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# Interpretation of negative values of the interaction parameter in the adsorption equation through the effects of surface layer heterogeneity

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## Abstract

The problem of the negative values of the interaction parameter in the equation of Frumkin has been analyzed with respect to the adsorption of nonionic molecules on energetically homogeneous surface.

For this purpose, the adsorption states of a homologue series of ethoxylated nonionic surfactants on air/water interface have been determined using four different models and literature data (surface tension isotherms). The results obtained with the Frumkin adsorption isotherm imply repulsion between the adsorbed species (corresponding to negative values of the interaction parameter), while the classical lattice theory for energetically homogeneous surface (e.g., water/air) admits attraction alone. It appears that this serious contradiction can be overcome by assuming heterogeneity in the adsorption layer, that is, effects of partial condensation (formation of aggregates) on the surface. Such a phenomenon is suggested in the Fainerman–Lucassen–Reynders–Miller (FLM) ‘Aggregation model’. Despite the limitations of the latter model (e.g., monodispersity of the aggregates), we have been able to estimate the sign and the order of magnitude of Frumkin’s interaction parameter and the range of the aggregation numbers of the surface species.

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**Keywords:** Adsorption; Interactions; Surface heterogeneity; Aggregation

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## 1. Introduction

The adsorption behavior of non-ionic surfactants on air/water interface has been a subject of a particular interest in the area for the past decades [1–6].

Intriguing phenomena, related to possible changes in their adsorption state, are revealed. An illustration is the established decrease in surface charge and potential above certain adsorption levels of the individual surfactants [1–3].

The adsorption behavior of nonionic surfactants is usually described in the literature through the simple model of Szyskowski–Langmuir [7], which does not take into account interactions between the adsorbed species. From our experimental data, we have found [8–10] that while the model of Szyskowski–Langmuir holds well for tetraethyleneglycol-octylether ( $C_8E_4$ ), for longer-chained surfactants, it is insufficient. When investigating [11] the adsorption behavior of  $C_{10}E_8$ —alone and in combination with tetrapentyl-ammonium bromide (TPeAB)—we had to employ models of wider validity, such as Frumkin’s approach [12].

In the model of Frumkin [12], the parameter of interaction  $\beta$  is considered always positive; it admits only attraction between the adsorbed molecules. The same model is described in the book of Adamson [13] where the parameter of interaction is similarly assumed always positive (attractive). In Hill’s [14] description of the lattice adsorption theory, again, repulsion between the adsorbed species is not considered, presuming that the excluded area of the adsorbed species accounts it for. The values of the interaction parameter ( $\beta$ ) that we have arrived at with the Frumkin model [9–11] vary significantly. Moreover, what is theoretically unexpected  $\beta$  may change its sign. It turns from positive for the mixed adsorption layer (i.e., attraction) to substantially negative values for the single  $C_{10}E_8$  (i.e., repulsion).

In contrast, Fainerman et al. [15] have stated that in some cases, the parameter of interaction is not related to the nature of the adsorption layer and is only a matching parameter. It seems inconsistent, however, to think that in some cases, this parameter is related to the surface interactions, while in other cases it is not. Moreover, the negative  $\beta$ -values that we have obtained [9–11] imply repulsive forces in an adsorption layer built of uncharged species, which is inexplicable in terms of the classical lattice theory. According to this theory, such adsorption behavior can only be observed on energetically heterogeneous substrate (e.g., Temkin’s equation for adsorption on solids, see Ref. [16]), which is not the case treated here (water/air interface). Thus, we have been challenged to attack the problem of the origin of this serious contradiction between the theory and the experimental findings.

It must be pointed out that the problem of the negative parameter  $\beta$  is considered already in the literature [17–19]. The explanations there include dipole–dipole repulsion between the heads of the nonionic molecules. We have investigated this idea [10] by calculating  $\beta$  on the base of energy of dipolar interaction and rejected it, for the

calculations resulted in  $\beta$  values of much lower order of magnitude.

