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# Comparison between heterogeneous multi-Langmuir and homogeneous electrostatically modified Langmuir models in accounting for the adsorption of small organic ions in reversed-phase liquid chromatography

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ABSTRACT

Adsorption isotherm data were measured by frontal analysis (FA) for sodium nicotinate (anionic species, ${}^{S}_{W}$pH 9.14) and atenololium chloride (cationic species, ${}^{S}_{W}$pH 2.60) on a column packed with hybrid porous particles (BEH-$C_{18}$), eluted with an aqueous solution of methanol at two different ionic strengths. These data were well accounted for by both a heterogeneous bi-Langmuir adsorption isotherm model and a homogeneous electrostatically modified Langmuir isotherm. In the case of the former model, two different types of adsorption sites are available for the ions. The saturation capacity and the binding constant of the stronger type of adsorption sites are nearly independent of the ionic strength of the eluent. These sites could be consistent with residual, accessible silanol groups, the surface concentration of which was estimated at 0.08 $\mu$mol/m$^2$. In contrast, the equilibrium constant of the weaker type of adsorption sites markedly increases with increasing elution strength of the eluent, a result consistent with a salting-out process. These weak adsorption sites are likely located at the interface between the $C_{18}$-bonded layer and the bulk eluent. In the case of the latter isotherm model, there is only one type of adsorption sites, its equilibrium constant increases with decreasing eluent ionic strength, consistent with classical electrostatics, but its saturation capacity strongly decreases when the ionic strength drops. This last result suggests that the homogeneous electrostatic adsorption model is physically inconsistent.

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## 1. Introduction

The adsorption mechanism of small ionic molecules on reversed-phase liquid chromatography (RPLC) stationary phases is not yet fully understood. This issue is important because most samples considered in food, biological, and pharmaceutical analyses contain numerous ionic or ionizable species. The heterogeneous adsorption behavior of small, polar but neutral compounds was demonstrated long ago, based on the measurement of their adsorption isotherms [1] and on the calculation of their adsorption energy distributions [2]. These neutral compounds are generally adsorbed onto two different types of sites and their adsorption data are well accounted for by the bi-Langmuir isotherm model. The ratio of the saturation capacities on the adsorption sites of types 1 and 2 is usually of the order of two to ten for small molecules [3]. The difference between the adsorption energies on these same adsorption sites is of the order of 5 kJ/mol. Although thermodynamic data cannot provide any microscopic insight regarding the adsorption process, it was speculated, based on these results, that the sites of the first type were located at the very interface between the top of the $C_{18}$-bonded layer and the bulk phase. The sites of the second type would be located deeper within the $C_{18}$-bonded layer [4]. This microscopic view is consistent with recent series of molecular simulations which establish the existence of a bi-modal equilibrium constant distribution for small molecules, such as n-butane or 1-propanol [5–7].

The experimental adsorption behavior of ionized compounds onto RPLC stationary phases was shown to be significantly different. For a large variety of commercial $C_{18}$-bonded silica phases, an enhanced peak tailing is usually observed when small samples are injected [8]. As the sample size decreases, the peak shape becomes rapidly more symmetrical to a point where peak tailing cannot be detected anymore [9]. This general observation is consistent with the existence of few and very strong adsorption sites which become saturated even at relatively high dilution. The ratio of the saturation capacities of the sites of type 1 and 2 is usually of the order of 100 [10]. In contrast to what is observed with neutral samples, the difference between the adsorption energies on the weak and strong adsorption sites is larger than 10 kJ/mol. The adsorption

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mechanism of small ionic molecules is then consistent with a negligible adsorption at the $C_{18}$-bonded layer/bulk phase interface and a strong adsorption onto very few specific active sites. There is no partitioning of ionic molecules amidst the $C_{18}$ chains at intermediate adsorption energies. Yet, to our knowledge, this microscopic description of the adsorption behavior of ions in RPLC has not been confirmed by molecular dynamics simulation.

An alternate interpretation of the adsorption data of ions in RPLC is based on the electrostatically modified Langmuir isotherm model. This model assumes that the surface of the adsorbent is homogeneous and hydrophobic and it takes into account the repulsive surface potential created by the adsorption of the amphiphilic ions [11–13]. As the surface concentration in the adsorbed monolayer increases, the electrostatic surface potential increases and the adsorption of additional molecules is made more and more difficult, due to electrostatic repulsion. As a result, the higher the concentration of the ionic sample in the bulk, the faster its propagation velocity, not only because the surface monolayer is being filled but also due to the increasing repulsion of the ions from the adsorbed phase. This results in an enhanced peak tailing, consistent with the experimental adsorption data.

