A Simple Model to Describe the Effect of Electrostatic Interactions on the Composition of Mixed Self-Assembled Monolayers

Th. Doneux*[,†,§] and Y. De Decker[‡]

Chimie Analytique et Chimie des Interfaces, Faculté des Sciences, Université Libre de Bruxelles, Boulevard du Triomphe 2, CP 255, B-1050 Bruxelles, Belgium, and Interdisciplinary Center for Nonlinear Phenomena and Complex Systems (I-CENOLI), Université Libre de Bruxelles, Boulevard du Triomphe 2, CP 231, B-1050 Bruxelles, Belgium

Due to intermolecular interactions, the surface composition of mixed self-assembled monolayers often differs markedly from the solution composition. In the case of charged surfactants, large deviations from the ideality have been reported. The effect of the electrostatic interactions between charged compounds on the surface composition is examined using a simple gas lattice model, in the Bragg–Williams approximation. The interaction potential is obtained from the Debye–Hückel treatment of electrolytic solutions. The model is able to explain and reproduce the deviations observed experimentally, both qualitatively and quantitatively. The key role played by the ionic strength on the surface composition is emphasized.

1. Introduction

Self-assembled monolayers (SAMs) composed of two (or more) compounds present a wide range of interest and potential application.[1,2] Numerous biosensors are based on the formation of mixed monolayers, where the compound providing the specific recognition toward a target molecule is diluted in a matrix of a second compound, whose role is to prevent any signal transduction from nonspecific recognition.[3,4] Mixed SAMs have also been designed to control the extent of adsorption of proteins and cells on surfaces,[5–11] whether promoting the adsorption to study electron transfer characteristics[12–17] or on the contrary preventing the adsorption to build nonfouling materials.[18–23]

The properties of the modified surfaces depend on different factors such as the chemical nature of the components, the surface composition, and the structure of the films (homogeneous versus phase segregated, presence of defects). Adjusting these factors in a controlled fashion allows one to confer unique properties to the modified surfaces. Several strategies have been followed to achieve this goal,[1,2] involving either the coadsorption of the

two compounds in one step or postassembly modifications of an initial SAM containing only one of the surfactants. Among these figure the inclusion of the second compound in the defects of the first SAM, the chemical or electrochemical replacement method, patterning techniques such as microcontact printing, and photolithography. While the postassembly modifications are of great interest for large-scale device production, the coadsorption method has the advantage of a greater simplicity and has therefore been widely used. It is well accepted that the coadsorption process involves a surface-bulk equilibrium so that the surface composition reflects, to some extent, the concentrations ratio of the two surfactants in the immersion solution.[1] Nevertheless, the numerous studies on mixed SAMs formed by coadsorption have resulted in very different types of behavior, ranging from ideal mixing (where the ratio of the two compounds at the surface is identical to that in the immersion solution) to largely nonideal systems, and from homogeneous to phase segregated monolayers. This fact arises from the key role played by intermolecular interactions in the formation of the monolayers. Since many interactions can be involved (van der Waals, hydrogen bonding, multipole–multipole, electrostatic), the actual adsorption behavior depends

* To whom correspondence should be addressed. E-mail: tdoneux@ ulb.ac.be.

† Chimie Analytique et Chimie des Interfaces.

‡ I-CENOLI.

§ Present address: Institute of Biophysics ASCR, v.v.i., Královopolská 135, 61265 Brno, Czech Republic.

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on the very nature of the two compounds and it is not surprising that many different results have been reported.