For this purpose, we decided to explore the available systematic literature data (surface tension isotherms) [20] for a series of homologous nonionic surfactants: the alkyl-polyoxyethylene ethers  $C_9E_8$ – $C_{15}E_8$ . We have developed here an optimization procedure based on the model of Frumkin to determine the adsorption parameters.

The present paper is an attempt to explain the appearance of negative  $\beta$  in Frumkin’s model. We describe the adsorption behavior of the systems, comparing several different models: of Szyskowski–Langmuir [7], Frumkin [12] and Fainerman–Lucassen–Reynders–Miller (‘Orientation’- and ‘Aggregation’-FLM models) [15].

## 2. Theoretical background

*Szyskowski–Langmuir Model* [7] does not assume interactions in the adsorption layer. The only fitting parameter in it is the equilibrium adsorption constant.

*Frumkin Model* [12]. The nonionic surfactant molecules are not charged, but only possess a dipole moment and the adsorption isotherm does not account for the presence of surface charge. The model of Frumkin can be presented through Eqs. (1) and (2).

$$Kc = \frac{\Gamma}{\Gamma_{\infty} - \Gamma} \exp\left(\frac{-2\beta\Gamma}{RT}\right) \quad (1)$$

$$\sigma = \sigma_0 + RT\Gamma_{\infty} \ln\left(1 - \frac{\Gamma}{\Gamma_{\infty}}\right) + \beta\Gamma^2 \quad (2)$$

Here  $K$  is the equilibrium adsorption constant,  $c$  is the bulk concentration of surfactant,  $\Gamma$  is the surfactant adsorption,  $RT$  is the thermal energy per mole,  $\Gamma_{\infty}$  is the maximum adsorption,  $\beta$  is the interaction parameter and  $\sigma$  and  $\sigma_0$  are, respectively, the surface tensions of the surfactant solution and pure solvent (water).

*FLM model assuming different adsorption states* [15]. The basic assumption of the model is that the adsorbed surfactant molecules orientation can differ, thus forming “mixed” adsorption layer. The size of the elementary cell  $\omega$  [15,24] for two possible orientations is:

$$\omega = \frac{\Gamma_1\omega_1 + \Gamma_2\omega_2}{\Gamma_1 + \Gamma_2} \quad (3)$$

Here,  $\Gamma_1$  and  $\Gamma_2$  are adsorption levels of the two states,  $\omega_1$  and  $\omega_2$  denote the “partial molar surface area” of the sites of different orientation and  $\omega$  is “average partial molar

surface area” [15]. The presence of two adsorption states requires two adsorption isotherms:

$$Kc = \frac{\Gamma_1 \omega}{[1 - (\Gamma_1 + \Gamma_2)]^{\frac{\omega_1}{\omega}}} \exp\left(-\frac{\omega_1}{\omega}\right) \exp(-2\beta(\Gamma_1 + \Gamma_2)\omega) + \beta\left(1 - \frac{\omega_1}{\omega}\right)(\Gamma_1 + \Gamma_2)^2 \omega^2 \quad (4)$$

$$Kc = \frac{\Gamma_2 \omega}{[1 - (\Gamma_1 + \Gamma_2)]^{\frac{\omega_2}{\omega}}} \exp\left(-\frac{\omega_2}{\omega}\right) \exp(-2\beta(\Gamma_1 + \Gamma_2)\omega) + \beta\left(1 - \frac{\omega_2}{\omega}\right)(\Gamma_1 + \Gamma_2)^2 \omega^2 \quad (5)$$

and the following equation of state:

$$\sigma = \sigma_0 + \frac{RT}{\omega} (\ln[1 - (\Gamma_1 + \Gamma_2)\omega] + \beta\{(\Gamma_1 + \Gamma_2)\omega\}^2) \quad (6)$$

This model operates with four fitting parameters:  $K$ ,  $\beta$ ,  $\omega_1$  and  $\omega_2$ . We employ it to check the sign of  $\beta$ .

