



Fractional statistical theory of finite multilayer adsorption



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ARTICLE INFO

Article history:

Received 5 August 2015

Received in revised form 5 October 2015

Accepted 28 October 2015

Available online 2 November 2015

Keywords:

Adsorption isotherms

Multilayer adsorption

Equilibrium thermodynamics and statistical mechanics

BSA protein adsorption

ABSTRACT

In the present paper, finite multilayer adsorption is described as a fractional statistics problem, based on Haldane's statistics. In this scheme, the Helmholtz free energy and its derivatives are written in terms of a parameter g , which relates to the configuration of the molecules in the adsorbed state. For values of g ranging between 0 and 1 the formalism is used to model experimental data of bovine serum albumin (BSA) adsorbed onto an ion exchange resin for different values of pH and temperature. Excellent agreement between theory and experiments was found.

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1. Introduction

A major bottleneck in dealing with generalized lattice gases within the framework of classical statistical mechanics is to properly calculate the configurational entropic contributions to the thermodynamic potential; this means the degeneracy of the energy spectrum compatible with given number of particles and adsorption sites [1–7]. In the simple case of adsorption of monomers (small adsorbates with spherical symmetry), this is usually done through the mean-field assuming that the particles are distributed randomly over the sites regardless their mutual interactions [1]. However, the entropic effects due to adsorbate–adsorbate interactions [1], multilayer adsorption [3], multicomponent adsorbates [4] and multisite-occupancy adsorption [5] are by no means negligible. For instance, the configurational entropy of linear k -mers (particles that occupy k lattice sites when adsorbed) is strongly dependent on the size k even for noninteracting particles [8]. Thus, configuration counting in the case of particles that occupy more than one lattice site (dimers, trimers, etc.), seems a hopeless task, and it limits the analytical developments in the field of adsorbed polyatomic gases.

Quantum fractional statistics proposed by Haldane [9] and Wu [10], is a theoretical frame that allows us to characterize a system of

interacting particles confined in a finite region of the space by a “statistical parameter” g , accounting for the number of states that are excluded from the states spectrum when a particle is added to the system. Fermions, bosons, and particles with fractional statistics correspond to $g = 1$, $g = 0$ and $0 < g < 1$, respectively.

In recent work [11,12], we extended the ideas of Haldane [9] and Wu [10] and presented the basis of a fractional statistics thermodynamic theory of adsorption (FSTA) of polyatomics as to describe the thermodynamic properties of the adlayer when the adsorbate occupies more than one adsorption site. FSTA was applied to a variety of adsorption problems: non-interacting chains adsorbed flat on a one-dimensional lattice [8,11,12]; molecules of different shape and size adsorbed on square, honeycomb and triangular lattices [13]; interacting k -mers adsorbed on two-dimensional lattices [14]; multicomponent adsorption of polyatomic species [15]; effects of excluded surface area on adsorption equilibria [16]; and modeling of experimental data of $C_3H_8/5A$ [11–13], $O_2/13X$ [11–13], methane–ethane mixtures in zeolites [14], and bovine serum albumin adsorbed on sulfonated microspheres [17].

In our previous work [11–16], we assumed that the molecules exclude more than one site when adsorbed and, consequently, g is greater than 1. The results obtained showed that adsorption of structured lattice gases can be treated in the framework of a generalized statistics with $g > 1$. Here, the theory presented in Refs. [11,12] is extended for the case $0 < g < 1$ in order to describe finite multilayer adsorption [3]. The present study is a natural

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continuation of our previous work and focuses on the thermodynamic properties of adsorbed phases in which adsorption proceeds beyond monolayer coverage. The theoretical scheme is applied to study adsorption of bovine serum albumin (BSA) onto an ion exchange resin, providing a simple model from which experiments may be interpreted.

