



Article A New Adsorption Equation for Nano-Porous Shale Rocks and Its Application in Pore Size Distribution Analysis

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Abstract: Adsorption equations are important to analyze the pore size distribution (PSD) of shale and the adsorption behavior on it. However, the accurate description of nitrogen adsorption on shale by current adsorption equations is difficult to achieve due to the heterogeneous pore structure of shale. In our study, new adsorption isotherms that can properly depict the adsorbed amount of nitrogen were built for shale rocks considering both the processes of nitrogen adsorption and the cylindrical pore shape property of shale. When performing a regression analysis on five sets of experimental adsorption data using the developed adsorption equations, the R-square ranged from 0.739 to 0.987. Based on the pore shape determined by adsorption–desorption curves, the distinct R-square indicated that our equation is not valid for shale samples with ink-bottle pores and pores formed by schistose materials, but that it is suitable for shale rocks based on the developed adsorption equations as capillary condensation volume is involved in the total adsorbed amount. Thus, the PSDs of shale rocks with cylindrical pore and slit pore were analyzed by the new adsorption equation.

Keywords: cylindrical pore model; adsorption equation; capillary condensation; pore size distribution

1. Introduction

As an unconventional gas reservoir, gas shale has become one of the major natural gas exploration targets in recent years [1,2]. Furthermore, the majority of nanopores in shale, which is a porous material, provide a large pore surface area for the storage of gases, such as methane, carbon dioxide and hydrogen. Because of shale's gas storage property and its potentially large recoverability s, it attracts much attention; many investigations into the gas adsorption behavior in shale pore networks and the pore structures of shale reservoirs have been conducted to advance shale gas exploration [3,4].

Unlike in conventional reservoirs, the pores in shale reservoirs are predominantly nanopores in organic matter and clay minerals because shale contains large amounts of total organic carbon (TOC) and clay minerals [5–7]. Therefore, it is difficult to characterize shale pore structures by using common techniques [8]. Furthermore, the components of shale result in complex pore characteristics and wide pore size distributions. To investigate the pore structure of such heterogeneous reservoirs, a N₂ adsorption–desorption experiment is normally performed to analyze the pore size distribution of shale [9]. However, there is no appropriate equation for the adsorption of N₂ on shale. Thus, the PSD of shale can only be derived from discrete measuring points.

Unlike high-pressure methane adsorption, low-pressure and low-temperature N_2 adsorption is dominated by monolayer adsorption, multilayer adsorption and capillary condensation, which is clarified by BDDT (Brunauer, Deming, Deming and Teller) adsorption isotherm classification [10,11]. As we know, the Langmuir adsorption equation



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). is widely accepted to describe monolayer adsorption, which assumes only one type of adsorption site on the surface of the adsorbent [12–24]. In addition, the BET (Brunauer, Emmett and Teller) adsorption equation is the most popular equation for multilayer adsorption, which assumes that the interaction on the adsorbent surface is much larger than that between neighboring adsorbate molecules [25–31]. Moreover, capillary condensation obeys Kelvin theory, and it is depicted by empirical liquid-adsorption equations [32,33]. Thus, these frequently used adsorption equations, which are based on homogeneous models, cannot be applied to interpret the coexistence of monolayer adsorption, multi-layer adsorption, and capillary condensation simultaneously. In our previous work, we built an adsorption equation that includes adsorption processes such as monolayer adsorption, multilayer adsorption, and capillary condensation [10].

Adsorption behavior is not only influenced by the adsorption process but also by pore shape. Nanopores in shale are confirmed by the de Boer classification method as cylindrical pores closed at one end, parallel-plate pores, wedge-shaped pores, and slit pores [34]. Furthermore, pore models are widely considered in studies of adsorption properties, especially for conditions in which capillary condensation and desorption hysteresis take place during the pore size distribution analysis.

