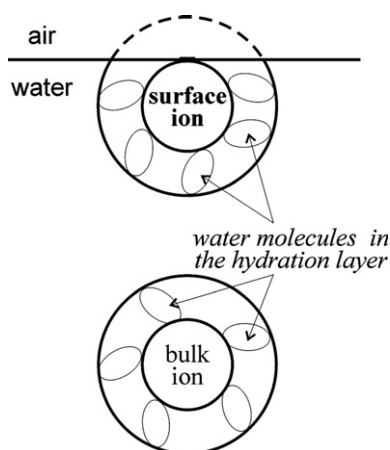


Fig. 8. Schematic presentation of the process of adsorption of a hydrated ion from the bulk at the surface: the hydrating molecules might be pushed away by the interface, so that the bare ion of radius  $R_i$  can touch it.

integral  $r$  varies in the limits  $R_h^2 - z^2 < r^2 < \infty$  and in the second one  $0 < r < \infty$ . The result

$$u_i^s = -\frac{2}{3} \frac{\pi \rho_w L_{iw}}{R_h^3} \left( 1 - \frac{3 R_i}{4 R_h} \right), \quad (4.25)$$

must be combined with  $u_i^b$  to obtain  $\Delta u_i$ . The bulk energy  $u_i^b$  is found in a similar way as  $u_i^s$  by integrating the interaction energy of the ion with a shell of water of radius  $r$  and thickness  $dr$  from  $R_h$  to infinity. The result is  $u_i^b = -4\pi \rho_w L_{iw} / 3R_h^3$ . The respective expressions for  $\Delta u_w$  are obtained by simply changing  $L_{iw}$  to  $L_{ww}$  but keeping in mind that the number of water molecules in the ensemble is  $N_w$ , so that in the expression for  $\Delta u_w$  one must replace  $\alpha_{ow}$  by  $N_w \alpha_{ow}$ . Substituting these results in Eq. (4.23) one finds:

$$u_0 = \frac{2}{3} \frac{\pi \rho_w}{R_h^3} \left( 1 - \frac{3 R_i}{4 R_h} \right) (L_{iw} - L_{ww}) \quad (4.26)$$

The respective expression for an ion totally immersed in the water is obtained by simply setting  $R_i = R_h$  in Eq. (4.26):

$$u_0 = \frac{\pi \rho_w}{6 R_h^3} (L_{iw} - L_{ww}) \quad (4.27)$$

Since both  $L_{iw}$  and  $L_{ww}$  contain  $\alpha_{ow}$  and  $I_w$ , it is convenient to rearrange the expression for  $L_{iw} - L_{ww}$ :

$$L_{iw} - L_{ww} = \frac{3}{2} \alpha_{ow} I_w \left( \frac{I_i}{I_i + I_w} \alpha_{oi} - \frac{N_w \alpha_{ow}}{2} \right) \quad (4.28)$$

If  $I_i = I_w$ , the expression in parentheses becomes identical with the excess polarizability  $\alpha^*$  as defined by Ninham and Yaminsky [39].

#### 4.2.2. Choice of the system parameters and comparison with experiment

Although the obtained equations for the adsorption energy seem simple, their use is by no means clear, both because of the

scattering of the experimental values for polarizabilities, ionization potentials and ion radii as well as sometimes because of the lack of clarity about their meaning. We begin by considering the degree of hydration (the number,  $n_w$ , of the hydrating molecules) and the radius  $R_h$  of the hydrated ion. The values of these quantities depend strongly on the experimental method used for their determination and can vary widely (see [75], p. 143). It seems that more reasonable results can be obtained by model calculations, rather than experimentally. Very careful calculations were performed by Marcus [76]. He found that the hydration number  $n_w$  for all ions is reasonably well represented by the empirical relation  $n_w = A_v |z_v| / R_i$ , where  $z_v$  is the ion valence and  $A_v = 3.6 \text{ \AA}$  for all ions. He further assumed that the water molecules, considered as spheres with radius  $R_w = 1.38 \text{ \AA}$  and volume  $V_w = 11 \text{ \AA}^3$ , form a dense layer of water around the ion, so that

$$\frac{4\pi}{3} (R_h^3 - R_i^3) = n_w V_w \quad (4.29)$$

The values of  $n_w$  and  $R_h$  calculated by Marcus [76] in this way are shown in Table 3 (the values of  $n_w$  and  $R_h$  for  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $-\text{SO}_4^-$  were calculated by us). Robinson and Stokes used basically the same approach (see Eq. (9.27)) in [74] but for  $V_w$  they used the value  $30 \text{ \AA}^3$ , which follows from the water density. However, they used different values of  $n_w$ , which were calculated from the ion diffusivity (see Table 11.10 in [74]). We used their data for  $n_w$  and Eq. (4.29) with  $V_w = 30 \text{ \AA}^3$  to calculate by their method the values of  $R_h$  in Table 3 — the results for  $R_h$  are not very different from those obtained by the method of Marcus. Both sets of  $R_h$ , those calculated by the method of Marcus and by the method of Robinson and Stokes, differ however much from the often quoted values [73] (in  $\text{\AA}$ ) 3.8, 3.6, 3.3, 3.5, 3.3 and 3.3 for  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  respectively. Since the ion–ion interaction energy depends on  $R_h^3$  and the adsorption energy of the ions on  $R_h^3$ , the precise value of  $R_h$  is of crucial importance.