Protein adsorption on solid surfaces has great practical and theoretical interest in technological and industrial processes [18]. The extensive use of immobilized proteins, the development of the microarrays and solid miniaturized devices involving proteins, combined with the special interest of the therapeutic protein separation for industrial biotechnology, has increased the need for understanding the interactions involved in such processes [19–22]. Thus, a wide variety of theories have been proposed for modeling experimental data of protein adsorption processes. An extensive overview of this field can be found in excellent work by Rabe et al. [23] and the references therein. The theories range from the well-known Langmuir equation [24], which was developed for monolayer adsorption, to the Brunauer–Emmett–Teller (BET) theory [25] for infinite multilayer adsorption. The FSTA presented here includes the Langmuir theory as a particular case ($g = 1$), reproduces the BET equation for $g = 0$, and also allows to describe intermediate cases of finite multilayer adsorption ($0 < g < 1$). In addition, FSTA is a simple model, with few adjustable parameters and each having a precise physical meaning. Other multilayer adsorption models have also been proposed [26–28] although they are complex and usually contain too many parameters which make them difficult to use.

The paper is organized as follows. In Section 2, the theoretical approximation for finite multilayer adsorption is developed. In order to test the applicability of the proposed model, Section 3 is devoted to the analysis of experimental data for bovine serum albumin (BSA) adsorbed on an ion exchange resin. Finally, the conclusions are drawn in Section 4.

2. Theory

In 2004, a new theory to describe adsorption of polyatomic adsorbates was introduced [11]. FSTA is based on a generalization of the formalism developed by Haldane [9,10]. Haldane's statistics relies on the fact that, given $(N - 1)$ identical particles confined in fixed volume, each of which having G accessible states at infinitely low density, the number of states available to a N th particle added to the volume is

$$d_N = G - \sum_{N'=1}^{N-1} g(N') = G - G_0(N), \quad (1)$$

where $g(N)$ is the number of states excluded per particle (a measure of the statistical interactions). In addition, the number of configurations for a system of N particles and G states is:

$$W(N) = \frac{(d_N + N - 1)!}{[N!(d_N - 1)!]} = \frac{[G - G_0(N) + N - 1]!}{\{N![G - G_0(N) - 1]!\}}. \quad (2)$$

Clearly, $g(N) = 0$ [$G_0(N) = 0$] and $g(N) = 1$ [$G_0(N) = N - 1$] hold for bosons and fermions, respectively.

In Refs. [11,12], the Haldane's theory was extended as to describe classical systems like the adsorption of molecules on solid surfaces. In this framework, the interaction of one isolated molecule with a solid surface confined in a fixed volume can be represented by an adsorption field having a total number G of local minima in the space of coordinates necessary to define the adsorption configuration (usually rendered by lattice sites in a discrete representation of the field). Thus, G can be rationalized as being the number of equilibrium states of a single molecule at infinitely low density. Depending on the configuration of the molecule in the adsorbed

state, some states out of G are prevented from occupation by the adsorption of another molecule. Moreover, because of possible concurrent exclusion of states by two or more molecules, the number of states excluded per molecule, $g(N)$, depends in general on the number of molecules N within the volume. Accordingly, given $(N - 1)$ identical molecules adsorbed on a surface of M sites, the number of states available to a N th one added to it can be obtained from Eq. (1) with $g(N) \geq 0$.

From Eq. (2), the canonical partition function $Q(N, M, T)$ can be easily calculated [1]. Thus,

$$Q(N, M, T) = W(N) \exp(-\beta N U_0) q_i^N, \quad (3)$$

where $\beta = 1/k_B T$, k_B is the Boltzmann constant, T is the temperature, U_0 is the adsorption energy per particle and q_i is the partition function of a single molecule in the adsorbed state. In addition, the Helmholtz free energy $F(N, M, T)$ relates to $Q(N, M, T)$ through [1]

$$\beta F(N, M, T) = -\ln Q(N, M, T). \quad (4)$$

The remaining thermodynamic functions can be obtained from the general differential form [1]