In terms of the conditions for the occurrence of capillary condensation, the cylindrical pore model is applied to analyze the key factors in capillary condensation, such as pore radius, solid–liquid surface tension, and temperature [35–37]. The slit pore model is the most popular method with which to analyze capillary condensation in micro scale [38,39]. In addition, the sphere pore model is chosen to analyze the influential factors in capillary condensation [40]. The adsorption–desorption hysteresis resulting from capillary condensation is also studied by given pore models. To clarify the hysteresis mechanism, the nucleation mechanism in nanopores, and the differential pressure between condensation and evaporation, pore models with cylindrical geometry are widely used [41,42]. Moreover, ink-bottle pores and the cone pore model are utilized to analyze hysteresis behavior [43,44]. Based on previous studies, the ink-bottle pore model, slit pore model and cylindrical pore model are frequently used to analyze the characteristics of adsorption in porous materials, and the cylindrical pore model was adopted to build a new adsorption equation in our study [45–52].

Additionally, the pore size distribution analysis of shale is usually dependent on nitrogen adsorption experiments. The common macroscale thermodynamic method of PSD analysis, the BJH (Barrett, Joyner and Halenda) method, the SF (Saito and Foley) theory, and the HK (Horváth–Kawazoe) model are widely used to fit in with the adsorption experimental data in pore size distribution algorithms [53]. The former two methods are developed considering cylindrical pores, in which the BJH method is the technique used for estimating the pore volume critically based on the Kelvin equation, and the SF model focuses on the pore potential equation. The third method, the HK model, evaluates the PSD through the differentiation of the adsorbate amount adsorbed [54]. All these methods estimate the PSD with a uniform interface model, which ignores the heterogeneous properties of shale caused by its complex components and pore structure.

In this study, we built an adsorbed volume occupied by multilayer adsorption and capillary condensation in shale based on the cylindrical pore model, and then integrated this into the developed adsorption equation. Furthermore, the experimental nitrogen adsorption data from different shale samples were also integrated into the new adsorption equation. Finally, in this study, the applicability of the developed adsorption equation to the pore size distribution calculation of shale is discussed.

2. Materials and Methods

We collected one shale sample (A3) from the Lower Sinian Doushantuo Formation and two shale samples (A1 and B2) from the Lower Cambrian Niutitang Formation in the Sichuan Basin, China, and two shale samples (A2 and B1) from the Yanchang Formation in the Ordos Basin in northern China, deposited in the late Triassic (Figure 1). These three shale formations were identified as prospective shale gas target layers in China due to their widespread burial thickness distribution and relatively high organic matter content, which indicate considerable gas-bearing potential and, therefore, that they should be given priority for shale gas exploration [55–57]. Geological characteristics of shale samples are shown in Table 1.



Figure 1. Images of shale samples selected from Ordos basin and Sichuan basin.

Sample ID	Basin	Lithology	Formation
A1	Sichuan basin	Dark-black shale	Niutitang
A2	Ordos basin	Dark-black shale	Yanchang7
A3	Sichuan basin	Black shale	Doushantuo
B1	Ordos basin	Pale-black shale	Yanchang7
B2	Sichuan basin	Pale-black shale	Niutitang

Table 1. Geological characteristics of shale samples.

The tests were conducted by the Quadrasorb SI surface area and pore-size analyzer (Figure 2). In our experiment, nitrogen was used as the adsorbate. The lower limitation of the specific surface area was $0.01 \text{ m}^2/\text{g}$ for nitrogen. In the pore size distribution analysis, the minimum pore volume was $0.0001 \text{ cm}^3/\text{g}$ (at standard temperature and pressure), and the pore-size range was 0.35 to 400 nm.



Figure 2. Diagram of the Quadrasorb SI instrument.