Another effect, which must be accounted for, is the real density of the hydration layer. Indeed, the hydrating molecules are not melted to form a dense sheath, as it is assumed in Eq. (4.29), but are better represented as spheres, touching the ion surface, whose centers are at a distance  $R_i + R_w$  from the center of the ion. If for simplicity one replaces the spherical surface, where the centers of the water molecules are, by a plane, simple calculation shows that the respective area is approximately 9 times larger for the ion  $\text{Li}^+$

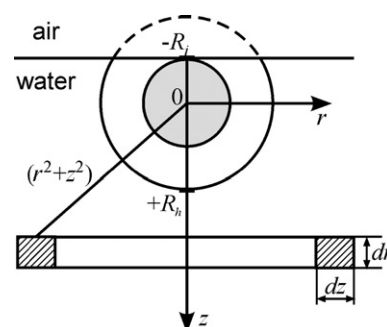


Fig. 9. Illustration of the integration procedure applied to derive the energy of an ion (as depicted in Fig. 8) at the water/air surface.

than the cross-sectional area  $\pi R_w^2 = 6.15 \text{ \AA}^2$  of the water molecule, while for the ion  $\text{K}^+$  this ratio is 16. Having in mind that the respective hydration numbers are 5.2 and 2.6, one may conclude that the hydrating molecules of  $\text{K}^+$  have much more freedom for lateral motion than those of  $\text{Li}^+$ . The comparison between  $\text{F}^-$  and  $\text{Br}^-$  leads to similar conclusions for the mobility of the hydrating molecules of  $\text{Br}^-$ .

When the hydrated ion interacts with another surface it can loose in principle part of its hydrating molecules. This is, however hardly possible during adsorption, since the adsorption energy of the counterions is of the order of  $k_B T$  (see Table 3 or Fig. 10 below) and their electrostatic energy does not exceed 6 to 8  $k_B T$ . This is much less than the hydration energy per molecule, which according to the data in [76], is of the order of 40  $k_B T$ . However, the displacement of the water molecules along the ion surface does not involve significant energy change. Hence, when the ion is pressed against the interface the hydrating molecules from the contact area can move inside the solution (as shown in Fig. 8) provided that there is enough room to accommodate them without dehydration. By using the approach of Marcus and deriving an equation for the volume of the truncated hydration shell (with the

configuration shown in Fig. 8) we calculated how much the radius of the truncated solvation layer must increase in order to accommodate all  $n_w$  hydrating water molecules. For the largest ions,  $\text{K}^+$  and  $\text{Br}^-$ , this radius turned out to be practically equal to the original one,  $R_h$ , but for the other ions it is considerably larger. The latter is another indication that the displacement of the water molecules for all ions, besides  $\text{K}^+$  and  $\text{Br}^-$ , probably requires detachment of some of these molecules, which is hardly possible, as shown above. That is why when calculating the adsorption energy of  $\text{K}^+$  and  $\text{Br}^-$  we accounted for the fact that at the interface their hydration shell is truncated (as shown in Fig. 8) and used Eq. (4.26), whereas for the other ions Eq. (4.27) was used.

Relatively less controversial is the situation with the ion polarizability,  $\alpha_{0i}$ . The existing data for ions in solution [11,51,77] do not differ dramatically. We used the data from Tavares et al. [51] not only because they are the newest ones, but also because they lead to the best final results shown in Table 3.

It is not quite clear how to define the number of water molecules,  $N_w$ , in Eq. (4.28). The problem is related to the polarizability of the hydrating water. Kunz et al. [11] suggested to define  $N_w$  as the number of water molecules filling the same volume as the bare ion, i.e.

$$N_w = V_i / V_w \quad (4.30)$$

where  $V_i$  is the volume of the bare ion and  $V_w$  is the volume of one water molecule. This definition in fact assumes, that the water molecules, hydrating the ion, have the same polarizability as the free water molecules, so that these molecules do not contribute to the excess polarizability  $\alpha^*$ . This is certainly not entirely correct. According to [78], the “freezing” of the hydrating molecules prevents them from moving, which leads to marked reduction of the dipole polarizability. Marcus [76] also argued that due to electrostriction the relative permittivity of the hydrating water is much lower than in bulk water.