More specifically, some studies on mixed SAMs involving charged surfactants have shown very large deviations from the ideality. The group of Kakiuchi has demonstrated[24] that, upon self-assembly of the positively charged 2-aminoethanethiol with the negatively charged 2-mercaptoethanesulfonic acid, the surface ratio of the two components amounts to unity almost regardless of their ratio in the immersion solution (from 10% to 95% of the negatively charged molecule). This behavior, qualified as "ideal nonideality",[24] was also observed more recently by Chen et al.[23] for a variety of mixtures of cationic and anionic compounds. They showed that the 11-mercaptotrimethylammonium mixes in such a way with thiols of similar length bearing a negatively charged, monovalent headgroup such as sulfonate, carboxylate, or methylphosphonate. Interestingly, these "zwitterionic" surfaces (composed of positive and negative groups in a 1:1 ratio) exhibit a very strong resistance to protein adsorption.[18,23] Another kind of deviation to ideality has been observed when an ionic compound is mixed with a neutral one. In this case, the adsorption of the neutral compound is highly favored.[7,25-29] For some systems, the structures of the two compounds were so different that the nonideality could not be assigned to the sole effect of the charge. However, large deviations were also observed in few systems where the two compounds were structurally very close, and it is thus expected that the charge plays a major role in the final surface composition. For instance, we have recently reported[26] that the coadsorption of 2-mercaptobenzimidazole (MBI, neutral) and 2-mercaptobenzimidazole-5-sulfonate (MBIS, negatively charged) on Au(111) resulted in a MBI-rich monolayer and that the actual surface composition can be adjusted by the ionic strength of the immersion solution. In the present work, we propose to develop a very simple model that is able to explain and reproduce the large deviations observed experimentally. Some general models of binary self-assembled monolayers have already been published in the literature.[30-36] Our contribution focuses on mixed SAMs made of thiolated molecules containing at least one charged component. We will show that, for simple systems, the deviations can be explained by the sole effect of the electrostatic interactions among adsorbates. This interpretation is supported by a very simple model, based on a mean-field approach, whose performance is discussed and compared, both qualitatively and quantitatively, to some experimental results extracted from the literature.

2. The Model

The formation of the monolayers is performed by the traditional self-assembly technique, where a gold (or another coinage metal) substrate is immersed in a solution containing the two thiolated surfactants. The adsorption of the compounds proceeds spontaneously, with the formation of strong gold–sulfur bonds being the main driving force of the process. Contrary to the approach of Pugnaloni et al.[32] who assumed the irreversible adsorption of one of the components, the adsorption should be considered in the present case as reversible for both of them, and therefore, the reactions are written as

$$A(\text{aq}) \rightleftharpoons A(\text{ads}) \qquad K_A \qquad (1)$$

$$B(\text{aq}) \rightleftharpoons B(\text{ads}) \qquad K_B \qquad (2)$$
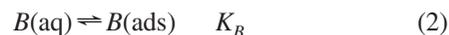
The chemical potentials of the different species are written as

$$\mu_i^{\text{aq}} = \mu_i^{\text{aq},0} + RT \ln a_i^{\text{aq}} \qquad (3)$$

$$\mu_i^{\text{ads}} = \mu_i^{\text{ads},0} + RT \ln \frac{\theta_i}{1 - \theta_T} + U_i \qquad (4)$$

where the subscript i stands for A or B, R is the gas constant, T is the temperature, a_i^{aq} are the activities in the solution, θ_i is the coverage, U_i is the effective interaction energy, and θ_T is the total coverage given by $\theta_T = \theta_A + \theta_B$. Note that eq 4 is obtained within the framework of the lattice gas approximation. The fulfillment of the equilibrium condition (eqs 1 and 2) requires the equality of the chemical potentials between the two phases for each species i. Recalling that the equilibrium constants are given by $K_i = \exp[-(\mu_i^{\text{ads},0} - \mu_i^{\text{aq},0})/RT]$, the adsorption isotherm of each component is described by

$$K_i a_i^{\text{aq}} = \frac{\theta_i}{1 - \theta_T} \exp\left(\frac{U_i}{RT}\right) \qquad (5)$$

which is equivalent to the Frumkin isotherm.

