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# Electrostatic and specific binding to macromolecular ligands A general analytical expression for the Donnan volume

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## Abstract

The dependence of the apparent acid dissociation constant of charged polyacids on the ionic strength and on the degree of dissociation is analysed in terms of the Donnan model. We introduce a new approximate analytical expression for the Donnan volume which depends on the ionic strength and on the degree of dissociation with only one adjustable parameter. This expression stems from analytical solutions of the non-linear Poisson–Boltzmann equation (NLPB) under different geometries. Two kinds of polyelectrolytes are studied: polyacrylic acid (PAA), as a model of homogeneous ligand, and Aldrich humic acid (HA), a heterogeneous ligand which exhibits a p$K_a$ dependent on the pH, even when the polyelectrolytic correction is applied. The new approximate Donnan volume expression allows to justify the empirical dependence of previous expressions found in the literature on the ionic strength, gives rise to master curves well behaved in all the range of macromolecular charges and can fit experimental results in good agreement with classical treatments like NLPB, used as a reference, involving a greatly simplified numerical treatment. Three different complexation isotherms are independently used to account for the specific binding. The robustness of the results is evidenced by the fact that similar central moments of the affinity distribution underlying each isotherm and of the adjustable parameter of the Donnan volume are obtained in each case.

*Keywords:* Macromolecular complexation; Polyelectrolytic effects; Specific binding; Polyacrylic acid; Humic acid; Donnan volume; Natural organic matter

## 1. Introduction

The binding to natural organic matter (NOM) is a relevant topic in the circulation of ions in environmental systems. Since acid–base ionisable groups participate in the binding sites of NOM, two components have been recognized in the binding energy: one of electrostatic origin, giving rise to the electrostatic or "atmospherical" binding, and a second chemical component responsible for the specific binding [1].

The electrostatic binding renders the apparent constants dependent on pH and ionic strength, *I*, the so-called polyelectrolytic effect. As a first approximation, mean field theories, mainly the non-linear Poisson–Boltzmann equation (NLPB) [2,3], have been used to account for the electrostatic binding. Different approximate models have been developed in order to avoid the numerical solution of the NLPB equation. Some are based on the assumption of a small deviation of the electroneutrality inside a certain volume [4,5]; counterion condensation model [6,7] proposes that, in cylindrical geometry, when the charge spacing along a rod of infinite length increases above a critical level, counterions "condense" ("territorial binding") depending on the dielectric constant of the solvent and on the charge of the counterions [8–10]. Another approximate model (the Donnan approach, D) is based on a biphasic concept: polyions are immersed in separate permeable gel phases. This approach assumes complete electroneutrality inside and outside the permeable gel phase, and the potential difference across the semipermeable membrane of the gel phase (Donnan potential) is then obtained from Donnan equilibrium conditions [11,12]. In some cases, it is difficult to obtain reliable measurements of

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the volume of this gel phase and empirical expressions for the Donnan volume have been reported for different polyions. The Donnan volume increases as $I$ decreases, and a linear relationship in the log–log scale has been suggested for the humic matter [13]. However, the results obtained are not fully satisfactory in all the range of macromolecular charges.

Moreover, NOM, in general, and humic matter, in particular, usually presents binding sites with different chemical functionalities. This property is closely related to the mixture character of these ligands made up of different chemical structures that have a common behaviour in front of a fractionation process [1,14]. This kind of ligands are called heterogeneous ligands, in contrast to the homogeneous ligands which are characterized by sites made up of only one functional group. Accordingly, the specific binding energy to a heterogeneous ligand is not a constant, but has to be described by a discrete or a continuous distribution function [15–17]. It has been shown that different affinity distributions can reproduce the binding data at wide intermediate coverage ranges with similar accuracy [17] so that results between different assumed distributions have to be compared in terms of the moments of the distribution. The first central moment of the distribution approximates the description of the data with a homogeneous binding having the average binding energy of the distribution, while the second central moment (the variance, $\sigma^2$) provides information on the spread of the distribution, i.e. on the degree of heterogeneity.

Both, the electrostatic and specific bindings are coupled, since the macromolecular charge depends on the specific binding, which at the same turn, depends on the concentration of complexing agents at the macromolecular surface (ruled by the polyelectrolytic effect). Thus, both, the set of parameters characterizing such distribution of affinities and the set describing the polyelectrolytic correction, have to be simultaneously fitted from experimental data in a general procedure.