Therefore, the assumption on which Eq. (4.30) is based is problematic. In the other extreme case, very low permittivity, as suggested by Marcus, one may assume that the hydrating molecules have zero polarizability. Then  $N_w$  must be the number of free water molecules occupying the same volume  $V_h$  (instead of  $V_i$ ) as the *hydrated* ion. The truth is probably between these two extreme cases. We checked both possibilities and found that the assumption of Kunz et al. (i.e. Eq. (4.30)) leads to better agreement of the calculated values of the adsorption constants  $K$  with the experimental results.

The second problem with  $N_w$  is related to the choice of  $V_w$  in Eq. (4.30). There are again at least two possibilities: (i) to take the average volume per molecule, based on the water density,  $30 \text{ \AA}^3$ , or (ii) to take the proper volume of a water molecule,  $11 \text{ \AA}^3$ , corresponding to a molecular radius  $R_w = 1.38 \text{ \AA}$ . Kunz et al. [11] and Robinson and Stokes [74] used the first option and Marcus [76] the second one. In fact both options have physical ground. The first option follows from the fact that in the free water a molecule indeed occupies  $30 \text{ \AA}^3$ . The second option can be justified by the fact that when calculating  $R_h$  from Eq. (4.29) we assumed  $R_w = 1.38 \text{ \AA}$ . We checked both options and obtained better agreement between the calculated and experimental values

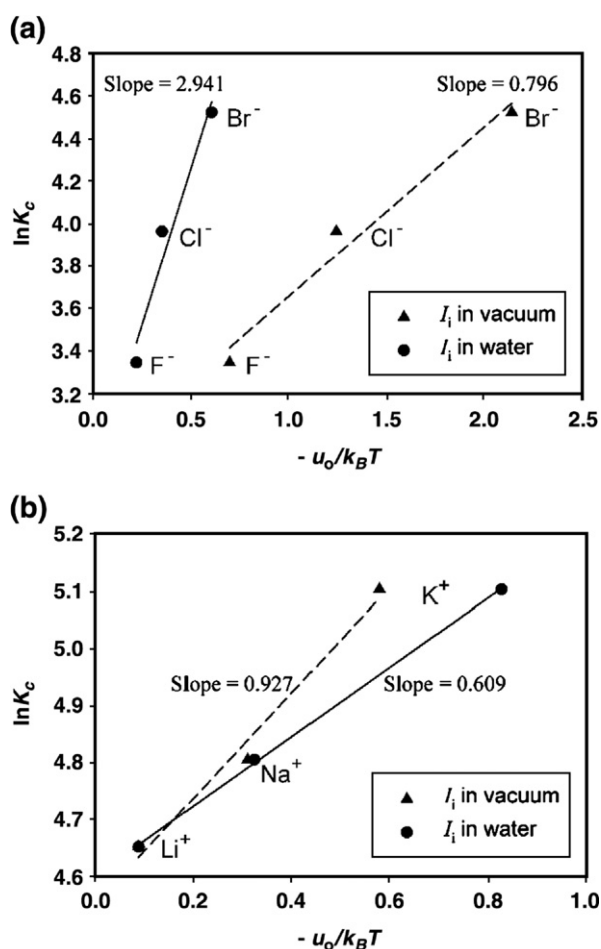


Fig. 10. Plot of  $\ln K_c$  vs.  $-u_0/k_B T$  for (a) dodecyl sulfate with  $\text{Li}^+$ ,  $\text{Na}^+$ , and  $\text{K}^+$  as counterions, and (b) dodecyl trimethyl ammonium with  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  as counterions. Note that the adsorption energy,  $-u_0/k_B T$ , is calculated with Eq. (4.26) for  $\text{K}^+$  and  $\text{Br}^-$  and with Eq. (4.27) for the other ions.

of  $K$  with  $R_w = 1.38 \text{ \AA}$ . In summary, in Eq. (4.30) we used for  $V_i$  the volume of the bare ion and for  $V_w$  the value  $11 \text{ \AA}^3$ .

There is also a problem with the meaning of the ionization potential  $I_i$ . In fact the exact London equation does not contain ionization potential, but contains instead the vibrational energy of the electron  $\hbar\nu_0 = E_e - E_0$ , where  $\hbar$  is Planck constant,  $\nu_0$  is frequency and  $E_e$  and  $E_0$  are the electron energies in the excited and non-excited state [79]. It was found empirically that  $\hbar\nu_0$  is close to the ionization potential i.e. to the energy needed to bring one electron from the initial energy  $E_0$  to energy zero. Both energies  $E_0$  and  $E_e$  are related to electron transfers *inside the atom or the molecule*. This means that any change of the electron energy after it has left the atom or the ion is not related to the characteristic frequency  $\nu_0$ . Since during ionization the outmost electrons are most likely to be knocked out, it is there ionization potential which should be taken. For the cations this is the second ionization potential, since the first potential corresponds to ionization of the respective atom, not ion. Since the anions have accepted one extra electron, their ionization potential must be equal to the negative value of the electron affinity. The ionization potential of the water is  $I_w = 2 \times 10^{-11} \text{ erg}$ .

