
Analytical solution for the three-parameter BET equation in liquid systems

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Abstract

This work presents significant contributions to the theoretical understanding of the Brunauer-Emmett-Teller (BET) isotherm applied to liquids. An analytical solution has been developed using multiple linear regression from the rearrangement of the BET equation into a quadratic form. A profound analysis of the BET equation revealed intriguing relationships, including equations to determine the concentration at which the adsorption capacity reaches its maximum, the concentration at the inflection point of the isotherm, and the concentration resulting in 50% coverage of the adsorbent surface. The analytical solution was tested against data from the literature, demonstrating its capability to provide results very close to those reported in the original studies, which were obtained using numerical methods. This validation underscores the accuracy and reliability of the proposed analytical approach. By offering a precise and computationally efficient alternative, comparable to numerical methods, this analytical solution advances the application of the BET isotherm in liquid systems, potentially enhancing the modeling and prediction of adsorption behaviors in various scientific and industrial contexts. The findings contribute to a deeper theoretical insight and practical utility, paving the way for more effective and simplified analysis of adsorption phenomena in liquid-phase systems.

Keywords: BET isotherm; Analytical solution; Adsorption modeling; Multiple linear regression.

1. Introduction

The BET (Brunauer, Emmett, and Teller) isotherm, developed in 1938, represents a cornerstone in adsorption science, providing a robust framework for understanding the behavior of adsorbate molecules on solid surfaces [1]. The model assumes a homogenous surface and monolayer adsorption, making it particularly useful for studying gas-solid interactions. By analyzing the adsorption data, the BET isotherm allows for the determination of crucial parameters such as the monolayer capacity (related to surface area) and the heat of adsorption [2,3].

One of the key strengths of the BET isotherm is its versatility. It can be applied to a wide range of adsorbates and adsorbents, making it a valuable tool in various fields, including material science, environmental science, and catalysis [4]. The model

has been instrumental in characterizing the surface properties of materials such as activated carbons, zeolites, and metal oxides [3].

While originally developed for gas-phase adsorption, researchers have adapted the BET equation for use in liquid-phase adsorption studies. Ebadi et al. [5] proposed a modified form of the BET isotherm equation specifically tailored for liquid-phase adsorption. However, unlike the gas-phase BET equation, which contains two degrees of freedom, the liquid-phase BET equation has three degrees of freedom. This additional complexity arises from the interactions between the adsorbate molecules in the liquid phase, leading to a non-linear form of the equation [5].

Despite the challenges posed by its non-linear nature, the modified BET equation for liquid-phase adsorption remains a valuable tool for studying adsorption phenomena in liquid systems. Advances in computational techniques and data analysis have

facilitated the application of numerical methods to solve the non-linear BET equation, enabling researchers to obtain accurate estimates of adsorption parameters and deepen their understanding of adsorption processes in liquid systems.

Throughout this work, the derivations of the proposed equations will be presented, discussing their applicability in explaining the experimental data, and exploring the implications of their parameters for understanding adsorption processes in solid-liquid systems. This contribution aims not only to expand the repertoire of available theoretical tools but also to enrich the general understanding of adsorption phenomena at solid-liquid interfaces, promoting significant advances in the practical applications of these processes.

The objective of this work is not to compete with numerical solutions in terms of applicability and precision in determining the coefficients of the isotherms, but rather to provide a deeper insight into the physical meaning and implications of the terms in the equation that describes the theory.

2. Derivation of the analytical solution

This derivation starts from the BET equation adapted for liquids by Ebadi and coworkers, presented in Equation 35 in the original article [5], written below:

$$q = q_m \frac{K_S C_{eq}}{(1 - K_L C_{eq})(1 - K_L C_{eq} + K_S C_{eq})} \quad (1)$$

Once the BET equation adapted for liquids has three degrees of freedom (q_m , K_S and K_L) cannot be written in the linear form, however it does not mean that there is no analytical solution.

Henceforth in the text, we will replace the symbology term K_L , proposed by Ebadi, by K_M . This will serve to avoid confusion with the Langmuir constant (K_L) that will also appear during the development of this work. Becoming K_S for denote single-layer constant and K_M for multi-layer constant.

