Non-Dissociative Gas Adsorption with Different Chemisorption Geometries on Nanoporous Surfaces

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Abstract

Isotherm equation is one of the important scientific bases for adsorbent selection. There are different isotherms that do not account for an adsorbate, different chemisorption geometries on the nanoporous surface. It is interesting to introduce a general isotherm, which considers different chemisorption geometries of an adsorbate on nanoporous surfaces. In this study, an isotherm for non-dissociative gas adsorption on nanoporous surface was derived by classical thermodynamics. Theoretical study of thermodynamics of adsorption leads to the concept of a constant parameter α which shows the ratio of the number of occupied sites to the number of adsorbed molecules. The derived isotherm was analyzed by several experimental systems of non-dissociative gas adsorption on nanoporous surfaces. By using experimental data, a comparison between the derived isotherm with some famous isotherms like Langmuir, Sips, Toth and Frumkin was provided.

1. Introduction

The reduction of gaseous pollution emissions to atmosphere is a matter of great concern nowadays. Simultaneously, a developing research by the invention of a wide range of treatment technologies with varying levels of successes has accelerated a dramatic progress in the scientific community. Of major interest, adsorption of gases by nanoporous material has experienced considerable growth in recent years. Nanoporous solids are attractive materials for energetically efficient and environmentally friendly catalytic and adsorption separation processes [1-5]. Open framework nanoporous materials are gaining increasing interest because of their exceptional adsorption properties. Zeolites are one of the most famous nanoporous that now widely used in industry as adsorbents and catalysts [6].

Since Isotherm equation is one of the important scientific bases for adsorbent selection, it is important to investigate both experimental and fundamental theories of adsorption. The selection
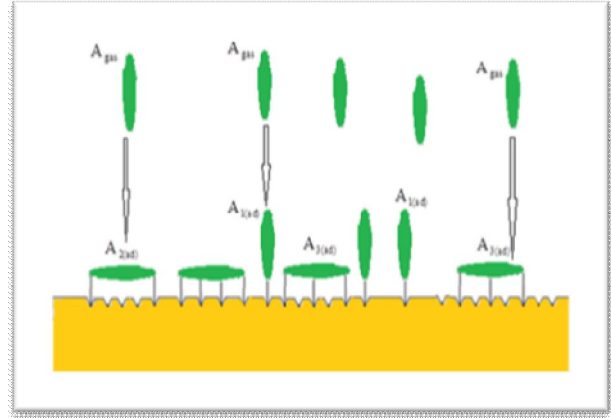
of the appropriate adsorption isotherm is one of the fundamental problems faced during analysis of experimental adsorption data. The most widely used isotherms are Langmuir [7], Frendlich [8], Sips (Langmuir-Freundlich) [9], Toth [10] and Frumkin [11]. However, these isotherms, though simple and effective, have the disadvantage of not accounting for an adsorbate with different chemisorption geometries on the nanoporous surface. The Azizian–Volkov (AV) isotherm has been provided for an adsorbate with two different chemisorption geometries on solid surface. It has been derived by classical and statistical thermodynamic [12, 13]. Some of molecules can be adsorbed with several chemisorption geometries on the nanoporous surface. In this study, we are going to derive an isotherm for non-dissociative gas adsorption with different chemisorption geometries on the nanoporous surface by using classical thermodynamics.

2. Theory

Let us consider that there is a two-dimensional lattice of vacant sites on the nanoporous material and 'A' molecules is adsorbed with different chemisorption geometries on the surface. A typical example for adsorption of 'A' molecules is shown in Scheme 1. In Scheme 1, $A_{1(ad)}$ is used to show one ad-molecule which occupies one site on the surface. $A_{2(ad)}$ is used to show one ad-molecule which occupies two sites on the surface. In a general case, when one 'A' molecule occupies 'i' vacant sites on the surface of nanoporous solid (i=1,2,…), $A_{i(ad)}$ is used to show its chemisorption geometry on the surface. The following process occurs for adsorption of 'A' molecule on the surface:
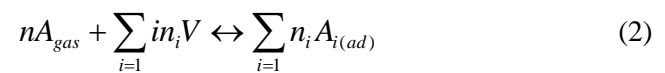
$$A_{gas} + iV \leftrightarrow A_{i(ad)} \qquad (1)$$

where A_{gas} represents 'A' molecule in the gas phase and V represents active vacant site on the surface of the nanoporous solid.