The ionization potentials in gaseous phase are known with good precision, which is not the case with ions in solution. So far there is probably no other way to account for the effect of the solvent besides calculating the hydration energy of the ions. The problem is that what is needed for the calculation of the intermolecular interactions is the effect of the solvent on  $\nu_0$ , i.e. on the energy  $E_0$ , and it is not clear how the change of the total energy of the ion upon hydration is related to  $E_0$  and thereby — to the ionization potential. For the lack of better possibilities we assumed, following Tavares et al. [51], that the change of the ionization potential of the ion is equal to the hydration energy. We used the thermodynamic procedure developed by Tavares et al. [51] to calculate the change of the hydration energy  $\Delta G_{\text{hyd}}^n$  of the ions for the processes



(where  $X$  and  $Y$  denotes cation and anion respectively) and added them to the respective ionization potentials in gaseous phase. These energies were calculated from the formula [51]:

$$\Delta G_{\text{hyd}}^{z_v \pm 1} = \left( \frac{z_v \pm 1}{z_v} \right)^2 \Delta G_{\text{hyd}}^{z_v} \quad (4.32)$$

where  $z_v + 1$  is the valence of the unstable cation and  $z_v - 1$  is the valence of the unstable anion. The ionization potentials in Table 3 do not contain the hydration energy of the electron for reasons, explained above.

We checked numerically all the physically reasonable options enumerated above. It turned out that many of them lead to results incompatible with the experimental data such as unrealistic trend of the dependence of  $\ln K$  on  $u_0/k_B T$  (non-monotonous change of  $u_0/k_B T$  with the ion order,  $\text{Li}^+ - \text{Na}^+ - \text{K}^+$  or  $\text{F}^- - \text{Cl}^- - \text{Br}^-$ ) or negative slope of the dependence of  $\ln K$  vs.  $-u_0/k_B T$ . The only possibility to avoid these problems was to

represent the excess polarizability as:

$$\alpha^* = \alpha_{0h} \frac{I_i}{I_i + I_w} - \alpha_{0w} \left( \frac{R_i}{R_w} \right)^3 \quad (4.33)$$

where  $\alpha_{0h}$  is the polarizability of the hydrated ion and  $R_w = 1.38 \text{ \AA}$ .

However, even in this case we did not have serious arguments for or against accounting for the role of ion hydration on the ionization potentials of the ions (see above). That is why we performed calculations with both options. The results are presented in Fig. 10 and the calculated adsorption energies in Table 3. The linear dependence of  $\ln K$  vs.  $-u_0/k_B T$  is good in all cases, and the slopes are relatively close to the theoretical one,  $1/2$  (see Eq. (4.16)). For  $\text{K}^+$  and  $\text{Br}^-$  we have calculated the energies  $u_0$  also by using Eq. (4.27) i.e. without accounting for the possible deformation of the hydration shell as illustrated in Fig. 8. If the obtained respective values for  $u_0/k_B T$ ,  $-0.40$  and  $-1.35$ , are used instead of the values calculated with deformed shell, the slopes of the lines (not shown) will not be very different from the theoretical one, but the correlation coefficients will be much worse.

It turned out that the slopes of the dependence  $\ln K$  vs.  $-u_0/k_B T$ , are closer to the theoretical one,  $1/2$ , when taking the ionization potential in water for the cations and in vacuum for the anions. The precise physical reason for this difference between cations and anions is unclear. It may be related to the much lower ionization potentials in vacuum of the anions vs. the cations, which makes the calculations of the adsorption energies of the anions very sensitive to the value of the hydration energy. Indeed, the data in Table 3 show that the low ionization potentials of the anions in vacuum lead to an almost twofold increase of the ratio  $I_i/(I_i + I_w)$  due to the hydration energy, whereas this change for the cations is only several percents. As a consequence, the calculated values of  $-u_0/k_B T$  for anions are more than three times smaller for ionization potentials in water than in vacuum.

Note that we obtained these results without using any free adjustable parameter. This fact lends support to the hypothesis that the effect of the type of the counterions on the adsorption constant  $K$  is due to van der Waals interactions rather than to steric reasons, related to the ion size as it is sometimes assumed [29–31].

