Research Article

Study on Shale Adsorption Equation Based on Monolayer Adsorption, Multilayer Adsorption, and Capillary Condensation

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Shale gas is an effective gas resource all over the world. The evaluation of pore structure plays a critical role in exploring shale gas efficiently. Nitrogen adsorption experiment is one of the significant approaches to analyze pore size structure of shale. Shale is extremely heterogeneous due to component diversity and structure complexity. Therefore, adsorption isotherms for homogeneous adsorbents and empirical isotherms may not apply to shale. The shape of adsorption-desorption curve indicates that nitrogen adsorption on shale includes monolayer adsorption, multilayer adsorption, and capillary condensation. Usually, Langmuir isotherm is a monolayer adsorption model for ideal interfaces; BET (Brunauer, Emmett, Teller) adsorption isotherm is a multilayer adsorption model based on specific assumptions; Freundlich isotherm is an empirical equation widely applied in liquid phase adsorption. In this study, a new nitrogen adsorption isotherm is applied to simultaneously depict monolayer adsorption, multilayer adsorption, and capillary condensation, which provides more real and accurate representation of nitrogen adsorption on shale. In addition, parameters are discussed in relation to heat of adsorption which is relevant to the shape of the adsorption isotherm curve. The curve fitting results indicate that our new nitrogen adsorption isotherm can appropriately describe the whole process of nitrogen adsorption on shale.

1. Introduction

Shale gas has attracted much attention in United States, China, Canada, and so forth, because of the gas storage mechanism and recovery potential of shale gas reservoirs [1, 2]. To investigate gas adsorption capacity and pore size distribution of shale rocks, high-pressure methane adsorption and low-pressure nitrogen or carbon dioxide adsorption experiments are conducted, respectively. Many researches have been done to find and modify adsorption equations suitable for describing methane adsorption. Considering methane adsorption as monolayer adsorption, Langmuir equation, L-F (Langmuir-Freundlich) equation, and M-L (modified Langmuir) equation are successfully applied to evaluate methane adsorption [3–5]. Furthermore, D-R (Dubinin-Radushkevich) equation, D-A (Dubinin-Astakhov) equation, and S-D-R (supercritical Dubinin-Radushkevich) equation are also used with consideration of methane adsorption as

micropore filling [6–8]. For carbon dioxide adsorption, to take into account the monolayer adsorption property, both Langmuir equation and L-F equation are applied to depict variations of the adsorption capacity with pressure [9–11]. On the contrary, it is hard to find an equation to depict low-pressure nitrogen adsorption because of the complicated adsorption mechanism. On the basis of BDDT (Brunauer-Deming-Deming-Teller) adsorption isotherm classification, nitrogen adsorption belongs to type IV, which indicates that it includes three processes: monolayer adsorption, multilayer adsorption, and capillary condensation. Unfortunately, the majority of adsorption equations are developed based on only one kind of adsorption mechanism, and they can be categorized into three aspects: monolayer adsorption, multilayer adsorption, and micropore filling.

In terms of monolayer adsorption, a widely accepted one is Langmuir adsorption equation which assumed only one type of adsorption sites on the surface of adsorbent [12, 13].

When extending the Langmuir equation for gas-liquid-phase adsorption studies, two types of sites are considered and the relationship between equilibrium concentration and amount of adsorbate is obtained [14–19]. Because the Langmuir equation describes adsorption on homogeneous surface, Gaussian energy distribution is used to adjust monolayer adsorption theory to heterogeneous surface [20–22]. To study multicomponent, monolayer adsorption of multicomponent gas, the assumption that the saturated amount of adsorption for each component is equal based on Langmuir equation was derived [23, 24].

In the aspect of multilayer adsorption, BET (Brunauer, Emmett, and Teller) equation is the most popular one, and it proposes a multilayer adsorption model which assumes that the interaction on adsorbent surface is much larger than that between neighboring adsorbate molecules [25–27]. The theory is appropriate for adsorption on solid surfaces with homogeneous chemical properties, which is frequently applied to calculate specific surface area for porous media. To extend BET equation to multicomponent adsorption, three kinds of n -component BET equations were proposed considering that adsorbed layers have evaporation-condensation characters for liquid mixture, supposing that the adsorbed layer of gas mixture is an ideal solution according to statistic thermodynamics and assuming gas mixture is immiscible liquid [28–31].