All samples were crushed to 60 to 80 mesh (180 to 250 μ m). The pulverized samples were dried and vacuumed at 353.15 K for 12 h for degassing in order to prepare the samples for the gas adsorption method. In the gas expansion process, the crushed samples were added in low-temperature-resistant test tubes in the experimental instrument, and N₂ adsorption–desorption isotherms were obtained under relative pressure ranging from 0.01 to 0.995 at 77 K. The adsorption isotherm was derived point by point by measuring the quantity of nitrogen adsorbed (*V*) and the equilibrium pressure as the relative pressure (*P*/*P*₀) increasing. By contrast, the desorption isotherm could be obtained by measuring the quantities of gas removed from the sample as pressure decreasing. With the QuadraWin software, the adsorption–desorption isotherm curves were generated automatically. The measured adsorption isotherms of N₂ on shale samples are shown in Figure 3.



Figure 3. Shale adsorption isotherms (A1).

3. Results

3.1. Adsorption Volume Constitution in Cylindrical Pores

Nitrogen adsorption isotherms belong to type IV, based on the BDDT adsorption isotherm classification [11], which indicates that the processes of nitrogen adsorption on shale includes monolayer adsorption, multilayer adsorption, and capillary condensation. At the initial stage of adsorption, only monolayer adsorption occurs, and free gas molecules are present in the pores. The number of molecule layers increases with the pressure and there are still some free gas molecules in the rest space of the pores. When the pressure rises to a certain value, capillary condensation starts to take place and all pores are filled gradually by gas molecules. Thus, the adsorbed volume can be divided into the volume of the multilayer adsorption and the volume of the capillary condensation [10].

Assuming that pores with various pore radii randomly distribute in the shale matrix (Figure 4), at any given pressure P_i , pores with radii of less than r_i are filled by adsorbate. Subsequently, all the filled pores can be simplified as an equivalent cylindrical pore model, characterized by length L_i and radius r_{pi} (Figure 5). Obviously, the radius of the equivalent model r_{pi} is the same as the radii of the pores (r_i) which can be filled by adsorbate at pressure P_i . Furthermore, the length of the equivalent cylindrical pore L_i is affected by the length $l_i (j \le i)$ of the pores with radii of less than r_i , which is given as:

$$L_{i} = \frac{\sum_{j=1}^{i} l_{j} \pi r_{j}^{2}}{\pi r_{pi}^{2}}$$
(1)



Figure 4. Schematic diagram of cylindrical pores in shale.



Figure 5. Equivalent cylindrical pore model for pore network in shale.

After assuming that the pores in the shale are cylindrical pores, the adsorbed adsorbate in shale nanopores can be depicted as the schematic in Figure 6. The cores of the cylindrical pores imply condensed liquid formation due to capillary condensation, and the external annular zone represents multilayer adsorption starting from the pore wall.



Figure 6. Volume division of cylindrical pore.

3.2. Construction of Adsorption Equation

It is clear that the main challenge of establishing the new adsorption equation is calculating the volumes occupied by multilayer adsorption and capillary condensation, respectively (Figure 4). When the pores are filled with adsorbate, the adsorbed volume is calculated by:

$$V_{ad} = V_{multi} + V_{cc} \tag{2}$$

As we know, the BET equation is usually used to determine the adsorbed amount of multilayer adsorption; thus, we discuss the applicability of the BET equation first. At low relative pressure, the BET equation depicts the adsorption data well. However, as the pressure increases ($P/P_0 > 0.4$), the BET curve deviates from the experiment data (Figure 7). Compared to the adsorption–desorption curve in Figure 3, when $P/P_0 > 0.4$, a hysteresis loop exists, which indicates that capillary condensation occurs at this pressure condition. Therefore, we infer that capillary condensation inhibits multilayer adsorption behavior, and that the BET equation is not applicable for multilayer adsorption when capillary condensation starts to take place.



Figure 7. Regression of experimental data by BET adsorption equation.