**FLM ‘Aggregation’ model** [15]. This model assumes the presence on the surface of monomers at equilibrium with monodisperse aggregates. The following relation gives the area of the elementary cell  $\omega$  (which is a function of the adsorption level for the mixture of monomers and aggregates):

$$\omega = \frac{\omega_1 + \left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1} \omega_n}{1 + \left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}} \quad (7)$$

Here  $\omega$  is “average partial molar surface area”;  $\omega_1$  and  $\omega_n$  denote “partial molar surface area” of monomers and of aggregates (each containing  $n$  monomers;

$\omega_n \approx n\omega_1$ ), respectively;  $\Gamma_1$  is monomer adsorption;  $\Gamma_c$  is the “critical aggregation adsorption” (equal to the adsorption of monomers [15]). The adsorption isotherm is:

$$Kc = \frac{\Gamma_1 \omega}{\left\{1 - \Gamma_1 \omega \left[1 - \left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}\right]\right\}^{\frac{\omega_1}{\omega}}} \quad (8)$$

and the respective equation of state is:

$$\sigma = \sigma_0 + \frac{RT}{\omega} \ln \left\{1 - \Gamma_1 \omega \left[1 - \left(\frac{\Gamma_1}{\Gamma_c}\right)^{n-1}\right]\right\} \quad (9)$$

For this model, we developed an optimization procedure, based on Eqs. (7)–(9) with five fitting parameters:  $K$ ,  $\omega_1$ ,  $\omega_n$ ,  $\Gamma_c$ ,  $n$ .

### 3. Results and discussion

The surface tension isotherms for the homologue series of alkyl-octaethyleneglycol surfactants, from nonyl- ( $C_9E_8$ ) to pentadecyl- ( $C_{15}E_8$ ) ethers analyzed here are taken from the work of Ueno et al. [20].

The four adsorption models described briefly in the previous section were subjected to testing through optimization over the respective free parameters. Since the ‘Szyskowski–Langmuir’ model and the ‘Different adsorption states’ (‘Orientation’)-FLM model reveal marked inconsistency, the results of their optimization are not presented. The attention has been focused instead onto the other two: the Frumkin model (Eqs. (1) and (2)) and the ‘Aggregation’ FLM model (Eqs. (7)–(9), with which the values of the adsorption parameters are estimated.

In the Frumkin model, we have split the interaction coefficient  $\beta$  into two parts:  $\beta_{\text{tail}}$ , accounting for interaction

Table 1

Data obtained from the model of Frumkin (Fr) and Fainerman–Lucassen–Reynders–Miller (FLM) aggregation model

Surfactant	$\Gamma_{\infty}$ $\mu\text{mol}/\text{m}^2$ (Ref.[20])	$\Gamma_{\infty}$ $\mu\text{mol}/\text{m}^2$		$\Delta\mu_{\text{tab}}$ kJ/mol (Ref.[20])	$\Delta\mu_{\text{com}}$ kJ/ mol		$\beta \times 10^{-7}$ J m <sup>2</sup> /mol (Frumkin)		$(\beta_{\text{tail}} + \beta_{\text{head}}) \times 10^{-7}$ J m <sup>2</sup> /mol (Frumkin)	$n$ (FLM)
		Fr	FLM		Fr	FLM	$\beta_{\text{tail}}$	$\beta_{\text{head}}$		
$C_9E_8$	2.20	2.20	2.10	34.93	36.60	35	134.7	−217.7	−83.1	1.5–2
$C_{10}E_8$	2.42	2.42	2.23	38.40	38.93	37.38	172.6	−268.4	−95.8	2–3
$C_{11}E_8$	2.50	2.50	2.41	42.00	41.91	39.65	181.3	−290.9	−108.9	3–5
$C_{12}E_8$	2.72	2.72	2.12	45.20	45.00	44.62	246.9	−377.9	−131.0	5–40
$C_{13}E_8$	2.87	2.87	2.41	48.66	48.4	44.54	289.8	−409.9	−120.1	40–80
$C_{14}E_8$	3.33	3.33	2.70	51.63	49.4	45.74	390.2	−540.5	−150.4	80–130
$C_{15}E_8$	3.67	3.67	2.37	51.50	54.9	48.76	483.6	−740.0	−256.4	130–250