It is the aim of the present paper to check the use of a new analytical expression for the Donnan volume in the description of the proton binding to two different kinds of ligands: the polyacrylic acid (PAA), as an example of homogeneous polyelectrolyte, and the humic acid (HA), as an example of heterogeneous polyelectrolyte. The new expression for the Donnan volume can be deduced from a combination of the Donnan ideas and the NLPB results aiming at describing a wide range of macromolecular charges, ionic strengths and geometries. Actually, present results will be compared with the NLPB equation, used as a reference approach (see Appendix A).

## 2. Theoretical background

Acid–base equilibria of polyions are generally described by the Henderson–Hasselbach equation:

$$\mathrm{p}K_{\mathrm{app}} = -\log c_{\mathrm{H}} - \log\left(\frac{\alpha_{\mathrm{d}}}{1-\alpha_{\mathrm{d}}}\right) \tag{1}$$

where $\mathrm{p}K_{\mathrm{app}}$ indicates the apparent dissociation constant of the polyacid, $\alpha_{\mathrm{d}}$ the degree of dissociation of the macromolecule and $c_{\mathrm{H}}$ is the bulk proton concentration.

Splitting the binding energy into an intrinsic or specific chemical component, $-RT\ln K_{\mathrm{c}}$, and an electrostatic work, which within the mean field approximation can be written as $F\psi_{\mathrm{S}}$, $K_{\mathrm{app}}^{-1}$ can be factorized as

$$\mathrm{p}K_{\mathrm{app}} = \log K_{\mathrm{c}} - \frac{1}{\ln 10}\frac{F\psi_{\mathrm{S}}}{RT} \tag{2}$$

where $\psi_{\mathrm{S}}$ is the electrostatic potential close to the binding sites with respect to the bulk solution (which is used as the origin), $F$ the Faraday constant, $R$ the gas constant, and $T$ is the temperature. $K_{\mathrm{c}}$ is also called average equilibrium function [1,16] and measures the chemical or specific binding energy so that

$$\begin{aligned}\log K_{\mathrm{c}} &= -\log c_{\mathrm{H_S}} + \log\left(\frac{1-\alpha_{\mathrm{d}}}{\alpha_{\mathrm{d}}}\right)\\ &= -\log c_{\mathrm{H_S}} + \log\left(\frac{Q_{\max}-Q}{Q}\right)\end{aligned} \tag{3}$$

where $Q$ and $Q_{\max}$ are the charge and the maximum charge in the fully deprotonated macromolecule and $c_{\mathrm{H_S}}$ labels the concentration of protons in a volume element close to the binding sites of the polyelectrolyte.

### 2.1. Specific binding

Both $K_{\mathrm{c}}$ and the coverage, $\theta = (Q_{\max} - Q)/Q_{\max}$, can be related to the distribution of affinities present in the heterogeneous macromolecules, the so-called affinity spectrum, $\mathrm{p}(\log k)$ [15]. In the simplest case, $\theta$ is a weighted addition of local Langmuir complexation isotherms:

$$\theta = \int_{-\infty}^{\infty} \mathrm{p}(\log k)\frac{1}{1+10^{-(\log k+\log c_{\mathrm{H_S}})}}\,\mathrm{d}\log k \tag{4}$$

Results obtained using different isotherms to fit binding data cannot be compared in terms of the isotherm parameters since the physical meaning and the dimensions of these parameters are specific of each isotherm. However, they can be compared by computing the moments of the respective affinity distributions underlying each isotherm. Actually, it has been shown [17] that the values of $\log K_{\mathrm{c}}$ at intermediate coverages are almost just function of the average, $\mu = \langle\log k\rangle$ and the variance, $\sigma^2 = \langle(\log k)^2\rangle - \mu^2$, of the affinity spectrum, and practically independent from the particular shape of the distribution for unimodal distributions. Thus, one expects to find an average affinity and variance almost independent of the isotherm used in the fitting of the specific binding for interemediate coverages, while divergent values of these parameters would be obtained when very low or very high coverage is included in the experimental binding data. Table 1 reports the relationships between the parameters and the moments of the underlying distributions for the complexation isotherms used in this work: Langmuir–Freundlich, Frumkin and uniform.

### 2.2. Donnan model for the electrostatic binding

In the Donnan approach, the polyelectrolyte is considered to behave as an electrically neutral gel phase having a particu-