In the forthcoming developments, the occupation of the sites by solvent molecules is not considered and so $\theta_T = 1$. This assumption is reasonable in the case of self-assembled monolayers. Replacing i explicitly in eq 5 and combining the results, we can write

$$\chi_A^{\text{aq}} = \frac{a_A^{\text{aq}}}{a_A^{\text{aq}} + a_B^{\text{aq}}} = \frac{\theta_A}{\theta_A + K(\theta_A)(1 - \theta_A)} \qquad (6)$$

where χ_A^{aq} is the molar fraction of the compound A in the solution (seen here as ideal) and

$$K(\theta_A) \equiv \frac{K_A}{K_B} \exp\left[\frac{U_B - U_A}{RT}\right] \qquad (7)$$

Equation 6 links directly the surface composition of the binary SAM to the composition of the immersion solution. For a given value of χ_A^{aq}, the surface composition depends on the relative values of the adsorption constants and on the effective interaction energies. Neglecting contributions arising from three-body interactions, these effective energies can be seen as due to a superposition of the pair interactions between the adsorbates in the monolayer. We propose here to evaluate these quantities using a "Bragg–Williams"-like mean field approximation, for which

$$U_A = \sum_r c_r \varepsilon_{AA}(r) \theta_A(r) + \sum_r c_r \varepsilon_{AB}(r) \theta_B(r) \qquad (8)$$

$$U_B = \sum_r c_r \varepsilon_{BB}(r) \theta_B(r) + \sum_r c_r \varepsilon_{AB}(r) \theta_A(r) \qquad (9)$$

where r is the distance between adsorbates, $\theta_i(r)$ is the occupation probability of the site at distance r by species i, ε_{ij} is the (space

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dependent) pair interaction potential, and c_r is the number of neighbors located at a distance r. These expressions can be further simplified by assuming that the adsorbates are distributed at random on the surface (forming a "perfectly mixed" layer), so that $\theta_i(r) = \theta_i$ and that

$$U_A = \theta_A u_{AA} + \theta_B u_{AB} \qquad (10)$$

$$U_B = \theta_A u_{AB} + \theta_B u_{BB} \qquad (11)$$

where $u_{ij} \equiv \Sigma_r c_r \varepsilon_{ij}(r)$.

The purpose of the present work being to investigate more closely the influence of electrostatic interactions between charged particles, it is convenient to separate the interaction potentials in two contributions:

$$\varepsilon_{ij}(r) = \varepsilon_{ij}^0(r) + \varepsilon_{ij}^{El}(r) \qquad (12)$$

and similarly

$$u_{ij} = u_{ij}^0 + u_{ij}^{El} \qquad (13)$$

In eq 12, the second term represents the purely electrostatic contribution to the interaction potential. It can be positive if the charges of two ions have the same sign, negative if the signs are opposite, and equal to zero if at least one of the molecules is nonionic. The first term takes into account all the other possible energetic contributions to the total interaction potential (van der Waals, dispersion, hydrogen bonding, multipoles). The determination of the value of $\varepsilon_{ij}^0(r)$ has been the object of different publications, both experimental and theoretical, in relation with single component or mixed monolayers.[30,31,37,38] For the most simple and most extensively studied structures, the linear alkanethiols, this attractive potential is known to increase linearly with the number of methylene units in the alkane chain.[37,39] For more complex structures, less experimental data are available, and the number of possible types of interaction makes the evaluation difficult. Some methods can nevertheless overcome this problem, as demonstrated by Yaliraki et al.,[31] who used molecular mechanics to compute the attractive potential existing between molecules having drastically different structures.