Table 2

The average errors per point (mN/m) for the model of Frumkin (Fr) and Fainerman–Lucassen–Reynders–Miller aggregation model (FLM)

	C <sub>9</sub> E <sub>8</sub>	C <sub>10</sub> E <sub>8</sub>	C <sub>11</sub> E <sub>8</sub>	C <sub>12</sub> E <sub>8</sub>	C <sub>13</sub> E <sub>8</sub>	C <sub>14</sub> E <sub>8</sub>	C <sub>15</sub> E <sub>8</sub>
Fr, mN/m	±0.5	±1.0	±0.65	±0.7	±0.8	±1.2	±1.55
FLM, mN/m	±0.95	±1.1	±1.05	±1.55	±1.35	±1.9	±2.2

between the hydrocarbon chains and  $\beta_{\text{head}}$ , for the polar heads, so that:

$$\beta = \beta_{\text{tail}} + \beta_{\text{head}} \quad (10)$$

The value of the term  $\beta_{\text{tail}}$  is estimated through the relation [21,23]:

$$\beta_{\text{tail}} = -N_A^2 \pi \int_{r_0}^{\infty} U(r) r dr \quad (11)$$

Here,  $N_A$  is the Avogadro constant,  $r_0$  is the minimum distance between the adsorbed species at close packing;  $r$  is current distance between the molecules,  $U(r)$  is the energy of pair interaction between the hydrocarbon chains [21,22], where:

$$U(r) = -\frac{3\pi CL}{8\delta^2 r^5} \quad (12)$$

Here,  $C$  is the London constant,  $L$  is length of the chain,  $\delta$  is distance between two adjacent methylene groups. On substituting Eq. (12) into Eq. (11) and integrating the latter one obtains:

$$\beta_{\text{tail}} = \frac{24N_A^2 \pi^2 CL}{\delta^2 d_1^3}, \quad (13)$$

and since  $1/\Gamma_{\infty} = N_A \pi d_1^2$ :

$$\beta_{\text{tail}} = \frac{24N_A^2 \pi^2 CL \sqrt{(\pi N_A \Gamma_{\infty})^3}}{\delta^2} \quad (14)$$

Analytical relation for  $\beta_{\text{head}}$  is not presently available. Therefore, we introduce it as a fitting parameter in Eq. (1).

Based on Eqs. (1), (2), (10) and (14), we have developed an optimization procedure operating with the following fitting parameters:  $K$ ,  $\beta_{\text{head}}$ , as well as  $\Gamma_{\infty}$ .

The results of the applied optimization procedure with the above two models are presented in Table 1.

Table 1 is arranged in the following manner:

- $\Gamma_{\infty}$  from the literature [20] (first reference point for assessing validity of the model);
- $\Gamma_{\infty}$  according the models of Frumkin (Fr) and Fainerman–Lucassen–Reynders–Miller ('aggregation' model; FLM);
- energy of adsorption  $\Delta\mu_{\text{tab}}^0$  from the literature [20] (second reference point);
- energy of adsorption  $\Delta\mu^0$ , obtained from the two models (Fr. and FLM);
- values of  $\beta_{\text{tail}}$ ,  $\beta_{\text{head}}$ ,  $\beta_{\text{tail}} + \beta_{\text{head}}$ , according to the Frumkin model and
- aggregation distribution number, according to FLM aggregation model.

Its values are obtained by varying the aggregation number  $n$  in the frame of the best theoretical fit for each one of the cases. The degeneration in the theoretical fits concerning the aggregation number reflects the expanding size distribution of the aggregates.

