International Journal of Innovation Scientific Research and Review
Vol. 03, Issue, 12, pp.2110-2113, December, 2021
Available online at http://www.journalijisr.com
SJIF Impact Factor 4.95

ISSN: 2582-6131

Research Article

THERMODYNAMIC ANALYSIS OF XIAYUKOU #11 COAL'S ADSORPTION

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Received 10th October 2021; Accepted 12th November 2021; Published online 20th December 2021

ABSTRACT

A series of isothermal adsorption experimental data of Xiayukou#11 coal sample in Shaanxi Hanchengmine is transformed into the isosteric adsorption data through a temperature-pressure-adsorption equation. The adsorption enthalpy is calculated by the Clausius-Clapeyron equation. Because the lnP~1/T produces a straight line with a negative slop, the adsorption must be a physical exothermic action. The unit isosteric adsorption enthalpy (IAE) decreases with the increasing of adsorption amount. This phenomenon indicates that the energy on the coal surface is uneven, and adsorption always occurs in the position with high energy first.

Keywords: Clausius-Clapeyron equation; temperature-pressure-adsorption equation; Isosteric Adsorption Enthalpy; unit IAE.

INTRODUCTION

Coal bed methane CBM, also known as gas, is the methane absorbed and flowing in the coal bed due to changes in temperature and pressure. Therefore, gas is the companion mineral resource of coal. Gas will cause disasters such as prominent coal gas outburst and gas explosion, so in the safety production of the coal mine, the gas should be reduced to meet the required low concentration. The gas drained into the atmosphere is a strong greenhouse gas that causes global warming. And CBM is a energy source cleaner than coal. Accurate CBM adsorption data is one of the essential parameters to calculate resources, which is related to the prediction and determines the prospect of CBM resources and the economic value of mining. The study of adsorption on coal seam is very important for evaluating adsorption capacity, and searching a reasonable engineering development scheme [1-3]. The discussion of isosteric adsorption enthalpy is also needed [4-8] for both temperature affect and the thermodynamic interaction between the adsorption medium surface and gas. The easiest way to conduct adsorption experiments in the laboratory is series isothermal adsorption, comparing with isosteric adsorption or isobaric adsorption. Even the series isothermal adsorption data can be reported according to the Langmuir Equation, but it is very hard to answer some thermodynamic questions, such as is the adsorption an endothermic process or an exothermic process? And why? This paper just wants to answer those questions.

THE CLAUSIUS-CLAPEYRON EQUATION

The Clapeyron equation is used to describe the equilibrium pressure P and equilibrium temperature T on a two-phase equilibrium of pure matter. The one of most common chemical processes of gas-liquid balance is gas adsorption. For gas adsorption, the indefinite integral of the Clausius-Clapeyron equation is presented as:

$$\ln P = \frac{\Delta_g^l H_m}{R}\frac{1}{T} + C \qquad (1)$$

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According to the indefinite integral of the Clausius-Clapeyron equation, the lnP vs. 1/T plot should be a straight line. From the slope of the straight line, the mole enthalpy of adsorption can be calculated. For adsorption, the initial state is a gas and the final state is a liquid. There are three approximation treatments in the derivation of the Clausius-Clapeyron equation:

1. Because the molar volume of the gas is much larger than the molar volume, the molar volume of the liquid is ignored;
2. The equation of state of the actual gas is approximately treated as the ideal gas equation of state;
3. It is assumed that the mole process enthalpy is a constant, and does not change with temperature T.

The mole process heat is numerically equal to the mole process enthalpy, but is always positive. The enthalpy could be positive or negative. If the lnP ~1/T line of the gas adsorption process has a negative slope, the mole adsorption enthalpy is negative, the adsorption process must be an exothermic process. Since the temperature increase is disadvantage for the exothermic process, then under the same conditions (adsorbent, pressure, coal sample), the adsorption amount will decrease with the temperature increasing.

TEMPERATURE-PRESSURE-ADSORPTION EQUATION

There are three variables in adsorption experiments, namely adsorption amount V, temperature T, and pressure P. The adsorption conducted at constant temperature is used to study the relationship between the adsorption amount and the pressure, and is called the isothermic adsorption, which is easy to be conducted in the laboratory. The data of isothermic adsorption is commonly treated by the Langmuir adsorption isothermal equation. The Clausius-Clapeyron equation requires the condition of isosteric adsorption. Therefore, the data of isothermic adsorption must be transform into usable isosteric adsorption. The connecting bridge between the isothermic adsorption and the isosteric adsorption is the temperature–pressure–adsorption equation (TPAE) [9-13]. To understand the interrelationship between temperature and pressure, the temperature T of adsorption and the adsorption quantity V are taken as the independent variables, and the pressure P is the dependent variable as:

$$\mathrm{lnP} = \frac{1}{\beta}\ln\left[\frac{V\sqrt{MT}-A}{BT^{1.5}\exp\left(\frac{\Delta}{T}\right)}\right] \quad (2)$$

The TPAE another form is presented as:

$$V = \frac{1}{\sqrt{MT}}\left[A + BP^{\beta}T^{1.5}\exp\left(\frac{\Delta}{T}\right)\right] \quad (3)$$

In Equation (3), the temperature and pressure are the independent variables, but the adsorption amount V is the dependent variable, looking like Langmuir adsorption isothermal equation.