$$dF = -SdT - \Pi dM + \mu dN, \quad (5)$$

where S , Π and μ designate the entropy, spreading pressure and chemical potential, respectively. Thus, a general form for the chemical potential of a system of adsorbed molecules on solid surfaces is obtained from Eq. (5) as:

$$\beta \mu = \beta \left(\frac{\partial F}{\partial N} \right)_{T, M} = \ln \left\{ \frac{n[1 - \tilde{G}_0(n) + n]^{(\tilde{G}'_0 - 1)}}{[1 - \tilde{G}_0(n)]^{\tilde{G}'_0}} \right\} - \ln K_e, \quad (6)$$

where $n = N/G$ is the density (n finite as N , $G \rightarrow \infty$). In addition, $\tilde{G}_0(n) \equiv \lim_{N, G \rightarrow \infty} G_0(N)/G$, $\tilde{G}'_0 \equiv d\tilde{G}_0/dn$ and $K_e = q_i \exp(-\beta U_0)$ is the equilibrium constant. Hereafter we examine the simplest approximation within FSTA, namely $g = \text{constant}$, which is rather robust as it will be shown below. Considering that $\tilde{G}_0 = gn$ and $\tilde{G}'_0 = g$, a particular isotherm function arises from Eq. (6),

$$K_e \frac{p}{p_0} = \frac{n[1 - n(g - 1)]^{g-1}}{(1 - ng)^g}, \quad (7)$$

where $p = p_0 \exp(\beta \mu)$ (p_0 is the relative pressure). As in the case of Langmuir and BET isotherms, Eq. (7) admits for total occupation of the first layer. In fact, our model belongs to a general class of statistical models, where the adsorption is reversible, the adsorbed phase is in equilibrium with the adsorbing gas, and the corresponding adsorption isotherm admits for total occupation of the first layer. In contrast, models of irreversible adsorption (as, for example, random sequential adsorption model) lead to a limiting or jamming state, in which the first layer is only partially covered due to the absence of free space of appropriate size and shape [23,29].

As mentioned in Section 1, the proposed formalism allows to deal with a wide variety of adsorption systems, each one characterized by a different value of the parameter g . To analyze some examples, it is useful to write the following condition for the function $\tilde{G}_0(n)$:

$$\tilde{G}_0(n_{\max}) = 1, \quad (8)$$

where $n_{\max} = N_{\max}/G$, being N_{\max} the maximum number of adsorbed molecules.

Let us consider the general case of adparticles composed by k elementary units in which k' out of k units of the molecule are attached to surface sites (occupying k' adsorption sites) and $(k - k')$ units are detached and tilted away from them. For a lattice of M sites, $G = mM$, where m is the number of distinguishable configurations of the molecule per lattice site (at zero coverage) and depends

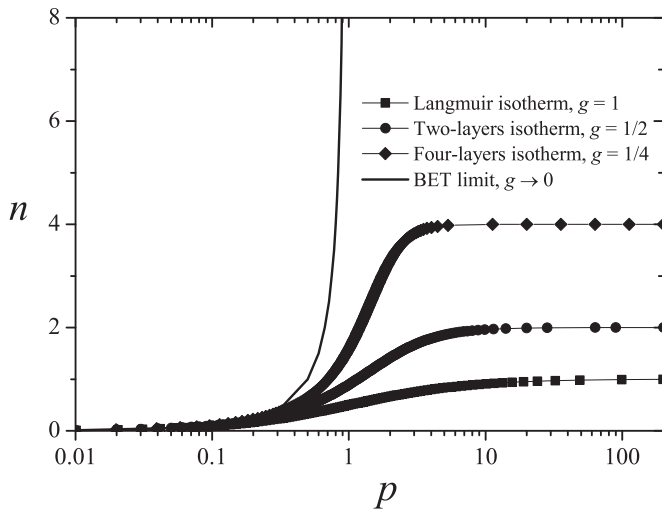


Fig. 1. Adsorption isotherms (from Eq. (7)) for different values of the parameter g as indicated.