Micropore filling is also a common adsorption mechanism, which is introduced on the basis of Polanyi adsorption potential theory [32]. According to thermodynamics, adsorption potential (ϵ) is transferring unit mass of adsorbate from gas phase to adsorbent surface. On account of thermodynamics, D-R and D-A equations were generated [33–36]. Changing micropore filling to surface coverage and keeping feature of Gaussian distribution of energy, D-R-K (Dubinin-Radushkevich-Kaganer) equation was built [37, 38]. For micropore filling on nonregular porous media, D-R equation was modified by fractal dimension function [39]. Furthermore, for supercritical fluid adsorption, S-D-R equation was built [7].

In fact, most adsorbents are heterogeneous porous media. Combination of adsorption equations is a solution to build equation for heterogeneous adsorbent. In studies of methane adsorption, empirical Freundlich equation was combined with Langmuir equation to obtain the L-F equation which is widely used in depicting CBM (coal bed methane) adsorption successfully [40, 41]. Moreover, heterogeneity of adsorbent surface has been taken into account, and an adsorption equation was built to express the relationship between equilibrium concentration and mass of adsorbate by combining Freundlich adsorption isotherm with Langmuir adsorption isotherm [42, 43].

It is clear that these adsorption equations only focus on one adsorption mechanism and cannot be applied to interpret monolayer adsorption, multilayer adsorption, and capillary condensation simultaneously. In addition, it is well known that shale consists of clay minerals (kaolinite, illite, chlorite, etc.), detrital minerals (quartz, feldspar, etc.), and some characteristic minerals (such as pyrite) [44–48], each with its specific adsorption property. On the other hand,

pore size distribution in shale is irregular [49], which results in an uneven distribution of adsorption potential. Compared with homogeneous materials used in other interfacial phenomenon studies, shale is an extremely heterogeneous adsorbent. However, most of current adsorption models assume that adsorbent is homogenous. Hence, our research is aiming at building a new adsorption equation for shale which enables us to depict complex adsorption including monolayer adsorption, multilayer adsorption, and capillary condensation.

2. Experiment

Adsorption and desorption data of shale measured by nitrogen at low temperature (77 K) is a fundamental method to analyze pore structure of shale. Samples were collected from Yanchang formation (Triassic, Ordos), Pingliang formation (Ordovician, Ordos), Wulalik formation (Ordovician, Ordos), Xujiahe formation (Triassic, Sichuan), Niutitang formation (Cambrian, Sichuan), and Doushantuo formation (Ediacaran, Sichuan). Properties of samples are described in Table 1. All samples were ground to pass a sieve size of 60 mesh (250 μm). For outgassing, the pulverized samples were dried and vacuumized at 80°C for 12 hours.

The apparatus used for nitrogen adsorption experiment is Quadrasorb SI surface area and pore size analyzer (manufactured by Quantachrome in USA) which is provided by State Key Laboratory of Oil & Gas Reservoir Geology and Exploitation (China). There are four stations of the experimental instrument. The lower limitation of specific surface area is 0.01 m^2/g for nitrogen. In the aspect of pore size distribution analysis, the minimum pore volume is 0.0001 cc/g (STP), and the pore size range is 0.35–400 nm. In our experiment, nitrogen is used as adsorbate. Measurement is conducted at temperature 77 K, and the minimum P/P_0 is 0.001.

All the experimental data are prepared to analyze nitrogen adsorption processes and determine the value of parameters in shale adsorption isotherm.

3. Adsorption Characteristics of Nitrogen Adsorbed on Shale

3.1. Adsorption Processes. According to BDDT (Brunauer-Deming-Deming-Teller) adsorption isotherm classification [50], nitrogen adsorption isotherms of shale belong to type IV (Figure 1), which indicates that adsorption on shale can be divided into three stages: monolayer adsorption, multilayer adsorption, and capillary condensation [51–54]. The three stages can be specifically expressed as follows: most adsorption isotherms of shale have an inflection point at low relative pressure, which refers to saturated adsorbed content in monolayer adsorption regime. Before this point, only monolayer adsorption takes place. As relative pressure increases, the thickness of adsorbed layers gradually increases and multilayer adsorption occurs. When relative pressure reaches initial capillary condensation pressure (usually around 0.4 P/P_0), adsorption-desorption curve forms hysteresis loop,

TABLE 1: Curve fitting parameters of shale adsorption isotherm for 80 samples.