ISOTHERMIC ADSORPTION DATA

Some scholars measured the #11 coal sample in Xiayukou of Shaanxi Hanchengmine. Those isothermic adsorptions are conducted with the temperature between 20 and 50 and with upper limit pressure of 8.0MPa.The Langmuir adsorption isothermal equation is presented as:

$$V = \frac{abP}{1+bP} \quad (4)$$

Table 1: Measured conditions of Xiayukou #11 coal samples and Langmuir parameters [1]

20℃		30℃		40℃		50℃	
a	**b**	**a**	**b**	**a**	**b**	**a**	**B**
63.1	0.62	52.3	0.65	35.8	0.74	26.5	0.77

RESULTS AND DISCUSSIONS

TPAE'sparameters regression

The adsorption amount of Xiayukou #11 coal at a specified temperature and a pressure is calculated by submitting Langmuir parameters into Equation (4). According to the original author, there were8 pressure points per temperature up to8.0MPa. In the regression, there are 14 pressure points per temperature up to14.0MPa. Therefore, total 56adsorption amount for four testing temperatures, are calculated and used for the regression of determining the four parameters A, B, Δ and β of TPAE [13]. Table 2 presents these four regressed parameters of Xiayukou #11 coal. It should be noticed that the TPAE with corresponding four regressed parameters only suitable for specified coal at certain temperature range (20 to 50) and certain pressure range (up to 14.0MPa).

TPAE's verification

With the four parameters A, B, Δ and β , Equation (3) can be used to create a three dimensional curvature surface in the certain temperature range (20 to 50) and certain pressure range (up to 14.0MPa). Figure 1 is the "measured points" and TPAE surfaces of the Xiayukou #11 coal samples used. The "measured points" are the points calculated by the Langmuir adsorption isothermal equation.

Table 2: four regressed parameters of Xiayukou #11 coal

A	**0.168**
B	0.0000167
β	0.2758
Δ	2964
$\bar{\delta}$ /%	6.05

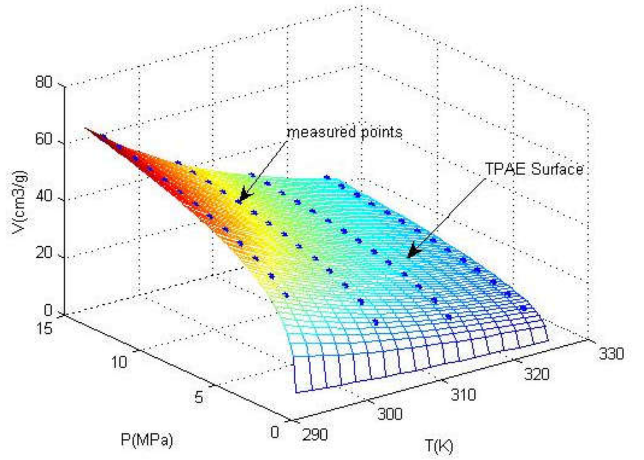

Figure 1: Measured point and TPAE surface of Xiayukou#11 coal of Shaanxi Hanchengmine

At the same time, TPAE can be used to calculate the 56adsorption amount at the exactly the same specified temperatures and pressures. The "calculated points" are the points calculated by the TPAE. The corresponding mean relative error $\bar{\delta}$ between the "measured points" and the "calculated points" is then calculated and listed in Table 2 too. Both figure 1 and the mean relative error have verified that the series isothermic adsorption can be perfectly represented by the TPAE.

lnP ~ 1 / T plots

The equation (1) can be used to calculate the isosteric adsorption enthalpy. For example, the adsorption amount is set up as a constant of 5.0cm^3/g, follow the steps of:

1. assumes a thermodynamic temperature T substitution equation (2);
2. then calculate the natural logarithm of adsorption pressure lnP;
3. the above steps are repeated for a series of temperature T, the corresponding series of the natural logarithm of adsorption pressure lnP are obtained.

According to the indefinite integral Clausius-Clapeyron Equation, the plot of 1/T~lnP at an adsorption amount of 5.0cm^3/g can be produced, and shown in Figure2.