Alternatively, the multilayer adsorption volume V_{multi} is a function of the adsorbed layer n and the maximum adsorbate volume of a single layer V_m , and given as:

$$V_{multi} = V_m n \tag{3}$$

The number of adsorbed layers *n* is depicted by the Halsey equation:

$$n = \left[\frac{-a}{RT\ln(P/P_0)}\right]^{\frac{1}{r}}$$
(4)

where *a* is a parameter that represents the homogeneity of uniform or non-uniform surfaces, and *r* reflects the attraction of the adsorbent for the adsorbate. The small *r* means that the force on the interface is van der Waals, which results in a greater attraction distance [58].

The volume of the capillary condensation V_{cc} derived from the cylindrical model with equivalent length *L* is:

$$V_{cc} = \pi r_k^2 L \tag{5}$$

where r_k is the radius of the capillary condensation, which is calculated by the Kelvin equation:

$$_{k} = -\frac{2\sigma\cos\theta V_{M}}{RT\ln(P/P_{0})} \tag{6}$$

The value σ is the surface tension, θ is the contact angle, and V_M is the molar mass of the adsorbate.

For the external annular zone, assume that it is filled by adsorbate, then:

$$V_m n = \pi L (2r_k t + t^2) \tag{7}$$

where *t* is the total thickness of the adsorbed layers and is given as:

I

r

$$t = t_m \left[\frac{-a}{RT \ln(P/P_0)} \right]^{\frac{1}{r}}$$
(8)

where t_m is the thickness of a single adsorbate layer.

Combining Equations (2) and (8), we develop a new adsorption equation, as follows:

$$V = \frac{V_m \left(\frac{a}{RT}\right)^{\frac{1}{r}}}{\left[-\ln\left(\frac{P}{P_0}\right)\right]^{\frac{1}{r}}} \left[1 + \frac{1}{\left(\frac{a}{RT}\right)^{\frac{1}{r}} \frac{t_m RT}{\sigma \cos\theta V_M} \left[-\ln\left(\frac{P}{P_0}\right)\right]^{1-\frac{1}{r}} + \frac{1}{4} \left(\frac{a}{RT}\right)^{\frac{2}{r}} \frac{t_m^2 R^2 T^2}{\sigma^2 \cos^2 \theta V_M^2} \left[-\ln\left(\frac{P}{P_0}\right)\right]^{2-\frac{2}{r}}}\right]$$
(9)

If we define $(a/RT)^{\frac{1}{r}}$ as A, $\frac{1}{r}$ as B, and $t_m RT/(\sigma \cos \theta V_M)$ as C, then we obtain the simplified adsorption equation:

$$V = \frac{V_m A}{\left[-\ln(P/P_0)\right]^B} \left[1 + \frac{1}{AC\left[-\ln(P/P_0)\right]^{1-B} + \frac{1}{4}(AC)^2 \left[-\ln(P/P_0)\right]^{2-2B}}\right]$$
(10)

4. Discussion

4.1. Adsorption Isotherm Confirmed by Adsorption Equation

The new adsorption equation was applied to perform a regression analysis on the adsorption isotherms of the nitrogen on the shales. The results are presented in Figure 8 and the fitting parameters are listed in Table 2.



Figure 8. Experimental adsorption data and relevant adsorption isotherms fitted by new adsorption equation.

Table 2. Value of variables for five shale sam	ples.
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Sample	V_m	A	В	С	R-Square
A1	0.16835	6.61549	0.32524	9.53452	0.98719
A2	0.365124	7.235891	0.34235	9.45812	0.95000
A3	0.38336	8.52541	0.20451	9.82451	0.97331
B1	0.20359	3.31599	0.65949	8.85840	0.76594
B2	0.90222	2.74084	0.12231	8.79350	0.73911

Obviously, the developed adsorption equation is partially applicable to shale samples. The calculated adsorption isotherms match well with the experimental data for shales A1, A2, and A3, while they fail to match the experimental data for shales B1 and B2. For B1 and B2, the determined adsorption isotherms are greater than the experimental data at low relative pressure, but less than these experimental data at high relative pressure. In addition, the R-squares of the five curve fittings range from 0.73911 to 0.98719. It can be seen that the R-squares are all greater than 0.9 for A1, A2, and A3.