Scheme 1. Non-dissociative gas adsorption with different chemisorption geometries of adsorbate on nanoporous solid surface.

Let us consider at equilibrium 'n' molecules of are adsorbed on the nanoporous solid surface. These molecules are adsorbed with different chemisorption geometries on the surface. The number of molecules that occupy 'i' vacant sites on the surface is n_i. The constraint for the value of n_i is $\sum_{i=1} n_i = n$. The overall adsorption process can be expressed as :

$$nA_{gas} + \sum_{i=1} in_i V \leftrightarrow \sum_{i=1} n_i A_{i(ad)} \qquad (2)$$

The condition of equilibrium is now given by

$$\sum_{i=1} n_i \mu_{A_{i(ad)}} - n\mu_{A_{gas}} - \sum_{i=1} in_i \mu_V = 0 \qquad (3)$$

where μ_v is the chemical potential of vacant site. $\mu_{A_{gas}}$ and $\mu_{A_{i(ad)}}$ are the chemical potentials of 'A' molecule in gas and adsorbed phases, respectively. Upon expressing the chemical potentials in adsorbed phase in terms of activities ($\mu_i = \mu_i^{\circ} + kT \ln a_i$) and the chemical in gas phase in terms of fugacity ($\mu_{A_{gas}} = \mu_{A_{gas}}^0 + k_B T \ln f_A$), one arrives at:

$$\frac{\prod\limits_{i=1}\left(a_{A_{i(ad)}}\right)^{n_i}}{\left(a_v\right)^{\sum\limits_{i=1} in_i}}=(f_A)^n e^{(\frac{-\Delta G^\circ}{kT})} \qquad (4)$$

where $a_{A_{i(ad)}}$ is the activity of ad- molecule and a_v is the activity of vacancy. f_A is fugacity of 'A' in the gas phase. ΔG° is standard free energy which is written as:

$$\Delta G^\circ = \sum_{i=1} n_i \mu_{A_{i(ad)}}^\circ - n\mu_{A_{gas}}^\circ - \sum_{i=1} in_i \mu_v^\circ \qquad (5)$$

Eq. 6 can be written as:

$$\frac{\prod\limits_{i=1}\left(\gamma_{A_{i(ad)}} X_{A_{i(ad)}}\right)^{n_i}}{\left(\gamma_v X_v\right)^{\sum\limits_{i=1} in_i}}=(\phi_A P_A)^n e^{(\frac{-\Delta G^\circ}{kT})} \qquad (6)$$

where $\gamma_{A_{i(ad)}}$ and γ_v are the activity coefficients of ad-molecule and vacancy, respectively. ϕ_A and P_A are fugacity coefficient and pressure of 'A' in the gas phase, respectively. $X_{A_{i(ad)}}$ is the surface mole fraction of $A_{i(ad)}$ expressed as:

$$X_{A_{i(ad)}} = \frac{in_i}{N_{V,max}} \qquad (7)$$

Where $N_{V,max}$ is the maximum number of vacant sites on the nanoporous solid surface. X_v is the surface mole fraction of vacancy written as:

$$X_V = \frac{N_V}{N_{V,max}} \qquad (8)$$

where N_V is the number of vacant sites on the nanoporous surface.

Surface coverage θ can be introduced as follows:

$$\theta = \frac{N}{N_{V,max}} \qquad (9)$$

where N is the number of occupied sites on the nanoporous surface. With respect to the overall process of adsorption, eq 9 can be written as:

$$\theta = \frac{\sum\limits_{i=1} in_i}{N_{V,max}} \qquad (10)$$

To obtain an isotherm, the surface mole fractions are written in terms of θ. The surface mole fraction of vacant sites is expressed by following equation:

$$X_V = 1-\theta \qquad (11)$$

and the surface mole fraction of adsorbate is obtained by combination of eqs 8 and 10:

$$X_{A_{i(ad)}} = \frac{in_i}{\sum\limits_{i=1} in_i}\theta \qquad (12)$$

By replacement of the surface mole fractions in eq 7, one arrives at:

$$\frac{(\theta)^{\sum\limits_{i=1} n_i}}{(1-\theta)^{\sum\limits_{i=1} in_i}}=\left(\gamma_v\right)^{\sum\limits_{i=1} in_i} \prod\limits_{i=1}\left(\frac{\sum\limits_{i=1} in_i}{in_i \gamma_{A_{i(ad)}}}\right)^{n_i} e^{(\frac{-\Delta G^\circ}{kT})}(\phi_A P_A)^n$$