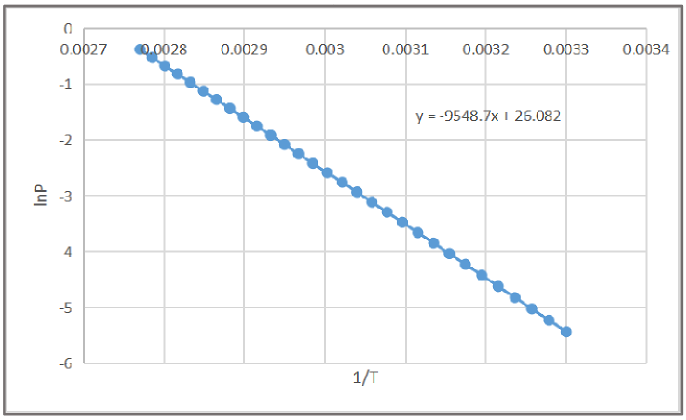

Figure2: 1/T~lnP at an adsorption amount of 5.0cm^3/g for Xiayukou #11 coal of Shaanxi Hanchengmine.

As can be seen from Figure 2, at the adsorption amount of 5.0cm^3/g, the lnP~1 / T forms a straight lines with a negative slope, -9548.7. That is to say, the isostericadsorption enthalpy (IAE) of Xiayukou #11 coal of Shaanxi Hanchengmine is negative. In other words, the adsorption of Xiayukou #11 coal is exothermic process.

Isostericadsorption enthalpy IAE

The IAE and an unit IAE can be obtained as:

1. The slope in lnP~1/T plot times by the gas constant R=0.008314KJ/ (mol K), results an IAE, KJ/mol;
2. The IAE was divided by the isosteric amount (here it is 5.0cm^3/g), an unit IAE would be obtained, KJ mol^{-1} cm^{-3} g.

Based on the procedure mentioned above, the IAE and an unit IAE at different adsorption amount can be obtained. Table 3 listed the unit IAE at different adsorption amount.

Table 3: unit IAE at different adsorption amount of Xiayukou #11 coal

adsorbed amount cm^3/g	unit IAE KJ.mol/(cm^3.g)
5.0	-15.88
7.5	-10.59
10.0	-7.94
12.5	-6.35
15.0	-5.29

The data in Table 3 show that the absolute value of unit IAE decreases with the increasing of adsorption amount. This phenomenon indicates:

1. The surface of the adsorption medium (coal seam) is not smooth, and the energy of the surface is uneven; and
2. Adsorption always occurs at higher energy (more negative) and more active positions first which can release more energy and make the system more stable.

Figure3 show the relationship between unit IAE and the adsorption amount of the Xiayukou #11 coal of Shaanxi Hanchengmine.

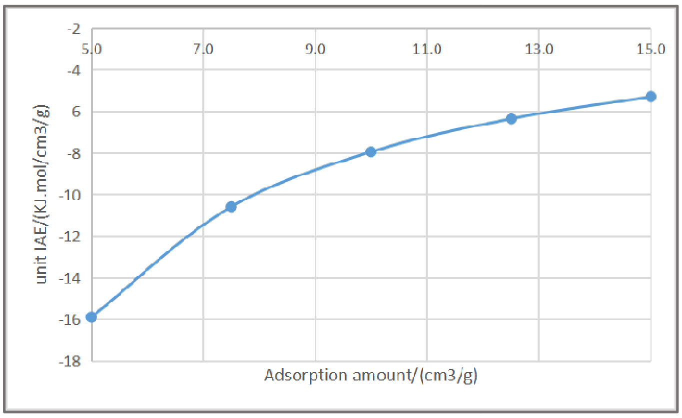

Figure 3: The relationship between unit IAE and the adsorption amount of Xiayukou #11 coal

CONCLUSION

The adsorption isotherm data of Xiayukou #11 coal has been used to regressed 4 parameters (A, B, Δ, β) of the temperature-pressure-adsorption equation (TPAE). TPAE can be transformed into appropriate format to deal with any one of isotherm adsorption, isosteric adsorption, or isobaric adsorption. Because the lnP~1/ T produces a straight line with a negative slop, so the adsorption of Xiayukou #11 coal bed gas is physical exothermic adsorption. Because the unit isosteric adsorption enthalpy (IAE) decreases with the increasing of adsorption amount, the energy on the coal surface is uneven. The adsorption always occurs in the position with high energy and large activity first, and then in the position with low energy and small activity.

Symbol Description

A	—	Micropore geometry form constant, dimensionless
B	—	Absorption flow coefficient, dimensionless
C	—	Integral constant
M	—	Adsorbed molecular weight, methane molecular weight is 16
$\Delta_\alpha^\beta H_m$	—	Enthalpy, KJ/mol
P	—	Adsorption pressure, MPa
R	—	Gas state constant；J/(mol.K)
T	—	Absorption temperature, K；
V	—	Adsorption quantity, cm^3/g；
a	—	Langmuir volume, cm^3.g^{-1}
b	—	the reciprocal of the Langmuir pressure, MPa^{-1}
β	—	Parameters of pressure influence dimensionless
Δ	—	The energy difference between the lowest potential energy and the activation energy of an adsorbed molecule. K；
$\bar{\delta}$	—	Average relative error, 100%

superscript, subscript

g	—	Gas phase
l	—	liquid phase
m	—	Moore
α	—	The initial state
β	—	The final state

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