A qualitative test of the theory can be performed also by calculating the adsorption of the counterions from our data for  $\sigma$  vs.  $C$  at constant surfactant concentration  $C_s$  and variable electrolyte concentration  $C_{\text{el}}$  (see Section 3). To avoid complicated notations we will illustrate the procedure by our data with the surfactant SDS with added electrolyte KCl. The respective form of the Gibbs isotherm is:

$$-\frac{d\sigma}{k_B T} = (\Gamma_s + \Gamma_{\text{Na}}) d\ln C_s + (\Gamma_{\text{K}} + \Gamma_{\text{Cl}}) d\ln C_{\text{el}} \quad (4.34)$$

where  $\Gamma_s$  is the adsorption of the surfactant ion. The first term in the right hand side is zero since  $C_s$  is constant. The ion  $\text{Cl}^-$  has negligible adsorption, since it has a charge of the same sign as the adsorbed surfactant. So one obtains:

$$-\frac{d\sigma}{k_B T} = \Gamma_{\text{K}} d\ln C_{\text{el}} \quad (4.35)$$

Hence, the adsorption  $\Gamma_{\text{K}}$  can be calculated from Gibbs Eq. (4.35). The electroneutrality condition allows the calculation of



the adsorption of  $\text{Na}^+$ :

$$\Gamma_{\text{Na}} = \Gamma_{\text{S}} - \Gamma_{\text{K}}$$

where we have neglected the adsorption of  $\text{Cl}^-$ . The surfactant adsorption  $\Gamma_{\text{S}}$  can be calculated from Eq. (4.15) with the values of the adsorption constants  $K$  from Table 1 for the respective counterion. The ion  $\text{K}^+$  has larger adsorption energy than  $\text{Na}^+$  (see Table 3). Besides the surfactant concentration is at least one order of magnitude lower than the added electrolyte concentration. Both factors must lead to small ratio of the adsorption of  $\text{Na}^+$  vs.  $\text{K}^+$ .

The obtained results are illustrated in Fig. 11 for the counterions  $\text{K}^+$  and  $\text{Li}^+$ . If there were no  $\text{Na}^+$  ions, the curves for the adsorption of the surfactant and the added counterion  $\text{K}^+$  should coincide. The small shift between the respective curves in Fig. 11a is due to the adsorption of  $\text{Na}^+$ , which is also shown in Fig. 11a. The relative adsorptions of  $\text{Na}^+$  with respect to  $\text{Li}^+$  and  $\text{K}^+$ ,  $\Gamma_{\text{Na}}/\Gamma_{\text{Li}}$  and  $\Gamma_{\text{Na}}/\Gamma_{\text{K}}$ , are shown in Fig. 11b.  $\Gamma_{\text{Na}}/\Gamma_{\text{K}}$  is smaller than  $\Gamma_{\text{Na}}/\Gamma_{\text{Li}}$  for all concentrations, which is due to the stronger adsorption of  $\text{K}^+$  than  $\text{Li}^+$ . The results for the other surfactants and counterions follow the same trend. The agreement of the results obtained by two independent calculations of the adsorptions confirms the reliability of our data and computational procedures.

We performed two additional tests of our theory. According to Eq. (4.16) the adsorption constant must depend on the type of the

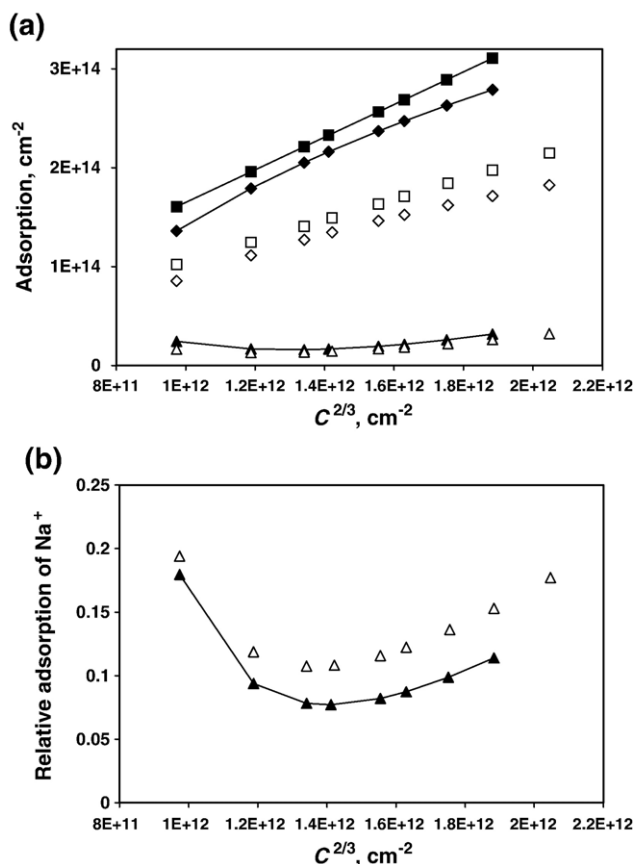


Fig. 11. (a) Adsorption of the dodecyl ion,  $\Gamma_{\text{S}}$  (squares),  $\text{K}^+$  or  $\text{Li}^+$  (diamonds), and  $\text{Na}^+$  (triangles) with added KCl (full symbol) or LiCl (empty symbol). See text for explanations. (b) Relative adsorption of  $\text{Na}^+$ : (i)  $\Gamma_{\text{Na}}/\Gamma_{\text{K}}$  (full symbol); (ii)  $\Gamma_{\text{Na}}/\Gamma_{\text{Li}}$  (empty symbol). See text for explanations.