on the lattice/molecule geometry. Then, from the definition of $\tilde{G}_0(n)$ and the condition in Eq. (8),

$$gn_{\max} = g \frac{N_{\max}}{G} = g \frac{M}{k'} \frac{1}{mM} = 1, \quad (9)$$

and

$$g = mk'. \quad (10)$$

In the case of monomers, $m=1$, $k'=k=1$, $g=1$ and Eq. (7) corresponds to the well-known Langmuir equation [24]. For non-interacting chains of size k adsorbed flat on a one-dimensional lattice, $m=1$, $k'=k$, $g=k$ and Eq. (7) reduces to the exact solution for 1D multisite-occupancy adsorption [8]. Other examples are given in the following. For instance, straight k -mers adsorbed flat on sites of a square lattice would correspond to $m=2$, $k'=k$ and $g=2k$. On the other hand, $m=1$, $k'=k=4$ and $g=4$ represents the case of $(a \times a)$ -squares (being a the lattice constant) adsorbed flat on a square lattice.

In all previous cases, each entity excludes one or more than one state when adsorbed and, consequently, $g \geq 1$. In what follows, FSTA will be used for values of g ranging between 0 and 1. To understand this, let us consider a system with the following properties: (1) each particle occupies one adsorption site when adsorbed on the lattice, and (2) a particle can be adsorbed onto an already adsorbed one, forming a finite number of layers z . Then, for a lattice of M sites, the condition in Eq. (8) results

$$gn_{\max} = g \frac{N_{\max}}{G} = g \frac{zM}{M} = 1, \quad (11)$$

and

$$g = \frac{1}{z}. \quad (12)$$

According to the last equation, the existence of a finite number of adlayers on the surface ($z > 1$) is associated with values of g between 0 and 1. In addition, and given that our model has a single energy parameter U_0 , the adsorption energy per particle is equal in all layers. In the language of the BET theory, this leads to the particular case of $c=1$ [25].

Fig. 1 shows the dependence of n with the pressure p [adsorption isotherm, Eq. (7)] for different values of g . Two well-known equations are obtained in the limit cases: (1) for $g=1$ ($z=1$, squares), Eq. (7) reduces to the Langmuir equation [24] and (2) for $g \rightarrow 0$ ($z \rightarrow \infty$, solid line), BET equation (with $c=1$) is recovered [25]. The curves corresponding to $g=1/2$ (two-layer isotherm, circles) and $g=1/4$

(four-layer isotherm, diamonds) are also shown in the figure. In all cases, the equilibrium constant and the relative pressure were set equal one, without any loss of generality.

To summarize the results obtained in this section, we can state that: (i) $g > 1$ means that more than one site is excluded when a molecule adsorbs on the surface at monolayer coverage, and FSTA allows to describe adsorption experiments ranging from simple species to elaborated polyatomics; and (ii) $0 < g < 1$ indicates the formation of a finite number of adsorbed layers, and FSTA provides a simple theoretical framework to model thermodynamic experiments of finite multilayer adsorption. This scheme will be used in the next section to analyze experimental data of protein adsorption.

3. Comparison with experimental results of protein adsorption

In this section, analysis of experimental results of protein adsorption has been carried out in order to determine the reaches and limitations of the theory. It is known that the protein molecules are large and complicated and an analysis of their interaction with a support is not simple. However, the protein (BSA) and the ion-exchange resin used in this study are well-known and characterized. This fact has allowed us to evaluate the application and scope of the theoretical model presented here.

It is clear that a complete analysis of this field is quite a difficult subject. For this reason, the examination of simple models with an increasing degree of complexity might help and guide us in establishing a general framework for the study of this kind of systems. In this context, the present work tries to contribute to the understanding of some of the characteristics of protein adsorption phenomena through the use of a simple model. Specifically, we will discuss the occurrence of finite multilayer adsorption in BSA adsorption experiments. In addition, the present study is a continuation of our previous work, where novel theoretical models have been applied to characterize the behavior of these systems [16,17,30].