The V_m , which represents the monolayer's adsorption behavior, reveals that the interaction force between the shale (adsorbent) and the first adsorbed nitrogen layer for A3 is stronger than the values for A1 and A1. This observation corresponds to the position of the inflection point in Figure 6. However, if B2 and B3 are included in the analysis, there is an anomalous trend. The inflection point of A3 is higher than that of B2, but the V_m for B2 is greater.

Combining Equations (8) and (10), the thickness of the adsorbed layer is calculated by:

$$t = t_m A [-\ln(P/P_0)]^B$$
(11)

The t-curves for the five samples are exhibited in Figure 9. As the relative pressure rises to 0.9, all the t-curves of the five samples show steep sections. This indicates external

interface adsorption at higher pressure. However, the curves are various when the relative pressure is less than 0.9. For A1, A2 and A3, the adsorbed layers increase rapidly at pressure $P_r < 0.1$, which may be caused by the strengthening of the interactions between the adsorbate and the adsorbent. At a pressure of $0.1 < P_r < 0.9$, the adsorbed layers stop increasing and capillary condensation is predominant [59]. In addition, the t-curves of B1 and B2 are totally different from those of A1, A2 and A3. The adsorbed layers of B1 increase gradually, and there is no inflection point of monolayer adsorption or multilayer adsorption. B2 shows a different variation tendency in that the amount of multilayer adsorption is small and the thickness of the adsorbed layers always remains around 1 nm, even if the pressure almost reaches saturated vapor pressure.



Figure 9. The t-curves of five shale samples.

After a comprehensive analysis of the curve fitting and physical meaning of variables *A* and *B*, it was found that the built adsorption equation is suitable for samples A1, A2 and A3, but not valid for B1 and B2. This may have resulted from the assumption of the pore shape in this study. As the pore model assumed cylindrical pores, only pore networks characterized by pores whose pore radius was constant could be depicted accurately by the new adsorption equation. When classifying the pore types of the five samples by de Boer classification [60], it was found that A1 and A3 belong to type B, with slit-shaped pores (Figure 10a) and that A2 belongs to type A, with cylindrical pores (Figure 10b).



Figure 10. Adsorption–desorption isotherms of shale samples. (**a**) Slit-pore samples (A1 and A3); (**b**) cylindrical pore sample (A2); (**c**) ink-bottle-shaped sample (B2); (**d**) micropore-dominated samples (B1).

Nevertheless, the pores in B2 are ink-bottle-shaped due to a typical type E adsorptiondesorption isotherm (Figure 10c). Since the capillary condensation is governed by the ratio and range of the fluid–fluid interaction and the fluid–matrix interaction [61,62], variations in the pore diameter result in the disorder of the interfaces in ink-bottle pores [63]. The potential of the adsorbent and adsorbate system is affected by the position of the liquid–vapor interface. As a result, capillary condensation mechanisms in pores with ink-bottle shapes and cylindrical shapes are significantly different [64], and the adsorption equation for the cylindrical pore model obviously fails to depict the adsorption behavior of ink-bottle pores.

The shapes of the pores in B1 were ambiguous when they were analyzed by de Boer classification. Furthermore, B1 was a typical micropore sample that belonged to the type B adsorption isotherm on the basis of the BDDT adsorption isotherm classification (Figure 10d) [11]. This may have resulted from the capillary condensation already having taken place in the micropores before the onset of capillary condensation in the mesopores [65]. Therefore, the adsorption behavior and nucleation in the micropore-dominated sample B1 was different from that in the other samples with large amounts of mesopores and macropores.

In summary, it is appropriate to use the developed adsorption equation for shale samples with cylindrical pores and slit pores.