The test of each model's applicability implies checking the deviations from the reference points  $\Gamma_{\infty}$  and  $\Delta\mu_{\text{tab}}^0$ . The increasing average error per point in the surface tension dependence is expressed in the deviations from the reference points. In our case the tolerable surface tension error per point is judged to be ca.  $\pm 1.0$  mN/m.

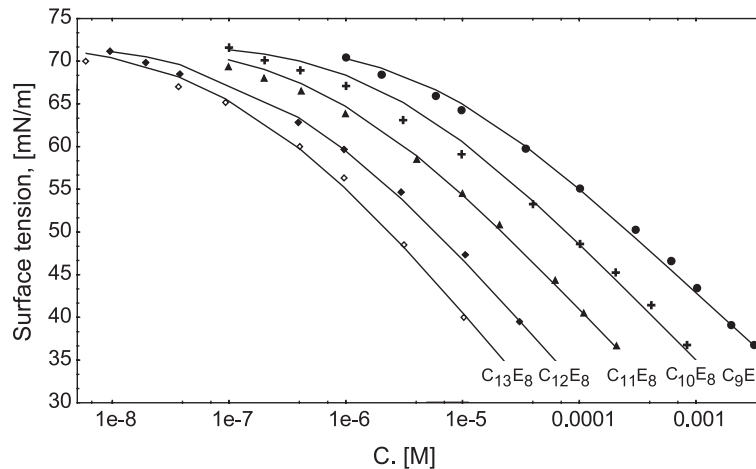


Fig. 1. Fits of the surface tension isotherms, based on the Frumkin model (solid lines) upon the experimental data [20] (points). The average error per point for C<sub>9</sub>E<sub>8</sub>–C<sub>13</sub>E<sub>8</sub> is in the range from 0.5 to 1.0 mN/m.

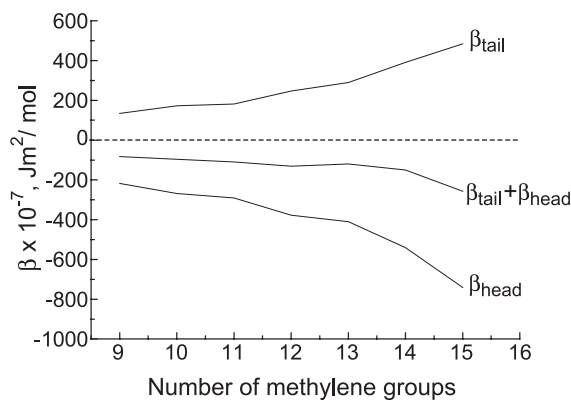


Fig. 2. Values of the interaction parameter  $\beta_{\text{tail}}$  of hydrophobic chains,  $\beta_{\text{head}}$  hydrophilic heads and the total  $\beta_{\text{tail}} + \beta_{\text{head}}$ .

The results obtained with the simple Szyszkowski-Langmuir model and the ‘Orientation’ FLM model are not essentially considered here. It suffices to say that these two models poorly describe the experimental isotherms. The deviations of the calculated isotherms from the experimental data are very significant ( $\Delta\mu - \Delta\mu_{\text{tab}} \geq 4$  kJ/mol;  $\sigma - \sigma_{\text{exp}} \geq 2$  mN/m) for both models. The latter model yields negative values for the parameter of interaction  $\beta$  in the range from  $-7.26 \times 10^8$  to  $-21.8 \times 10^8$  J m<sup>2</sup>/mol, as in the Frumkin model (see further).

The fits obtained from the model of Frumkin for surfactants from C<sub>9</sub>E<sub>8</sub> to C<sub>13</sub>E<sub>8</sub> are satisfactory (relatively low theoretical average error per point:  $\pm 0.5$  to 1.0 mN/m, which is quite acceptable for the theoretical analysis). The average error for C<sub>14</sub>E<sub>8</sub> and C<sub>15</sub>E<sub>8</sub> is slightly larger (respectively, 1.2 and 1.55 mN/m; see Table 2) and the deviation from  $\Delta\mu_{\text{tab}}$  is greater.