Before starting the comparison between experimental and theoretical data, and in order to analyze adsorption from liquid solutions, it is convenient to write the theoretical isotherm given in Section 2 in a more appropriate form. For this purpose, two modifications have been made in Eq. (7): (1) the pressure p has been replaced by the concentration of the solute in the liquid c , and (2) the quantity n has been written in terms of the ratio q/q_{\max} , where (q_{\max}) q represents the (maximum) amount of solute adsorbed on the surface of the adsorbent,

$$\frac{q}{q_{\max}} = \frac{N}{N_{\max}} = \frac{N}{zM} = gn. \quad (13)$$

Under these considerations, Eq. (7) adopts the form,

$$K_e c = \frac{(q/q_{\max})[g - (g-1)q/q_{\max}]^{g-1}}{[g - g(q/q_{\max})]^g}. \quad (14)$$

The experimental data were taken from the study of the adsorption of BSA on an ion exchange resin, Amberlyst 15 (A 15). BSA is a well-known globular protein and it is considered as a model protein commonly used in laboratory studies.¹ Its globular structure is achieved by the folding of its polypeptide chain into three domains, each one formed by six helices, and its secondary structure is essentially α -helix [32–34].

The resin A 15 was selected as support for this work. A 15, classified as a strongly acidic cationic exchanger, is a macroreticular polymeric material based on crosslinked styrene divinylbenzene copolymers. The resin presents a high degree of mechanical and

¹ In physicochemical experiments, BSA is widely used as a model protein to study adsorption due to its availability and low cost [31].

Table 1
Characteristics of ion exchange resin Amberlyst 15.

Functional group	Crosslinking	Particle size	Exchange capacity	Average pore diameter
-SO ₃ ⁻	20%	0.60–0.85 mm	4.1 meq H ⁺ /g	300 Å

Table 2
Fitting parameters corresponding to the data in Fig. 2.

Temperature (°C)	pH	q_{max} (mg BSA/g resin)	K_e	g
25	4	29.19	1.09	0.26
25	7.5	8.71	0.99	0.25
25	9.5	5.63	2.03	0.34
37	4	56.03	1.52	0.22
37	7.5	17.76	1.21	0.16
37	9.5	6.10	2.41	0.30
45	4	41.47	0.94	0.23
45	7.5	11.19	0.89	0.15
45	9.5	5.79	2.07	0.32

chemical stability for all values of pH. The main characteristics of A 15 are listed in Table 1. The support was activated by agitation with HCl (3 M) for 5 h. The ion exchange capacity (meq H⁺/g of resin dry) was determined by mean of the acid–base titration of the aqueous phase after 3 h of incubation into an aqueous solution of NaOH (1 M), see Table 1.

Finally, for obtaining the adsorption isotherms, 0.2 g of resin/mL of solution (dry weight) were incubated with buffer solution (0.1 M acetic/acetate buffer for pH 4 and 0.1 M Tris–HCl buffer for pH 7.5 and 9.5) containing different amounts of BSA (0.2–2 mg/mL) during 3 h. This procedure was carried out at 25, 37 and 45 °C. The amount of adsorbed BSA, q (mg BSA/g resin), was calculated as

$$q = \frac{(c_i - c_f)V}{w}, \quad (15)$$

where c_i (c_f) represents the initial(final) BSA concentration (mg BSA/mL); V is the solution volume (mL) and w is the amount of resin (mg). The protein concentrations were determined at 278 nm using a UV–Vis spectrophotometer (Hitachi UV–Vis spectrometer).

