Electrostatic Theory of Ion-Pair Chromatography.
Multi-Site Occupancy Model for Modifier and Solute Adsorption

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Summary
The adsorption mechanism of ionic surfactants on chemically modified phases combines the features not only of single ion adsorption but also those of polymer adsorption. Therefore the simple Langmuir-Stern isotherm used in electrostatic theories of ion-pair chromatography is not very realistic, as this equation is developed statistically for a one-site occupancy model of adsorption. The same concerns solute adsorption. This is why many predictions of the existing electrostatic theories are not fully in agreement with the experimental data. In this work the fundamental assumptions of these electrostatic theories are combined with some modern theories of surfactant and solute adsorption, based on a multi-site occupancy model. The theoretical expressions for the capacity coefficients obtained in this way are also able to explain experimental findings, previously classified as exceptional deviations from the predictions of the electrostatic theories.

Introduction
Recently Stahlberg et al. [1-5] published an interesting series of papers describing a new theoretical approach to ion-pair chromatography. In the previous classical approach adsorption of amphiphilic modifier molecules was considered as a process creating new electrically charged adsorption sites in the surface phase. The partition of solute between the bulk (mobile) phase and the surface (stationary) phase was seen as adsorption on these discrete electric charges, mostly due to electrostatic interactions. We are not going to review the literature based on that classical approach, as it is far too extensive.

Stahlberg's idea was to transfer to ion-pair chromatography the approach used in theories of the electric double layers formed by adsorption of ions at water-oxide interfaces. This was the theoretical treatment of the structure of the double layer relating the distribution of dissolved ions and the potential gradient near the surface to the composition of the aqueous phase first performed by Gouy [6, 7], and independently by Chapman [8]. Their detailed considerations and the modifications proposed by Stern [9] and Grahame [10] were accepted by Stahlberg. Thus, to describe both the modifier and solute adsorption, Stahlberg used the Langmuir-Stern adsorption isotherm.

Stern accepted the model of localized adsorption to describe adsorption of ions, using simultaneously the "smearing" mean-field approximation to describe electrostatic interactions. The "smearing" approximation is largely justified by the long-range nature of electrostatic interactions. Later, Stern's approach was elaborated in an even more sophisticated way in many papers classified now as the "site-binding" or "complexation" approach in theories of the electric double layer. In fact it is now the most popular and widely used approach, which is also evidence of its great success.

Thus, Stahlberg's employment of Stern's approach must be seen as remarkable progress. According to this approach the solute and modifier molecules interact via their charges "smared" on the solid surface. The finite size of these molecules is taken into account in terms of localized adsorption. This is the point where Stahlberg's approach needs to be greatly modified.

The molecules of amphiphilic modifiers applied in IPC (ion-pair chromatography), are usually large. They are composed of a polar head and a large hydrophobic moiety, often a long flexible alkyl chain. Usually surfactants are used as the modifiers. Adsorption of such long, highly flexible, hydrophobic moieties cannot be considered in terms of a one-site occupancy model of adsorption on which the theoretical, (statistical), derivation of the Langmuir equation is based. Adsorption of amphiphilic modifiers combines the features of both ion and polymer adsorption, and must therefore be considered in terms of a multi-site occupancy model. That point is now widely recognized. The mechanism of
hydrophobic chain adsorption is one of the most important factors governing adsorption of surfactants. The purpose of this work is to develop further Stahlberg’s application of the Gouy-Stern approach in IPC taking into account the multi-site occupancy character of adsorption of both amphiphilic modifiers and analytes.

Theory

The starting point is the theory of ionic surfactant adsorption published recently by Koopal and co-workers [11]. There are two versions of this theory, depending on whether the solid (stationary phase) surface and surfactant molecule have the opposite or the same charge. Theoretically, both these situations can be found in IPC depending on the PZC (point zero charge) of the sample and on the pH of the mobile phase. For this reason, we take here into account both versions of Koopal’s approach.

First we consider the situation where solid surface and surfactant molecule are oppositely charged. Below, we shall discuss briefly the assumptions underlying Koopal’s approach:

1. The surfactant molecule is a chain containing one charged group (valency τ) and (r - 1) apolar segments. As a first approximation each CH₂ group of the aliphatic chain can be considered as one segment.