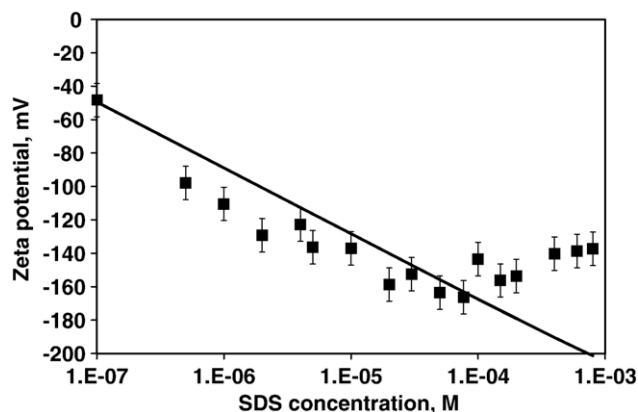


Fig. 12.  $\zeta$ -potential of hexadecane emulsion drops measured as a function of the concentration of SDS in presence of 10 mM NaCl. The straight line represents the theoretical surface potential  $\Phi_0$  calculated from Eq. (4.18).

counterion, but not on its concentration. This conclusion is tested on Fig. 6, where the effective concentration  $C$  includes also the electrolyte concentration (see Eq. (2.21)). The initial portions of the curves  $\sigma(C^{2/3})$ , shown in Fig. 6, practically coincide for all systems oil/water with electrolyte concentrations varying from zero to 0.5 M (the average slope is  $K = 143$ ). The same is true for the systems air/water. The small deviations from the straight line at larger concentrations are due to the fact that the area per molecule depends on the electrolyte concentration as explained in Section 2.3. These results confirm the theoretical predictions.

The quantitative check of the theory was done by comparing the theoretical values of the surface potential (calculated from Eq. (4.18)) with the measured  $\zeta$ -potential of emulsion droplets in the presence of SDS and 10 mM NaCl (the experimental details are given in Section 3). The adsorption isotherm obtained by Gurkov et al. [68] was used to determine the adsorption constant  $K = 140$  for this particular system. Fig. 12 presents the measured values of the  $\zeta$ -potential as a function of the concentration of SDS. The straight line represents the theoretical prediction according to Eq. (4.18) without any adjustable parameter.

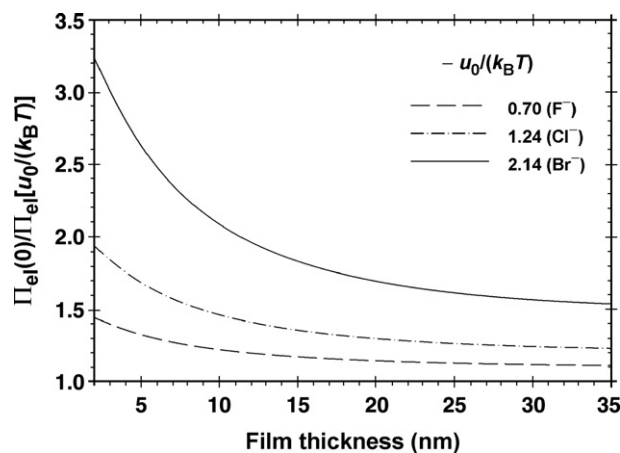


Fig. 13. Ratio of the disjoining pressure  $\Pi_{el}$  for the shown values of  $-u_0/k_B T$ , corresponding to the three halogen counterions:  $\text{F}^-$ ,  $\text{Cl}^-$  and  $\text{Br}^-$ , toward  $\Pi_{el}(0)$  (corresponding to  $u_0=0$ ) for surfactant concentration  $C_s=0.5$  mM. The calculations were performed by means of Eq. (5.1) and numerical solution of Eqs. (4.1) (with  $R=2.5$  Å), (4.5), (4.12) and (4.15).