(13)

or

$$\frac{\theta}{(1-\theta)^{\frac{\sum in_i}{n}}}=\left(\gamma_v\right)^{\frac{\sum in_i}{n}} \prod\limits_{i=1}\left(\frac{\sum\limits_{i=1} in_i}{in_i \gamma_{A_{i(ad)}}}\right)^{\frac{n_i}{n}} e^{(\frac{-\Delta G^\circ}{nkT})}\phi_A P_A$$

(14)

Finally, eq 14 can be simplified as:

$$\frac{\theta}{(1-\theta)^\alpha} = KP_A \qquad (15)$$

where K is a constant, which relates to the Gibbs standard free energy of adsorption. This constant parameter (K) equals to

$$K = \left(\gamma_v\right)^{\frac{\sum in_i}{n}} \prod\limits_{i=1}\left(\frac{\sum\limits_{i=1} in_i}{in_i \gamma_{A_{i(ad)}}}\right)^{\frac{n_i}{n}} e^{(\frac{-\Delta G^\circ}{nkT})}\phi_A \qquad (16)$$

α in eq. 15 is a constant parameter and equals to

$$\alpha = \frac{\sum\limits_{i=1} in_i}{n} \qquad (17)$$

The ratio of the number of occupied sites to the number of adsorbed molecules is α. By finding the α it is possible to find the ratio of different

chemisorption geometries of a nanoporous adsorbent. The same parameter was previously provided by Azizian and Volkov for gas adsorption with two different chemisorption geometries on solid surfaces and was shown by 'η' in Av-isotherm [15, 16]. With respect to definition of α (eq 17), it can be concluded that $\alpha \geq 1$. In the case of $\alpha = 1$, one adsorbate occupies only one site on the surface and it is adsorbed by only one chemisorption geometry on the nanoporous surface. Therefore, eq 15 reduces to Langmuir isotherm, when $\alpha = 1$.

Eq 15 is a simple isotherm equation for non-dissociative gas adsorption, which accounts different adsorbate chemisorption geometries on the nanoporous surfaces. Nitta et al [14] derived the same adsorption isotherm, neglecting adsorbate-adsorbate interactions, from a localized model in which one molecule occupies multi-site on a homogeneous surface. The resultant expression is essentially the same as that of Honig and Mueller [15] for single-component adsorption derived from the vacant solution theory. Honig and Mueller suggested essentially the same expression as eq 15 from the vacant solution theory in which one molecule is assumed to occupy one site and an imaginary site occupies a fractional site [15]. Henry [16] suggested a similar expression for single-and multi-adsorptions from the kinetic theory. Eq 15 can be written in linear form as:

$$\ln \frac{P_A}{\theta} = \alpha \ln (1 - \theta) - \ln K \qquad (18)$$

Therefore, $\ln \dfrac{P_A}{\theta}$ is a linear function of $\ln (1 - \theta)$.

The plot of $\ln \dfrac{P_A}{\theta}$ vs ln(1-θ) will be a straight line with the slope of α and the intercept of $-\ln K$.

In addition, eq 15 can be written as in terms of q as:

$$\frac{q}{(q_m - q)^\alpha} = K' P_A \qquad (19)$$

K' in eq 19 is a constant parameter and equals to

$$K' = q_m^{\alpha - 1} K \qquad (20)$$

In the next section, we will discuss the advantages of eq 19 for modeling of experimental data. In addition, a comparison between eq 19 and some famous isotherms, which are listed in Table 1, to fit empirical data of gas adsorption on nanoporous materials will be provided.

Table 1. Some of the important isotherm models which have been used in the present work.