4.2. Pore Size Distribution Derived from Adsorption Equation

As mentioned in the BJH (Barrett, Joyner and Halenda) theory, pore volume substantially relates to the volume of capillary condensation. Based on Figure 6, the calculation of the pore volume V_p is derived from the geometrical relationship between the Kelvin radius r_k , the pore radius r_p , and the inner capillary volume, V_{cc} , as in [66]:

$$V_{pi} = V_{ki} \frac{r_{pi}^2}{r_{ki}^2}$$
(12)

Assume that when capillary condensation takes place in the pores, these pores are all filled with adsorbate at any given pressure *P*. Subsequently, the pore radius is given as:

$$_{p} = r_{k} + t \tag{13}$$

Combining Equations (6) and (10), the Kelvin radius can be expressed as:

$$r_k = -\frac{2t_m}{C\ln(P/P_0)}\tag{14}$$

Rearranging Equations (11), (13), and (14), r_p is:

$$r_p = t_m A \left[-\ln(P/P_0) \right]^{-B} - \frac{2t_m}{C \ln(P/P_0)}$$
(15)

Substituting Equations (14) and (15) into Equation (12), the pore volume V_{pi} is:

$$V_{pi} = \left[1 + \frac{AC(-\ln(P_i/P)^{1-B})}{2}\right]^2$$
(16)

Analyzing the pore size distribution of the shale samples A1, A2, and A3 with the new adsorption equation (Figure 11), the dominant pore diameters of these three shale samples are 3.32 nm, 16.94 nm, and 12.44 nm, respectively. Meanwhile, as shown in Figure 11, the pore volume of A2 is obviously larger than those of A1 and A3, and A1 has the smallest pore volume. This result matches the finding of Thommas's research based on adsorption–desorption isotherms. Adsorbents with large pores result in the higher relative pressure of the start-point of capillary condensation and a wider hysteresis loop [67]. Analyzing the

adsorption–desorption isotherms of three shale samples (Figure 10a,b), the pores in A1 are the smallest due to the lowest relative pressure. It is difficult to compare dominant pore sizes for A2 and A3 only from the start-point of capillary condensation because of their nearly identical relative pressure. However, when considering the width of the hysteresis loop, the dominant pore size can be ranked as A2 > A3 > A1, which verifies the result derived from pore size distribution analysis.



Figure 11. Pore size distribution of shale samples. (a) A1; (b) A2; (c) A3.

5. Conclusions

In this study, a new adsorption equation was developed to depict the adsorption behavior of nitrogen in shale nanopores. The application of this new equation on five shale samples was discussed regarding the curve fitting and variable analysis. In addition, we built a new approach to calculate the pore size distribution based on the developed adsorption equation. The major conclusions are summarized as follows:

- 1 We propose a cylindrical pore model by simplifying complex pore networks as tubes with different radii. The model considers that the adsorption processes of nitrogen in shale nanopores are monolayer adsorption, multilayer adsorption, and capillary condensation. In addition, a new adsorption equation was derived from the cylindrical pore model by regarding the total adsorption volume as consisting of the inner capillary volume and the multilayer adsorption volume. The fitting results revealed that the adsorption equation is able to properly depict the experimental data for shales with cylindrical pores and slit pores.
- 2 The t-curves derived from the parameters of the adsorption equation demonstrate the multilayer adsorption behavior in shale nanopores. When the relative pressure is less than 0.9, the microporous shale shows a steadily increasing t-curve because of the micropore filling. However, the inflection points at relative pressure around 0.1 indicate the saturated monolayer adsorption in other samples. When the relative pressure is greater than 0.9, the adsorption on the external interface results in a steep section on the.
- 3 For the cylindrical pore model, the pore volume is proportional to the inner capillary volume. When the capillary condensation volume at any relative pressure is calculated by the new adsorption isotherm, the pore size distributions of the shales can be determined successfully. In summary, it is a time-saving method to evaluate the pore volume and the dominant pore size.

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