The experimental data were fitted using least-squares statistics [35]. Thus, suppose that n data points ($x_i, y_i, z_i; i = 1, \dots, n$) are being fitted to a model that has L adjustable parameters ($a_j; j = 1, \dots, L$). The model predicts a functional relationship between the measured independent and dependent variables,

$$z(x, y) \equiv z(x, y; a_1, \dots, a_L), \quad (16)$$

where the dependence on the parameters is indicated explicitly on the right-hand side. Then, the following function must be minimized over a_1, \dots, a_L :

$$\sum_{i=1}^{n_m} [z_i - z(x_i, y_i; a_1, \dots, a_L)]^2. \quad (17)$$

The parameters of the model are then adjusted to achieve a minimum in function (17), yielding best-fit parameters. The adjustment process is thus a problem in minimization in many dimensions.

The least-squares procedure was performed for each experimental isotherm. In this case, Eq. (14) was used as fitting function, with K_e and g as adjustable parameters. The maximum amount of solute adsorbed on the surface q_{max} was set using the experimental data. The results are shown in Fig. 2 and the fitting parameters are collected in Table 2. Symbols correspond to experimental data and lines represent theoretical results. Clearly, the FSTA model provides a very good agreement with the experimental data.

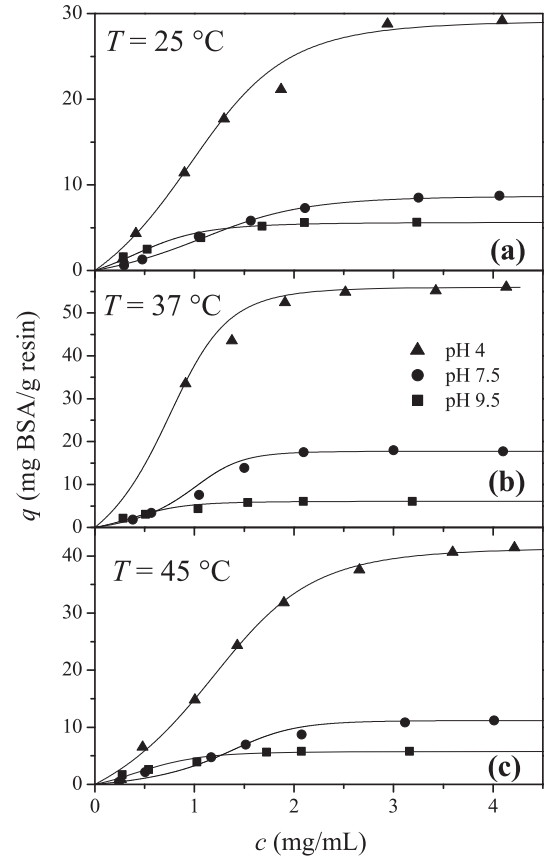


Fig. 2. (a) Adsorption isotherms of BSA on resin Amberlyst 15 for $T = 25$ °C and three different values of pH as indicated. Symbols correspond to experimental data and lines represent theoretical results from Eq. (14). (b) Same as part (a) for $T = 37$ °C. (c) Same as part (a) for $T = 45$ °C.

The results obtained from the theoretical modeling, particularly the g values varying between 0 and 1, suggest the occurrence of finite multilayer adsorption. This phenomenon has already been observed in previous research on BSA adsorption [36–39]. With respect to the equilibrium constant, the resulting values of K_e are of the same order of magnitude as those reported in the literature for similar systems.

For each value of pH, the influence of the temperature on the maximum amount adsorbed q_{max} can be analyzed from the behavior of the parameter g . This situation is reflected in Fig. 3, where q_{max} (solid symbols, left-vertical axis) and g (open symbols, right-vertical axis) are shown in terms of temperature. Parts (a), (b) and (c) correspond to pH 4, pH 7.5 and pH 9.5, respectively.