Observing the numerator in the BET equation, we see that the expression is quadratic with respect to C_{eq} .

$$q = q_m \frac{K_S C_{eq}}{(1 - K_M C_{eq})(1 - K_M C_{eq} + K_S C_{eq})} \quad (2)$$

Performing the polynomial expansion, we obtain:

$$q = q_m \frac{K_S C_{eq}}{(K_M^2 - K_M K_S) C_{eq}^2 + (K_S - 2K_M) C_{eq} + 1} \quad (3)$$

Rewriting the equation:

$$\frac{C_{eq}}{q} = \left(\frac{K_M^2 - K_M K_S}{q_m K_S} \right) C_{eq}^2 + \left(\frac{K_S - 2K_M}{q_m K_S} \right) C_{eq} + \frac{1}{q_m K_S} \quad (4)$$

Now, we can plot a graph with C_{eq}/q vs C_{eq} that should result in a parabola like graph representing the quadratic function.

The quadratic function:

$$y = ax^2 + bx + c \quad (5)$$

can be transformed to a linear domain, using

$$z = x^2 :$$

$$y = az + bx + c \quad (6)$$

The linear regression can be solved analytically using linear algebra:

$$\theta = (\mathbf{X}^T \mathbf{X})^{-1} \cdot \mathbf{X}^T \mathbf{y} \quad (7)$$

Where θ is an n by 1 vector representing all the coefficients of interest, \mathbf{X} is a m by n matrix, composed of m samples and $n = 3$ variables (C_{eq}^2 , C_{eq} , 1), and the symbol \mathbf{y} is a m by 1 vector representing the target values (C_{eq}/q).

Once the coefficients a , b and c , of the equation 5 are determined, the solution for parameters in equation 4 follows:

$$\frac{K_M^2 - K_M K_S}{q_m K_S} = a \quad (8)$$

$$\frac{K_S - 2K_M}{q_m K_S} = b \quad (9)$$

$$\frac{1}{q_m K_S} = c \quad (10)$$

Normalizing equations over c :

$$K_M^2 - K_M K_S = \frac{a}{c} = \alpha \quad (11)$$

$$K_S - 2K_M = \frac{b}{c} = \beta \quad (12)$$

Isolating K_M from equation 12:

$$K_M = \frac{K_S - \beta}{2} \quad (13)$$

and substituting in equation 11, we obtain:

$$\left(\frac{K_S - \beta}{2} \right)^2 - \left(\frac{K_S - \beta}{2} \right) K_S = \alpha \quad (14)$$

Performing the polynomial expansion:

$$\left(\frac{K_S^2}{4} \right) - \left(\frac{K_S^2}{2} \right) + \left(\frac{\beta K_S}{2} \right) - \left(\frac{\beta K_S}{4} \right) - \left(\frac{\beta K_S}{4} \right) + \left(\frac{\beta^2}{4} \right) = \alpha \quad (15)$$

$$K_S^2 = 4 \left(\frac{\beta^2}{4} - \alpha \right) \quad (16)$$

$$K_S = \sqrt{\beta^2 - 4\alpha} \quad (17)$$

$$K_S = \sqrt{\left(\frac{b}{c}\right)^2 - 4\left(\frac{a}{c}\right)} \quad (18)$$

Rewriting the equation 13, we obtain:

$$K_M = \frac{1}{2} \left(K_S - \frac{b}{c} \right) \quad (19)$$

Rewriting the equation 10:

$$q_m = \frac{1}{c K_S} \quad (20)$$

Equations 18, 19 and 20 demonstrate how to obtain the analytical solutions for the three BET degrees of freedom K_S , K_M , and q_m , respectively, starting from a regression of the quadratic function that describes C_{eq}/q vs C_{eq} .

It is important to note that the formation of the parabola is a mathematical implication of the C_{eq}/q vs C_{eq} plot for multilayer adsorption according to the BET model. This property presents an interesting characteristic: the possibility of visually evaluating the experimental adsorption points and/or how closely the data fit the BET model. In other words, if the data do not result in a concave parabolic graph, the adsorption process may not be suitable for BET modeling or may signal some deviation from the idealized BET model.

Furthermore, it is possible to identify potential outlier candidates. Values that do not fit the graph can be easily identified. Ideally, these points should be experimentally repeated in order to verify their reproducibility, confirming whether there is any deviation from the expected BET model.