As mentioned previously, a specific attention is drawn on the contribution from the electrostatic interactions between charged molecules. The central point of our approach is to take into account that the electrostatic potential acting between two charged particles can be partly screened due to the presence of electrolytes in the solution. More specifially, we assume that this potential is of the Debye–Hückel form, which reads

$$\varepsilon_{ij}^{El}(r) = \frac{Z_i Z_j e^2}{4\pi\varepsilon\varepsilon_0} \frac{e^{-\kappa(r-\sigma)}}{(1+\kappa\sigma)r} \qquad (14)$$

where σ is the closest approach distance, depending on the geometrical properties of the lattice and the monolayer, Z_i and Z_j are the charge numbers of the molecules, e is the elementary charge of the electron, ε is the relative dielectric constant of the immersion solution, and ε_0 is the permittivity of the vacuum. In this equation, κ^{-1} is the Debye length which is related to the ionic strength of the solution, $I = 1/2\Sigma_i Z_i^2 C_i$ (with C_i being the molar concentration of i in the solution) through

$$\kappa^2 = 2\frac{1000F^2}{\varepsilon\varepsilon_0 RT}I \qquad (15)$$

The numerical values of the constants used in these equations can be found in Table 1. The use of a Debye–Hückel potential is justified by the fact that the adsorption of the surfactants is a surface-bulk equilibrium and is thus influenced by the properties

Table 1. Numerical Values of the Constants Used in the Model

symbol	numerical value
ε_0	8.85418×10^{-12} C^2 N^{-1} m^{-2}
ε	24.6 (ethanol)
ε	78.4 (water)
F	96 487 C mol^{-1}
R	8.314 J mol^{-1} K^{-1}
T	298.15 K

Table 2. Nth Neighbor, Number of nth Neighbors, and Distance (in Terms of the First-Neighbor Distance σ) Relative to a Site of Reference in a Hexagonal Close Packed System

neighbor position	number of neighbors	distance (l/σ)
1	6	1
2	6	$\sqrt{3}$
3	6	2
4	12	$\sqrt{7}$
5	6	3
6	6	$2\sqrt{3}$
7	12	$\sqrt{13}$
8	6	4
9	12	$\sqrt{19}$
10	12	$\sqrt{21}$

of the solution. Indeed, the counterion distribution around a central charge (such as an adsorbed molecule in our case) depends on the presence of charges not only in the two-dimensional array formed by the SAM but also in the bulk. Therefore, the situation should not be reduced to a purely two-dimensional problem.

3. Results and Discussion

In this section, we propose to use the model presented above to discuss the implications of mixing surfactants bearing a charge, and to compare our results with some selected experimental data. To clearly distinguish the role of the electrostatic interactions from the other parameters, a few assumptions were made. The first is that all the nonelectrostatic interactions are equal (i.e., u_{ij}^0 = Cst), so that their respective contribution to the energetics of the system will cancel, as shown below. Physically, it would correspond to the situation where the two surfactants have very similar structures, such as, for example, linear alkanethiols with the same number of $-CH_2-$ groups. The second assumption is that K_A and K_B are equal. Here, again, this is reasonable in the case of thiolated compounds adsorbed on gold, for which it is established that the main contribution to the adsorption constant is the gold–sulfur bond. Finally, since SAMs of alkanethiols are known to form well-defined ($\sqrt{3} \times \sqrt{3}$)$R30°$ close packed layers on Au(111), we consider the adsorbates to be distributed following a hexagonal pattern. The distances r between neighbors and the corresponding value of c_r for this triangular lattice are given in Table 2. To estimate the interaction energy, we performed tests on the number of neighbors that should be considered in order to have convergence of the sum. We typically found that the isotherms converge when taking into account the 6–7 first neighbors for systems of low ionic strength and the 2–3 first neighbors in the case of moderate to high values of I. This difference can actually be rationalized based on the spatial extent of the interaction potential (see later). In the figures presented here, we always considered the 10 first neighbors to ensure the aforementioned convergence.