Number	A	B	K	M	N	R-Square
D1	0.0537	1.9980	2132.0000	1.4890	0.0993	0.9988
D2	6.9810	0.0150	203.5000	0.9568	203.3000	0.9129
D3	0.0780	2.3980	0.0000	0.9168	3.8730	0.7652
D4	2.0550	1.2430	3.7850	0.5093	5274.0000	0.9991
D5	2.3920	0.2903	783.3000	0.7181	538.0000	0.8952
D6	5.2550	1.5350	6.2590	0.1476	191.1000	0.9983
D7	1.6750	1.1630	3.2210	0.2803	144.5000	0.9999
D8	1.9080	1.5610	4.1690	0.3121	1422.0000	0.9994
D9	2.2440	1.3200	6.7910	0.2632	232.6000	0.9993
D10	1.6210	1.2640	5.0760	0.4035	2745.0000	0.9980
D11	0.9914	1.1540	5.6780	0.4159	6902.0000	0.9993
D12	5.4060	1.7330	191.1000	0.4047	201.7000	0.9003
D13	5.3580	0.3832	208.0000	0.4707	202.8000	0.8984
D14	4.2840	1.4770	1896.0000	0.2662	5.7960	0.9995
D15	8.5540	1.3940	59.1100	0.5487	7595.0000	0.9079
D16	3.0770	1.5530	2.5480	0.2783	817.0000	0.9995
D17	7.4640	0.1425	650.6000	0.6635	333.4000	0.9124
D18	3.4710	1.5220	6.1130	0.2741	427.4000	0.9995
D19	3.3230	0.0003	427.4000	0.5498	423.1000	0.9088
D20	3.9300	0.0836	561.5000	0.4809	334.3000	0.9303
D21	3.5090	1.4470	5.5610	0.2747	723.2000	0.9991
D22	1.3000	1.4950	292.4000	0.4657	4.5470	0.9998
D23	4.2450	1.4390	3.9790	0.2875	408.9000	0.9985
D24	2.8740	1.0500	53.0000	0.4740	53.6000	0.9213
D25	2.9540	0.4405	701.8000	0.4577	275.8000	0.9257
D26	3.5920	0.2153	209.1000	0.3085	208.2000	0.9436
D27	5.3050	1.5090	5.4720	0.2243	268.2000	0.9981
D28	5.1140	1.4920	4.6400	0.2279	346.7000	0.9986
D29	9.0830	1.5220	242.3000	0.1936	2.4390	0.9994
D30	7.0750	1.4830	6.5960	0.2288	2220.0000	0.9957
D31	2.7600	1.3680	6.0210	0.2718	156.4000	0.9990
D32	6.3140	1.4600	5.4280	0.2655	6569.0000	0.9966
D33	6.6460	1.5110	4.5510	0.2274	7304.0000	0.9943
D34	4.9060	1.9610	162.9000	0.5029	206.6000	0.9260
D35	6.0750	1.5820	4.5020	0.2520	642.7000	0.9998
D36	10.4800	1.5260	5.6510	0.2440	216.6000	0.9985
D37	5.4940	1.4900	6.4730	0.2477	194.1000	0.9984
D38	5.4510	1.5800	4.8690	0.2569	1299.0000	0.9991
D39	9.2010	1.5080	5.0390	0.2308	174.4000	0.9987
D40	3.6820	1.3920	3.6970	0.3226	2108.0000	0.9997
D41	0.2399	1.3620	7.7860	0.5925	153.7000	0.9969
D42	4.5800	1.5770	4.8860	0.3121	1525.0000	0.9991
D43	4.6990	1.3130	3.8670	0.3180	1697.0000	0.9993
D44	0.8405	1.7690	404.3000	0.3685	3.9270	0.9997
D45	0.5450	1.3380	15.3900	1.2740	2570.0000	0.9852
D46	1.6880	0.6039	176.0000	1.1490	0.0014	0.9834
D47	1.9000	0.5685	206.7000	1.3950	203.6000	0.9780
D48	3.2030	1.5100	3.9550	0.5210	1347.0000	0.9994
D49	0.1630	1.1610	3.9160	0.5117	124.4000	0.9996
D50	0.3986	1.2930	42.2300	1.7860	63.0900	0.9736
D51	3.0890	1.4760	5.7340	0.3389	897.6000	0.9988
D52	2.4900	1.3240	3.8420	0.4336	872.2000	0.9989

TABLE I: Continued.