2. In the adsorbed state each chain of r segments has a sequence (train) of m segments adsorbed in the first layer and the remaining (r - m) segments protrude into the solution as a tail.

3. Owing to coulombic attraction the charged head segment has a strong electrostatic affinity for the surface, so that all adsorbed head segments are present in the first adsorbed layer (closest to the surface).

4. In a poor solvent, as water is for surfactants, segments tend to cluster together. Thus, to a good approximation one can consider the segment density distribution as a homogeneous, (step-function), extending over (r/m) layers each with a volume fraction ϕᵣ equal to ϕ₁. For such a simplified segment density distribution [ϕᵣ] the calculation of the free energy of mixing is relatively simple.

5. The surfactant chain is flexible both in solution and in the adsorbed state.

With these assumptions Koopal et al. [11] arrive at the following isotherm equation

\[ \Phi_1 = W \left( \frac{m}{r} \right) \left( \frac{1 - \Phi_1}{1 - \Phi_*} \right)^r \exp \left[ m \chi'_s + 2r \chi'(\phi_1 - \Phi_*) - \tau Y_1 \right] \]

(1)

where the subscript (*) refers to the equilibrium bulk solution, and W is a combinatorial factor arising from the assumption about the density profile of the segment distribution.

In order to approximate W, more than one route can be followed. The simplest is to assume that only the train segments are restricted in their bond positions and that after the first layer the chain is as free as in the solution. For a chain of (r - 1) bonds, adsorbed with (m - 1) bonds in the first layer, bond m going from layer 1 to layer 2 and the remaining bonds distributed as in the solution phase, W will become

\[ W_m = \frac{\lambda_0^{m-1} \lambda_1}{\lambda_0^r} \]

(2)

where \( \lambda_0 \) denotes that a train of m segments is in the first layer and that the other segments are left “free”. In Eq. (2) \( \lambda_0 \) is the fraction of nearest neighbours in the same lattice layer and \( \lambda_1 \) that in each of the adjacent layers, hence \( 2 \lambda_1 + \lambda_0 = 1 \). This approximation underestimates the conformational entropy loss, \( -kT \lambda \), because the tail is assigned more freedom than it actually has.

Alternatively, W can be approximated by restricting the positions of the segments in order to satisfy the assumed segment-density profile. In this case, a train of (m - 1) bonds is followed by a segment m directed towards the solution and the remaining bonds distributed over layers 2 to (r/m), with ((r/m) - 2) steps from i to (i + 1) and (r - m - (r/m) + 1) steps parallel to the surface. In this case W can be approximated as

\[ W_{mb} = \frac{\lambda_0^{r - (r/m)} \lambda_1^{(r/m) - 1}}{[(r/m) - 2]! [r - m - (r/m) + 1]!} \]

(3)

where \( mb \) denotes that a train of m segments is in layer 1 and that the position of the remaining segments satisfies a block distribution. The approximation in Eq. (3) overestimates the loss in conformational entropy, because, in the adsorbed layer, the return from layer i to (i - 1) is forbidden, whereas in bulk solution there are no restrictions. Moreover, each chain is forced to remain within the assumed segment-density profile, which is an oversimplification.

The two approximations can be considered as extremes, the true value of W being somewhere between the two. Eq. (2) represents the simplest possible approximation but it cannot be applied if \( m \rightarrow 1 \).

The last exponential term on the r.h.s of Eq. (1) describes the interactions between the surfactant and surface, \( X_s \), then between the adsorbed surfactant molecules, \( 2r \chi' \phi_1 \phi_0 \), and between the polar head and the surface (-τ Yₙ). Above, \( \chi'_s \) is the weighted average, net-adsorption energy per segment,

\[ m \chi'_s = (\chi'_s + \chi_1 \chi_{P0}) + (m - 1) \chi_a \chi_{a0} \]

(4)

where \( \chi'_s \) is the polar segment(p)-surface(s) interaction energy, \( \chi_{P0} \) is the “exchange energy” parameter for polar segment-water(0) interaction, and the mean-