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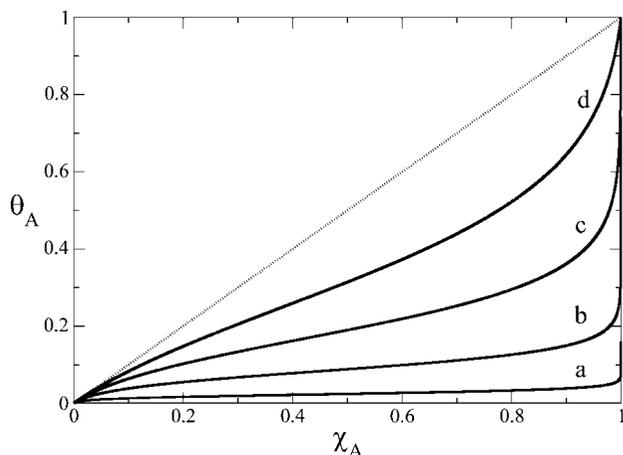
Figure 1. Theoretical surface composition versus solution composition for a prototypical mixture of a charged (compound A) and a neutral (coumpound B) alkanethiol ($\sigma = 2.55$Å, $Z_A = 1$) in ethanol. The ionic strength in (a) is given by $I = C_A$ (the molar concentration of A) and corresponds to the case where A is the only charged species in solution (no elecrolyte added). For the other curves, the ionic strength is (b) $I = 0.1$, (c) $I = 1$, and (d) $I = 2$ mol L $^{-1}$. The dashed line represents the ideal behavior.

3.1. Mixture of a Charged Compound and a Neutral Compound. Let A be the ionic (charged) surfactant and B the nonionic (neutral) one. From eqs 10 and 11, the difference between the two effective interaction energies can be rewritten as

$$U_B - U_A = u_{BB} - u_{AB} + (2u_{AB} - u_{AA} - u_{BB})\theta_A$$
$$\approx (u_{AB} - u_{AA})\theta_A \quad (16)$$

because of the conservation relation $\theta_A + \theta_B = 1$, and since for molecules with long aliphatic chains nonionic interactions should dominate $A - B$ interactions, so that $u_{AB} \approx u_{BB} \neq u_{AA}$. A very simple form can be obtained for the adsorption isotherm by noting that, in $u_{AB} - u_{AA}$, the nonionic interactions cancel each other, since A and B have the same number of $-CH_2-$ groups and thus $U_B - U_A \approx -u_{AA}^{El}\theta_A$.

With the two assumptions of equality made above ($K_A = K_B$), $K(\theta_A)$ takes from eq 7 the following simple form:

$$K(\theta_A) = \exp\left(-\frac{u_{AA}^{El}}{RT}\theta_A\right) \quad (17)$$

It is inferred from this equation that only the electrostatic interactions contribute to the value of $K(\theta_A)$ and hence to the surface composition. The value of u_{AA}^{El} is obviously positive, reflecting a repulsion between the ionized compounds; as a result, the adsorption of the neutral compound B at the surface should be favored as compared to that of the ionic one, and a large negative (relative to the compound A) deviation from ideality be obtained. This general tendency is confirmed by numerically solving eq 6 and plotting the corresponding isotherms for typical values of the different parameters. Curve (a) of Figure 1 presents the isotherm obtained in the hypothetical case of two alkanethiol-type molecules adsorbed on Au(111) from a millimolar ethanolic solution at room temperature. In these conditions, representative of those often used in the formation of SAMs, a very pronounced negative deviation from the ideal behavior (dotted line) is indeed observed, in agreement with experimental data reported in the literature.[7,25,27–29] Interestingly, the simple model we use here predicts that the amplitude of the deviation from ideality can be modulated by adjusting the experimental conditions. Indeed, from eq 14, it is expected that varying any of the parameters Z_A, κ^{-1}, or ε will affect the value of u_{AA}^{El}. For a given compound (Z_A fixed)

in a given solvent (ε fixed), it is, for example, extremely easy to change the value of the Debye length κ^{-1} by adding an electrolytic salt, since κ is connected to the ionic strength through eq 15. Curves (a)–(d) in Figure 1 illustrate this effect of the ionic strength on the surface composition of the binary mixture. Increasing the ionic strength of the surrounding solution results in an enhanced screening of the electrostatic repulsions between the charged molecules. As κ^{-1} decreases, so does u_{AA}^{El} and the deviation from ideality becomes less pronounced. It should also be noted that low values of κ^{-1} induce a rapid decrease (in space) of the screened electrostatic interaction potential, so that the system switches from a long-scale coupling between adsorbates at low ionic strength to a very short-scale coupling at high ionic strentgh.