## 5. Effect of the counterions on the disjoining pressure of foam films

Although the adsorption energies of the counterions,  $u_0$ , are not very large, they may change significantly the electrostatic component  $\Pi_{el}$  of the disjoining pressure  $\Pi$  of a thin film.  $\Pi_{el}$  is defined by the equation [80]:

$$\Pi_{el} = 2R_g T C_t (\cosh \Phi_m - 1) \quad (5.1)$$

Here  $R_g$  is the gas constant,  $T$  is temperature and  $\Phi_m$  is the minimum of the dimensionless potential at the midplane  $z=h/2$ , with  $h$  being the film thickness. As an example the potential  $\Phi$  was calculated by numerical solution of Eq. (4.5) along with Eq. (4.1) (with  $R=2.5$  Å) for surfactant concentration  $C_s=0.5$  mM. The boundary conditions are Eq. (4.12) and the requirement for minimum of  $\Phi$ :  $d\Phi/dz=0$  at  $z=h/2$ . The adsorption  $\Gamma$ , entering in Eq. (4.12), is calculated from Eq. (4.15) — this is equivalent to the so-called condition for “charge regulation”. The results were used to calculate  $\Phi_m$  and  $\Pi_{el}$  from Eq. (5.1). The total disjoining pressure,  $\Pi$ , is calculated from:

$$\Pi = \Pi_{el} - \frac{A_H}{6\pi h^3} \quad (5.2)$$

where the Hamaker constant for foam films is  $A_H=4 \times 10^{-13}$  erg.

The results for the halogen counterions are shown in Figs. 13 and 14. Fig. 13 presents the ratio of  $\Pi_{el}(0)$  (corresponding to lack of counterion adsorption i.e. to  $u_0=0$ ) to  $\Pi_{el}$  for the values of  $-u_0/k_B T$ , corresponding to the three halogen counterions:  $F^-$ ,  $Cl^-$  and  $Br^-$  (see Table 3). The decrease of  $\Pi_{el}$ , provoked by the counterions is significant — it is about three-fold for film thickness  $h=5$  nm. The effect of the counterions on the total disjoining pressure,  $\Pi$ , of a foam film, including also the Hamaker contribution, is illustrated in Fig. 14. The maximum around  $h=5$  nm, which controls the stability and the coalescence of the bubbles, drops almost 5 times in the presence of only 0.5 mM  $Br^-$ . Unfortunately, we are not aware of experimental measurements of the disjoining pressure  $\Pi$  with different

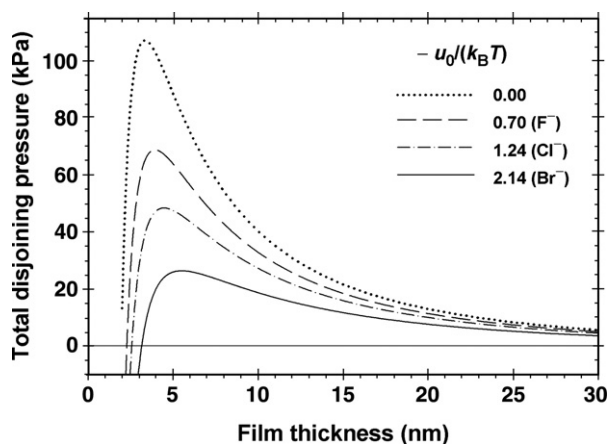


Fig. 14. Total disjoining pressure,  $\Pi$ , calculated from Eq. (5.2) with Hamaker constant  $A_H=4 \times 10^{-20}$  J for counterions F,  $Cl^-$  and  $Br^-$ . The other parameters are as in Fig. 13.

counterions, permitting comparison with the theoretical calculations, presented above.

## 6. Conclusion

We attempted to develop a theory accounting for the effect of the counterions on the adsorption constant  $K$ . The experimental values of  $K$  were determined by using surface and interfacial tension isotherms measured by us or available in the literature by plotting them vs. the effective surfactant concentration  $C^{2/3}$ . The new effect accounted now with respect to the theory in [42] is the van der Waals interaction energy of the counterions,  $u_s$ , with the interface, which must be added to the electrostatic energy to calculate the distribution of the counterions normally to the interface. This distribution, along with the Poisson–Boltzmann Eq. (4.5), allows calculating the potential distribution which is used to derive a generalization of Gouy Eq. (4.14) and a modified expression (4.16) for the adsorption constant  $K$ , which depends now also on the adsorption energy of the counterion,  $u_0$ .

The adsorption energy from solution is the energy needed to interchange the position of the hydrated ion in the bulk of the solution with that of the same volume of solvent at the surface. The respective energies were calculated from Eqs. (4.26) and (4.27) (see also Eq. (4.22)), which involve the ionic polarizabilities  $\alpha_{0i}$  and the ionization potentials  $I_i$  of the respective ions and the radii  $R_h$  or  $R_i$  of the hydrated or the bare ion respectively. By careful analysis of the available experimental data for  $\alpha_{0i}$ ,  $I_i$  and  $R_h$ , coupled with some reasonable hypothesis, we succeeded to obtain linear dependences between the calculated values of  $u_0$  and the experimental data for  $\ln K$  with slopes rather close to the theoretical one,  $1/2$  (see Fig. 10). The obtained results for the counterion adsorption energy  $u_0$  and the respective adsorption constant were used to investigate numerically the effect of the counterions on the disjoining pressure  $\Pi$  of foam films. The effect turned out to be significant especially for films of small thickness.