Although  $\Gamma_{\infty}$  and  $\Delta\mu$  (with the exception of C<sub>14</sub>E<sub>8</sub> and C<sub>15</sub>E<sub>8</sub>) are very close to those reported in the literature, the model of Frumkin yields  $\beta < 0$  in all cases. An illustration for the best agreements between theory and experiment (from C<sub>9</sub>E<sub>8</sub> to C<sub>13</sub>E<sub>8</sub>) is presented in Fig. 1.

The interaction parameters ( $\beta_{\text{tail}}$ ,  $\beta_{\text{head}}$  and  $\beta_{\text{tail}} + \beta_{\text{head}}$ ) are presented in Fig. 2 as a function of the number of methylene groups in the hydrocarbon chain. The parametric curves for  $\beta_{\text{tail}}$  (attractive) and  $\beta_{\text{head}}$  (repulsive) appear to be symmetrical, but the negative values of  $\beta_{\text{head}}$  prevail in the sum. This results in dependence, yielding persistently  $\beta < 0$  for the entire series of surfactants, from C<sub>9</sub>E<sub>8</sub> to C<sub>15</sub>E<sub>8</sub>. We shall remind here that, when investigating the adsorption behavior of C<sub>10</sub>E<sub>8</sub> in the presence of TPeAB [11], we have obtained considerable attractive forces in the mixed adsorption layer ( $\beta > 0$ ), which suggests that the presence of ionic surfactant can prevent the surface aggregation.

The FLM-“aggregation” model presumes monodispersity or-at most-very narrow size distribution of the aggregates (see Eq. (7)). Fig. 3 is an illustration for the theoretical dependence of the population variance of the aggregation distribution number (see Table 1) and  $\beta_{\text{total}}$  on the number of the methylene groups in the hydro-

carbon chain of the alkyl-octaethyleneglycol ether (C<sub>n</sub>E<sub>8</sub>) molecule.

Fig. 3 shows that the shorter representatives of the homologue series (C<sub>9</sub>E<sub>8</sub>, C<sub>10</sub>E<sub>8</sub> and C<sub>11</sub>E<sub>8</sub>) possess very low population variance of the aggregation distribution number, which means—if not always strict monodispersity—at least rather narrow size distribution of the surface aggregates, while the longer ones (C<sub>12</sub>E<sub>8</sub>–C<sub>15</sub>E<sub>8</sub>) exhibit increasing polydispersity of the aggregates.

It is worth pointing out here that Fainerman et al. [25] have reported recently aggregation number of 2.5 for C<sub>10</sub>E<sub>8</sub>. This result is in remarkable agreement with the value, which we obtain here for the same surfactant (see Table 1).

We have tried to investigate the origin of the discrepancies between the experimental results and the “aggregation” model from the point of view of “polydispersity” by varying (as a fitting parameter) the number of monomers in the aggregates. When considering the discrepancies between theory and experiment, it must be born also in mind that the probability of experimental error may be greater for the longer-chained surfactants, due to their low bulk concentrations and a possible time dependence of the experimentally measured surface tension values [26].

As a result, we obtain with the longer-chained surfactants a picture of rapidly increasing aggregation numbers and strongly expressed polydispersity (Table 1 and Fig. 3). Thus, the “inconvenient” results for C<sub>12</sub>E<sub>8</sub>–C<sub>15</sub>E<sub>8</sub> may actually yield new complementary information about the state in the adsorption layer.