Our results show that the presence of a charge on one of the two surfactants has a significant impact on the surface composition of the monolayer, which is markedly different from the solution composition. A direct, quantitative comparison with experimental systems reported in the literature is not easy. The investigated systems sometimes offer a complexity far beyond the assumptions made in the present contribution, and the nonelectrostatic interactions certainly contribute to the equilibrium surface composition. For example, the mixture of a long neutral alkanethiol with a shorter charged one leads to a SAM highly enriched with the neutral one,[28,29] but a comparable result would be obtained even in the absence of a charge on the shorter alkanethiol, because of larger attractive interactions between longer chains as compared to shorter ones.[30,40] Another issue deals with the effective charge of the molecules, whether in the immersion solution or at the surface. The charged groups can be subject to acid–base equilibria affecting the ratio of neutral to charged molecules in solution. Besides, the pK_a value for a given compound may differ in the adsorbed state as compared to its value in solution.[41,42] Finally, very little attention has been paid to the systematic investigation of the ionic strength effect.

To validate the approach and to highlight the contribution of the electrostatic interactions, the results given by the model were compared to the experimental data reported for the mixed monolayer of 2-mercaptobenzimidazole (MBI, neutral) and its sulfonated derivative (MBIS, charged). When the adsorption proceeded from pure water solutions, the SAMs were highly enriched in MBI. However, a marked increase in the amount of MBIS at the surface was obtained upon addition of 0.25 M CaCl$_2$ into the immersion solutions. Although very different from the alkanethiols, the structures of these two compounds are very close to each other, and it is thus expected that the assumptions made here are still valid.[26] As seen in Figure 2, our model reproduces the trends in the experimental data. In particular, the general tendency toward ideality upon addition of a strong electrolyte is observed in the experiments as well as in the theoretical predictions. The correspondence is fairly good for low to moderate coverages, but larger deviations are observed for high coverages. This is in fact expected, since the mean field approximation which was used is known to break down in the case of very dense systems of strongly interacting particles. It is noteworthy that the domain of validity of the model seems larger for higher values of the ionic strength. This is not unexpected, since the characteristic length of the electrostatic interactions is shorter at higher ionic strength and the interactions are less marked in that case.

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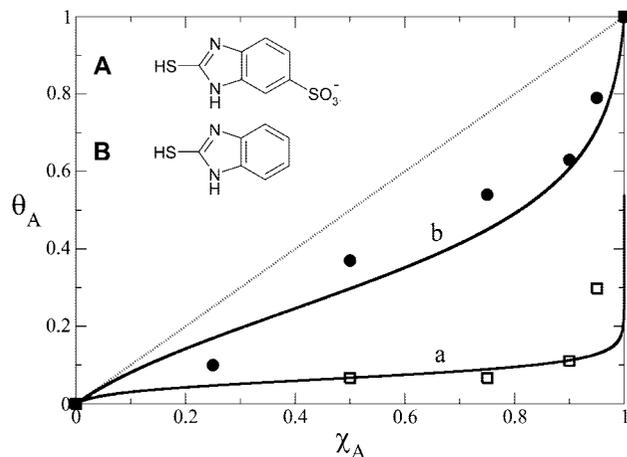
Figure 2. Comparison of the experimental (symbols) and theoretical (plain curves) adsorption isotherm for a MBIS (compound *A*)−MBI (compound *B*) mixture ($\sigma = 3.29$Å, $Z_A = 1$) in pure water (curve a, empty squares) and in a 0.25 M solution of $CaCl_2$ (curve b, solid circles). The ideal behavior is shown as a guide to the eye.