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## Appendix A. Numerical analysis of the main approximations used in the derivation of the expressions for the adsorption constant $K$ and the surface potential $\Phi_0$

The importance of the found effects calls for more detailed analysis of the two main approximations involved in the derivation of the final results for the adsorption constant  $K$  and the surface potential  $\Phi_0$

- (i) The iterational procedure consisting in replacing under the integral in Eq. (4.8) the true potential  $\Phi(z)$  by the potential  $\Phi^{(0)}(z)$  from Eq. (4.9b), valid for a system without specific counterion adsorption;
- (ii) The neglect of the correction term  $f_u$  in Eq. (4.10). We analyzed these problems by solving numerically the exact

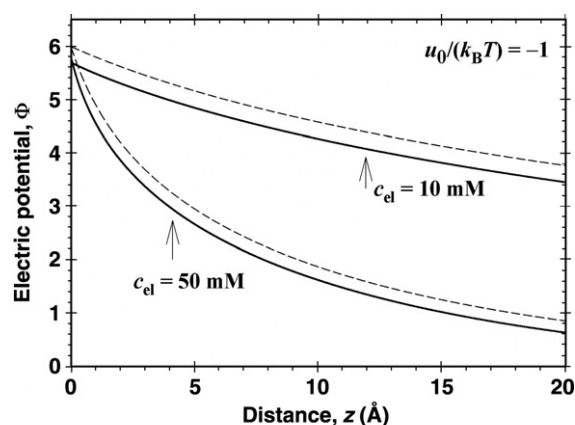


Fig. A1. Numerical solution for the electric potential  $\Phi(z)$  from Eqs. (4.1) and (4.5) for two different ionic strengths: 1 mM and 50 mM and  $u_0/k_B T = -1$  (solid lines). Exact solution, Eqs. (4.9a) and (4.9b), for  $u_0 = 0$  with  $\Phi_0^{(0)} = 6$  (dashed lines).

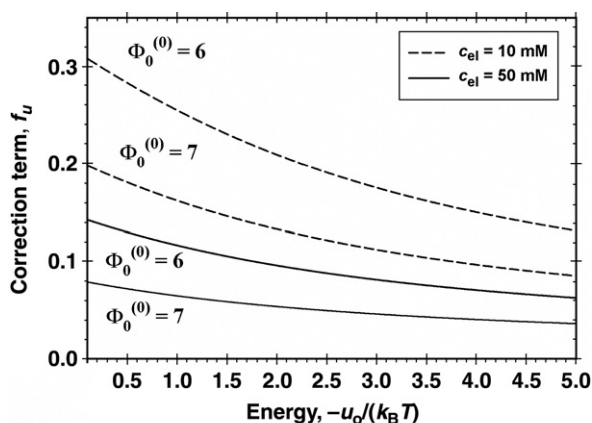


Fig. A2. Numerical calculation of the correction term  $f_u$  (Eq. (4.11)) as a function of the surface potential  $\Phi_0^{(0)}$ , electrolyte concentration,  $C_{el}$ , and adsorption energy  $-u_0/k_B T$ .

problem, formulated by Eq. (4.5) with some relevant values of the system parameters.

The first problem was analyzed by calculating numerically the electric potential  $\Phi(z)$  from Eqs. (4.1) and (4.5) for two different ionic strengths: 1 mM and 50 mM. The chosen value of the energy is  $u_0/k_B T = -1$  and of the radius is  $R = 2.5 \text{ \AA}$ . The results for  $\Phi(z)$  are shown by solid lines in Fig. A1. The dashed lines correspond to the exact solution, Eqs. (4.9a) and (4.9b), for  $u_0 = 0$  with potential  $\Phi_0^{(0)} = 6$ . The values of the surface potentials  $\Phi_0^{(0)}$  and  $\Phi_0$  are related through Eq. (4.20). Obviously, the electric potential decreases when the interaction energy is accounted for, but the difference between the two potentials is small (less than 10% according to Eq. (4.20)) and about the same for the two chosen electrolyte concentrations in spite of the large difference between them. This confirms the applicability of the approximation used.

This conclusion is also confirmed by the results from the numerical calculation of the correction term  $f_u$  shown in Fig. A.2 as a function of three relevant parameters: it decreases with increasing potential  $\Phi_0^{(0)}$ , electrolyte concentration,  $C_{el}$ , and adsorption energy  $-u_0/k_B T$ . The data presented in the last column

of Table 3 indicate that for the alkaline ions the correction factor  $1 - f_u$  is always larger than 0.8. However, for the halogen ions it can become close to 0.7 since they provoke larger decrease of the potential  $\Phi_0$  than the alkaline ions.

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