#### 4. Conclusions

Among the available models, these with a small number of fitting parameters are, as a rule, preferable. From this point of view, the model of Frumkin appears to be very good: with only two fitting parameters  $K$  and  $\beta$  ( $\Gamma_{\infty}$  usually is measured from the maximum slope of the surface tension isotherms in the figures). Negative values of the interaction

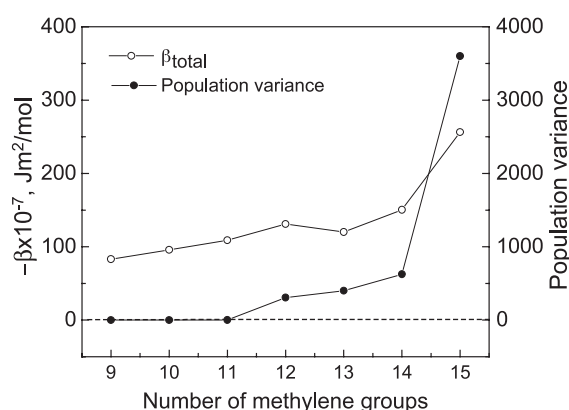


Fig. 3. Dependence of the (negative)  $\beta_{\text{total}}$  values (○) and the corresponding population variance (●) in the aggregate size on the number of methylene groups in the hydrophobic tails of the surfactant molecules.



parameter correspond to repulsion in the surface layer, i.e., diminishing capability for adsorption with increasing surface coverage. Such type of adsorption is often observed on energetically nonhomogeneous surface [16], like this of solids [27], and can be described by the well-known equation of Temkin [16]. However, in terms of the classical lattice theory of adsorption on energetically homogeneous (fluid) surface, negative values of the parameter of interaction are unacceptable, which makes the model of Frumkin unusable for many surfactant systems. The “aggregation model”, advanced by Fainerman et al. [15], has given us the hope that this serious contradiction can be solved.

Therefore, the main question is how the models of Frumkin [12] and Fainerman et al. [15] are related. One can find in the latter (Eq. (7)) that the size of the elementary adsorption cell is a function of the adsorption  $\Gamma_1$ :  $\omega$  increases with the adsorption and, consequently, the available sites (the number of the elementary cells) diminish, as compared to models assuming constant elementary cell area (Frumkin and Szyskowski–Langmuir). That is why the negative sign of  $\beta$  corresponds to the case of variable size of the elementary adsorption cell (Eqs. (7)–(9)). Thus, although the ‘Orientation’-FLM model operates with variable size of the elementary adsorption cell (see. Eq. (3)), the values of the interaction parameter  $\beta$  remain negative.

The surprising moment here is that, the “aggregation” model describing the heterogeneity in the adsorption layer, situated on energetically homogeneous surface, turns out to be equivalent to the case of homogeneous adsorption layer situated on energetically heterogeneous surface. For example, in Ref. [28], the adsorption of proteins on air/water interface is adequately described with the equation of Temkin.

It is worth to remind here that the presence of surface aggregation is related to the following form of the Gibbs adsorption isotherm [29]:

$$d\sigma/d\ln(c) = -RT(\Gamma_1 + n\Gamma_n) \quad (15)$$

and the equation for the averaged size of the adsorption cell [30]:

$$\omega = \frac{\sum_{i=1}^k \Gamma_i \omega_i}{\sum_{i=1}^k \Gamma_i} \quad (16)$$

Eq. (16) allows the presence of polydispersity as well. The question is whether a single monomer and an aggregate are equivalent as kinetic units. Based on Eqs. (15) and (16), one can conclude that, depending on the energy of intermolecular interaction, an aggregate (consisting of  $n$  monomers) could be equivalent to a certain (effective) number of monomers  $n_{\text{eff}}$ :  $1 \leq n_{\text{eff}} \leq n$ . Such an approach can be employed in the further development of the surface aggregation theory.

This article has aimed at investigating the origin of the negative values of  $\beta$  and proving that the model of Frumkin is applicable, even when such values are obtained in

contradiction to the classical lattice theory. Our final conclusion is that the existence of negative  $\beta$  supports the hypothesis of aggregation in the adsorption layer.

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