3.2. Mixture of Two Oppositely Charged Compounds.

We now turn the class of coadsorption systems involving two molecules with opposite charges, a situation to which our simple approach can easily be applied. Since in the present case each molecule is charged, none of the interaction parameters u_{ij}^{El} is equal to zero. However, the equality $|Z_A| = |Z_B|$ leads to the simplification that $u_{AA}^{El} = u_{BB}^{El} = -u_{AB}^{El}$, so that $K(\theta_A)$ is now written as

$$K(\theta_A) = \exp\left[\frac{2u_{AB}^{El}}{RT}(2\theta_A - 1)\right] \qquad (18)$$

Here, again, only the electrostatic interactions influence the surface composition. The molecules *A* and *B* being oppositely charged, the term is negative, reflecting attractive forces between the two components, while the electrostatic *A*−*A* and *B*−*B* interactions are repulsive. As a result, a deviation from ideality is observed, for which the ratio of the two components at the surface tends to be more balanced than the ratio in the solution. This is illustrated in Figure 3, which displays the curve obtained with our model (curve a) together with the experimental results of Ooi et al.[24] A very good agreement is found between the theoretical and experimental results, both exhibiting the "ideal nonideal" behavior, that is, a surface ratio equal to unity over a very large range of solution composition. It should be emphasized that the apparent symmetry of the isotherms can be deduced directly from eq 18, which is itself symmetric with respect to $\theta_A = 0.5$. Figure 3 also presents theoretical curves obtained for different values of the ionic strength. As for the previous case, it should be pointed out that the deviation from ideality becomes less
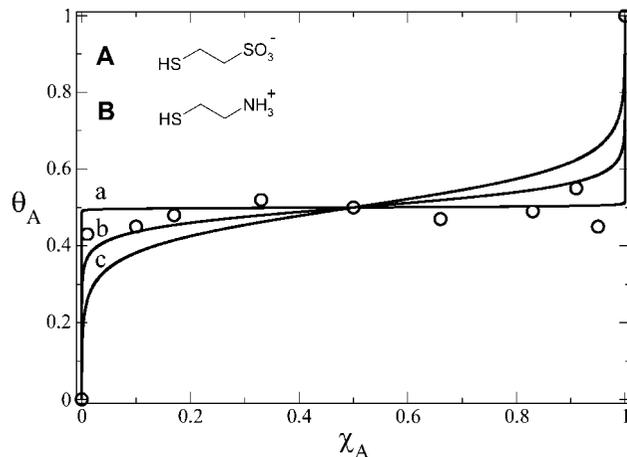

Figure 3. Surface composition versus solution composition for the mixture of 2-mercaptoethanesulfonic acid (compound *A*) and 2-aminoethanethiol (compound *B*). Open circles: experimental data from ref 24. Solid lines: theoretical curve ($\sigma = 2.5$ Å, $Z_A = -1$, $Z_B = +1$); curves a, b, and c, respectively, correspond to ionic strengths of 1×10^{-3} (experimental conditions), 1, and 5 M. The dashed line represents the ideal behavior.

pronounced at higher ionic strengths. Our model therefore points once again toward the possibility to effectively control the surface composition by playing with the ionic strength of the solution, though in this case relatively high values of *I* should be required to reach ideality.

4. Conclusions

The model presented in this paper, though extremely simple, satisfactorily explains and reproduces some results reported in the literature regarding the surface composition of mixed SAMs. We showed that electrostatic interactions between charged surfactants lead to surface compositions significantly different from the solution compositions. The model demonstrates that besides the solution composition the most important parameter influencing the surface ratio of the two components is the ionic strength. Therefore, this should be precisely controlled in experimental studies of SAMs, which is usually not the case. Often, the only significant source of charged species in the immersion solution are the surfactants themselves; consequently, the ionic strength is very low, resulting in large deviations from ideality. Varying the ionic strength allows one to modulate the amplitude of the electrostatic interactions and to adjust the surface composition. While some assumptions were made here to highlight the specific role of the electrostatic interactions, the model is sufficiently general to be used for more complex systems, provided enough experimental data are available.