The results in Fig. 3 can be interpreted as follows: an increase in the number of adsorbed layers (which means an increase in q_{max}) is accompanied by a decrease in g . Conversely, a decrease in the number of adsorbed layers (which means a decrease in q_{max}) is accompanied by an increase in g . In all cases, the maximum adsorption occurs at 37 °C, where the curve of g has a minimum. Thus, the parameter g (in the range $0 < g < 1$) appears as a measure of the capacity of the molecule to form multilayer. This finding represents evidence of the physical and experimental significance of

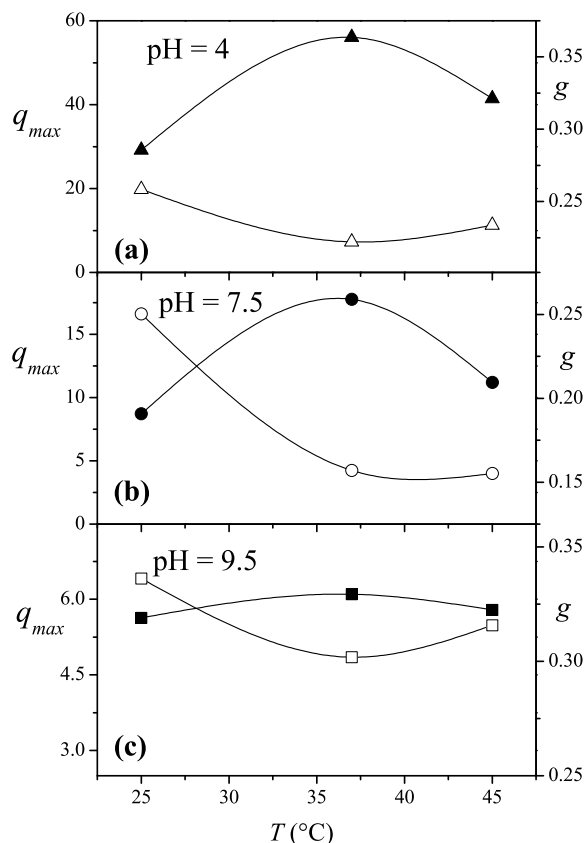


Fig. 3. (a) Comparison between q_{max} (solid symbols, left-vertical axis) and g (open symbols, right-vertical axis) for pH 4 and three different temperatures $T = 25, 37$ and 45 °C. (b) Same as part (a) for pH 7.5. (c) Same as part (a) for pH 9.5.

g , and shows the applicability of FSTA to model a wide range of adsorption systems.

4. Conclusions

A new theoretical frame to treat finite multilayer adsorption as a fractional statistics problem has been presented. The formalism is based on a generalization of the fractional statistics thermodynamic theory of adsorption. In this scheme, the Helmholtz free energy and its derivatives are written in terms of a parameter g , which relates to the configuration of the molecules in the adsorbed state. For $g > 1$, FSTA allows to model adsorption experiments ranging from simple species to elaborated polyatomics. For values of g between 0 and 1, this parameter can be written in terms of the number of adsorbed layers, and FSTA provides an adequate theoretical framework to describe finite multilayer adsorption.

The theoretical results were applied to model experimental data of bovine serum albumin adsorbed onto an ion exchange resin for different values of pH and temperature. A nonlinear regression technique was used in fitting the experimental data, where the isotherms were fitted with two free parameters: parameter g and equilibrium constant K_e . Excellent agreement was found between theory and experiment. The values obtained for the fitting parameters indicate the occurrence of finite multilayer adsorption.

Further comprehensive analysis of experimental isotherms through the proposed formalism appears necessary to discern its applicability, reliability, and accuracy. In this line, future efforts will be devoted to the analysis of some well-known systems, such as N_2 [40,41], Ar [42] and ethylene [43] on graphite, which present solid finite multilayer films below their respective bulk triple points.

Acknowledgments

E.A.T., E.Q. and N.A.O. thank support from Universidad Nacional de San Luis (Argentina) under project 21712. D.A. M-F. and A.J. R-P. thank support from Universidad Nacional de San Luis (Argentina) under project 322000, CONICET (Argentina) under project PIP 112-201101-00615 and the National Agency of Scientific and Technological Promotion (Argentina) under project PICT-2013-1678.

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