Langmuir	Langmuir-Freundlich	Toth	Frumkin
$\dfrac{\theta}{1-\theta} = KP$	$\dfrac{\theta}{1-\theta} = KP^n$	$\dfrac{\theta^n}{1-\theta^n} = KP^n$	$\dfrac{\theta}{1-\theta} = KP\, e^{-\beta\theta}$

3. Results and discussion

In this section, we are going to analyze the applicability of the derived equation (eq. 19) to fit equilibrium data of gas adsorption on nanoporous surfaces. In addition, we want to provide a comparison between some famous isotherms like Langmuir, Langmuir-Freundlich, Toth and Frumkin with eq 19 to fit empirical data of gas adsorption on nanoporous materials. For this purpose, the experimental data have been selected from the literatures to be analyzed [17, 18]. The chosen empirical system is C_2F_6 adsorption on zeolite 13x [17]. Adsorption of C_2F_6 on zeolite 13x has been studied by Ahn et al [17] at different temperatures (303.15, 323.15 and 343.15 K). Experimental data were fitted to eq 19 by MATLAB R2012a (The Mathworks, Inc).

Table 2. The obtained parameters of isotherms for C_2F_6 adsorption on zeolite 13x at 303.15 K.

Parameters	Eq 19	Langmuir	Langmuir-Freundlich	Toth	Frumkin
K	29.93	0.051	0.126	0.253	0.133
q_m(mol/kg)	2.01	1.84	1.95	1.98	1.90
n or α	1.70	---	0.73	0.67	---
$\square$	---	---	---	---	1.42
R^2	0.9957	0.9889	0.9928	0.9946	0.9937

The best fitting parameters were found at different temperatures and the results are shown in Tables 2, 3 and 4. It is shown in Tables 2, 3, and 4 that there is very good agreement between eq 19 and experimental data of C_2F_6 adsorption on zeolite 13x.

Table 3. The obtained parameters of isotherms for C_2F_6 adsorption on zeolite 13x at 323.15 K.

Parameters	Eq 19	Langmuir	Langmuir-Freundlich	Toth	Frumkin
K	32.82	0.037	0.058	0.091	0.0525
q_m(mol/kg)	1.81	1.71	1.77	1.79	1.75
n or α	1.34	---	0.87	0.81	---
β	---	---	---	---	0.58
R^2	0.9989	0.9977	0.9819	0.9964	0.9964

As expected, the values of α at different temperatures are bigger than one. It is shown in Tables 2, 3 and 4 that by increasing of temperature, the value of α decreases. Actually, at higher temperature, the number of adsorbed molecules of C_2F_6 that occupy more than one site on zeolite 13x surface decreases. The comparison between eq 19 and some famous isotherms such as Langmuir, Langmuir-Freundlich, Toth and Frumkin isotherm equations was provided. The results of fitting are presented in Tables 2, 3 and 4. As seen, eq 19 is more useful isotherm to predict the amount of

adsorbates on zeolite in comparison to other isotherms at different temperatures. The experimental data of C_2F_6 adsorption on zeolite 13x confirms the applicability of derived isotherm.

Table 4. The obtained parameters of isotherms for C_2F_6 adsorption on zeolite 13x at 343.15 K.

Parameters	Eq 19	Langmuir	Langmuir-Freundlich	Toth	Frumkin
K	45.44	0.024	0.028	0.035	0.0265
q_m(mol/kg)	1.67	1.61	1.63	1.65	1.63
n or α	1.16	---	0.96	0.92	---
β	---	---	---	---	0.18
R^2	0.9994	0.9992	0.9511	0.9993	0.9993

As another example, we applied the derived equation (eq 19) to correlate of empirical data of CO_2 adsorption on zeolite 13x at 313 K [18]. Eq 19 can correlate empirical data of CO_2 adsorption on zeolite 13x, successfully. The results of fitting are $q_m = 6.52$ (mol/kg), $K = 1.07$, $\alpha = 2.08$. As expected, the ratio of the number of occupied sites to the number of adsorbed molecules (α) is bigger than one. It can be concluded that CO_2 molecules adsorb with different geometries on zeolite surface.

4. Conclusion

In this paper, an isotherm for non-dissociative gas adsorption on nanoporous surfaces has been derived by classical thermodynamics. One constant parameter (α) in the derived isotherm was found that can interpret the ratio of the number of occupied vacant sites to the number of adsorbed molecules. The α parameter shows the average number of vacant sites which occupied by one adsorbed molecule. The derived isotherm has been analyzed by experimental systems of non-dissociative gas adsorption on nanoporous surface at different temperature. By using the experimental data, comparison between the derived isotherm and some famous isotherms like Langmuir, Langmuir-

Freundlich, Toth and Frumkin was provided. The comparison showed the derived equation has perfect conformity with experimental data of gas adsorption on nanoporous surface.

Acknowledgment

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