Exploring the deeper aspects of the equations (C_{eq} when $q = q_m$):

We can derive an equation that determines the C_{eq} for a complete monolayer q_m , based on the values of K_M and K_S . Based on equation 3, when $q = q_m$ the following equality must be truth:

$$\frac{K_S C_{eq}}{(K_M^2 - K_M K_S) C_{eq}^2 + (K_S - 2K_M) C_{eq} + 1} = 1 \quad (27)$$

So:

$$K_S C_{eq} = (K_M^2 - K_M K_S) C_{eq}^2 + (K_S - 2K_M) C_{eq} + 1 \quad (28)$$

$$K_M (K_M - K_S) C_{eq}^2 - 2K_M C_{eq} + 1 = 0 \quad (29)$$

Therefore, the solution for C_{eq} is given by the solution of the quadratic function:

$$C_{eq} = \frac{2K_M \pm \sqrt{(-2K_M)^2 - 4K_M(K_M - K_S)}}{2K_M(K_M - K_S)} \quad (30)$$

$$C_{eq} = \frac{K_M \pm \sqrt{K_M K_S}}{K_M(K_M - K_S)} \quad (31)$$

Once the term $(K_M - K_S)$ will always be < 0 , and consequently the ratio K_S/K_M always > 1 , the positive solution is given by:

$$C_{eq} = \frac{1 - \sqrt{\frac{K_S}{K_M}}}{(K_M - K_S)} \quad (32)$$

The term $(K_M > K_S)$ occurs in Type III isotherms, implying the non-formation of a monolayer over the entire surface.

3. Testing Equations for Experimental Data

Next, some isotherms from the literature that have already been modeled according to the BET isotherm for liquids were selected (Table 1). The analytical solutions proposed in this work was then tested to verify their accuracy against the data reported in the literature.

The isotherm data from the literature were extracted from the graphs using the WebPlotDigitizer program, version 4.6 [6].

Table 1. Comparison between the data of isotherms modeled with the BET equation for the liquid phase (literature data) and the parameters calculated from the analytical solution developed in this work (bold values).

q_m	K_S	K_M	Ref.
0.52 ^a	0.90 ^b	0.0045 ^b	[7]
(0.58)	(0.36)	(0.0039)	This work
103 ^c	1.169 ^b	0.031 ^b	[8]
(102)	(1.187)	(0.031)	This work
110.1 ^d	0.0736 ^e	0.0220 ^e	[9]
(110.0)	(0.0739)	(0.0220)	This work
89.66 ^d	0.0911 ^e	0.0218 ^e	[9]
(88.87)	(0.0940)	(0.0219)	This work
71.3 ^c	0.567 ^b	0.0342 ^b	[10]
(71.4)	(0.581)	(0.0343)	This work

a: mg m⁻² b: L mg⁻¹ c: mg g⁻¹ d: g L⁻¹ e: L g⁻¹

The data obtained in Table 1 demonstrate a high capacity of the analytical solution to reproduce the results given by the numerical methods used in the literature, validating the usefulness of this approach. Allowing for the exploring the additional data

extracted from the equations, as the inflection point and $q = q_m$ point, as shown in the Figure 1.

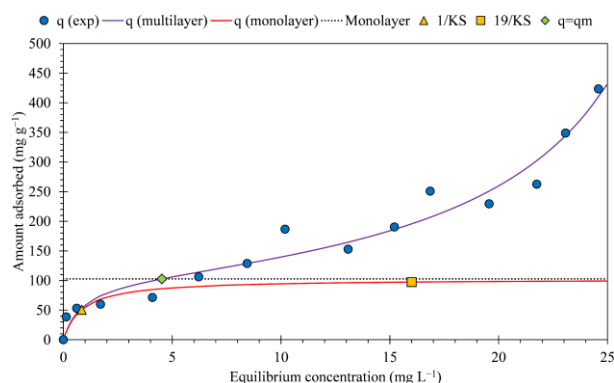


Figure 1. Adsorption isotherm of ritonavir on SBA-15 in a 50 mM phosphate buffer, pH 6.8, at 37 °C adjusted by the BET model for liquids. Experimental data published by Dening et al. [8]

Analyzing the point where $q = q_m$, it is evident that this point represents solely a mathematical relationship between the total adsorbed quantity and the amount adsorbed necessary for monolayer formation q_m . The process of multilayer formation occurs from the beginning of the isotherm, albeit in smaller proportions. When the total adsorbed quantity equals q_m , some of the adsorbate has already been in multilayer form, and the adsorbent surface has not yet been fully covered.

4. Conclusions

The analytical solution for solving the three-parameter isotherm proved to be effective. A thorough analysis of the BET equation for the liquid phase led to the discovery of other interesting relationships.

The proposed equation was compared to experimental data from adsorption isotherms for various solid-liquid systems, demonstrating excellent agreement. The ability of the equations to describe adsorption under different experimental conditions underscores its robustness and versatility.

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