The goal of this work was to compare the physical meanings of the electrostatically modified Langmuir adsorption isotherm and of the multi-Langmuir adsorption isotherm. We used a column packed with BEH-$C_{18}$, an adsorbent the specific surface area of which is known (172 $m^2/g$ before bonding), the ionizable compound sodium nicotinate ($^W_W\mathrm{p}K_{a,1} = 2.17$ and $^W_W\mathrm{p}K_{a,2} = 4.82$), and a methanol/water solution as the mobile phase (10/90, v/v). A most important feature of the $C_{18}$-bonded, endcapped hybrid organic (ethyl)/inorganic (silica) solid BEH-$C_{18}$ adsorbent is the quasi total absence of ion exchange sites in the pH range between 1 and 11, which was demonstrated by the total absence of retention of the cation $Li^+$ at pH values as high as 11 for the first generation of hybrid organic (methyl)/inorganic adsorbent, Xterra [14]. From this perspective, the behavior of BEH-$C_{18}$ is the same as that of Xterra. The pH of the eluent was kept constant at $^S_W$pH 9.14 by using the ammonium/ammoniac buffer at two different ionic strengths (50 and 250 mM). The adsorption data of sodium nicotinate were measured at 295 K by frontal analysis, in a large range of sample concentrations (0–85 g/L). Furthermore, in order to exclude the possible influence of fixed charges that might possibly exist on the surface of the adsorbent, the adsorption data of the β-blocker atenolol were measured at the same temperature, in the concentration range between 0.1 and 50 g/L. The $^S_W$pH was fixed at 2.60 with a phosphate buffer and the ionic strength was adjusted by adding NaCl at concentrations of 0 or 250 mM. In both cases, the isotherm data were modeled, the best adsorption isotherm parameters were determined; their physical meaning is discussed in order to determine which is the most realistic adsorption model for ions in RPLC when there is no charged group on the adsorbent surface.

## 2. Theory

### 2.1. Frontal analysis

Adsorption data were measured by the frontal analysis method. This method is very precise (±1%) and accurate (±2.5%), provided that the temperature of the column is controlled (±0.5 K), the hold-up time, $t_0$, of the column is accurately measured within 0.5%, and the extra-column time, $t_{ex}$ from the mixer to the detector, is known within 0.5% [1]. Even minor errors in the measurememt of the hold-up and extra-column times could lead to misinterpretation in the derivation of the best adsorption isotherm [15,16] especially when the elution time of the front of the breakthrough curve becomes close to the hold-up time $t_0$. In frontal analysis experiment, a concentration plug of height $C$ is injected during a time $t_p$, sufficiently long for thermodynamic equilibrium to be achieved all along the column between the stationary and the bulk phase. The breakthrough curve is recorded and the elution time of its front, $t_{eq}$, is measured. The equivalent area method was used to measure each $t_{eq}$ value, as explained in details in [1]. The amount of compound, $q^*(C)$, adsorbed at equilibrium per unit volume of adsorbent is then given by the mass conservation law:

$$q^*(C) = F_v C \frac{t_{eq} - t_0 - t_{ex}}{V_c - F_v t_0} \qquad (1)$$

where $F_v$ is the flow rate applied during the frontal analysis experiments and $V_c$ is the volume of the empty column tube. This experiment is repeated for a series of concentration steps, $C$.

### 2.2. Adsorption isotherm models

In this work, we consider two different adsorption models susceptible to account for the adsorption of ions in RPLC: (1) the simplest heterogeneous adsorption model, the bi-Langmuir isotherm [17] and (2) the simplest homogeneous adsorption isotherm for charged analytes, which considers the electrostatic surface potential created by the sole adsorbed compound itself, or the electrostatically modified Langmuir isotherm [11]. Note that, since we use as packing material endcapped BEH-$C_{18}$, which exhibits no ion exchange properties between pH 1 and 11 [14], we may neglect the possible effects of pre-existing, fixed charged group bound to the surface of the adsorbent, the charge of which could possibly change the surface potential (zero electrostatic potential). Yet, in order to eliminate the hypothesis of the presence of fixed charges on the surface, adsorption experiments were also carried out at the acidic pH 2.60.

The bi-Langmuir adsorption isotherm model is written:

$$q^*(C) = q_{S,1} \frac{b_1 C}{1 + b_1 C} + q_{S,2} \frac{b_2 C}{1 + b_2 C} \qquad (2)$$

where $q(C)$ is the amount adsorbed on the stationary phase in equilibrium with the bulk concentration $C$. $q_{S,1}$, $q_{S,2}$, $b_1$, and $b_2$ are the saturation capacities and equilibrium constants on the adsorption sites 1 and 2, respectively. The equilibrium constant, $b_1$, includes the contributions to adsorption of the overall effects of all the intermolecular interactions (hydrophobic, π–π, polar, acid–base, etc.) involving a given adsorption site on and/or within the stationary phase surface. By essence, like any other thermodynamic model, the model proposed here cannot provide a microscopic interpretation of the adsorption process on each adsorption site (structure of the electrical layer, local electroneutrality equation, etc.). In contrast, the values of $q_{S,1}$ and $b_i$ can be used to propose a consistent retention mechanism of ionizable compounds onto the stationary phase surface.

The Stahlberg adsorption isotherm model is written:

$$\Gamma(C) = \Gamma_S \frac{K\ \exp(-B\Gamma)C}{1 + K \exp(-B\Gamma)C} \qquad (3)$$

In this model, $\Gamma$ is the number of charged molecules adsorbed per unit surface area of the adsorbent material, $\Gamma_S$ is the saturation capacity of the adsorbent when the bulk concentration $C$ tends towards infinite. Note that $\Gamma_S$ is independent of the surface potential and the ionic strength of the bulk phase. $K$ is the chemical equilibrium constant of the same sample in the absence of electrochemical potential at the surface of the adsorbent. $B$ is a parameter which depends on the valence $z$ of the ions, the Faraday constant $F$ (96485 C/mol), the ionic strength $I$ in the bulk phase (mol/$m^3$), the permittivity $\varepsilon_0\varepsilon_r$ of the bulk phase ($\varepsilon_0 = 8.85 \times 10^{-12}\,J^{-1}\,C^2\,m^{-1}$), and the thermal energy $RT$ (J/mol). After solving the linearised

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