Number	A	B	K	M	N	R-Square
D53	3.1810	0.1210	556.3000	1.0080	276.6000	0.9509
D54	2.0150	1.4120	4973.0000	0.5012	4.8210	0.9991
D55	5.4370	1.4850	5.6280	0.2821	1196.0000	0.9994
D56	4.9370	1.5060	5.7860	0.3235	633.8000	0.9993
D57	1.1190	1.5900	2357.0000	0.8201	6.8430	0.9994
D58	2.5580	1.4510	3.8680	0.3408	690.5000	0.9988
D59	2.5710	1.3870	4.9770	0.4927	357.1000	0.9995
D60	0.7093	1.3030	3.2820	0.6943	282.8000	0.9996
D61	0.5753	1.5290	700.2000	0.4714	3.8960	0.9999
D62	0.2555	0.2743	32.7500	3.2820	0.1412	0.9609
D63	4.1530	1.4710	4.0830	0.3707	229.8000	0.9988
D64	0.3084	1.2180	3.3540	0.5845	172.4000	0.9989
D65	0.1870	0.5533	41.5700	1.5160	0.0292	0.9894
D66	0.1506	1.2430	1.9260	0.6289	102.3000	0.9997
D67	0.1322	1.1130	3.5120	0.4219	101.8000	0.9998
D68	1.8820	1.3280	4.1040	0.3971	193.7000	0.9989
D69	1.1050	1.2280	3.9960	0.4548	146.3000	0.9995
D70	3.5390	1.3730	297.5000	1.1020	389.5000	0.9095
D71	0.2066	1.8990	597.9000	0.5551	4.6210	0.9999
D72	1.7930	1.3680	5.0270	0.5813	291.4000	0.9997
D73	3.0830	1.4350	5.1210	0.5572	435.3000	0.9996
D74	1.5910	1.3670	7.1400	0.5368	11840.0000	0.9981
D75	2.7250	2.5950	159.2000	0.9335	174.9000	0.9170
D76	0.7462	0.1465	84.1800	2.1390	0.0039	0.9910
D77	3.8900	0.1753	500.5000	0.7077	264.5000	0.9242
D78	0.1222	1.9200	1187.0000	0.4956	7.9260	0.9999
D79	0.1362	1.8620	126.3000	0.4758	3.7370	0.9998
D80	0.1082	1.8330	96.1900	0.4922	2.8620	0.9996

which demonstrates that capillary condensation exists in the process of nitrogen adsorbed on shale.

3.2. Adsorption Equations and Adsorption Processes. As mentioned above, shale adsorption includes processes of monolayer adsorption, multilayer adsorption, and capillary condensation. Therefore, the generated new shale adsorption isotherm would be capable of depicting all features of these processes.

In terms of monolayer adsorption, Langmuir equation will be an appropriate choice. Langmuir built an adsorption model with the following assumptions: (1) surface of adsorbent has one type of adsorption sites and one site can accommodate only one adsorbate molecule or atom; (2) the surface is homogeneous and there is no lateral interaction between adsorbate molecules; (3) adsorption reaches dynamic equilibrium [55]. Based on these assumptions, the adsorption isotherm can be given as

$$V = \frac{V_m b P}{1 + b P}. \quad (1)$$

All terms used in the equations are defined in the nomenclature section.

For multilayer adsorption, BET adsorption isotherm is a representation of multilayer adsorption model generated by Brunauer, Emmett, and Teller, which assumes the interaction between adsorbate and adsorbent surface is much larger than that between neighboring molecules. The theory is appropriate for adsorption on surface of solid with homogeneous chemical properties, which is frequently applied to calculate specific surface area for porous media. The BET equation can be expressed as [25]

$$V = \frac{V_m c P}{(P_0 - P) [1 + (c - 1) (P/P_0)]}. \quad (2)$$

Capillary condensation is a process where gas phase transforms into liquid phase. Thus, an adsorption equation applicable to describe liquid adsorption is suitable for this adsorption stage. Among investigated adsorption equations, Freundlich adsorption isotherm is an empirical equation describing equilibrium concentration of solute in solution with respect to concentration of solute adsorbed on the surface of solvent. The adsorption equation is [56]

$$m = k P^{1/n}. \quad (3)$$

Figure 2 points out that if we only apply Langmuir isotherm to shale adsorption in low relative pressure section

FIGURE 1: Classification of BDDT adsorption isotherms (from Brunauer, Sing et al., 1940).

FIGURE 2: Application of Langmuir isotherm to nitrogen adsorption isotherm for shale at low relative pressure section.

FIGURE 3: Application of BET isotherm to nitrogen adsorption isotherm for shale before capillary condensation.

(before the inflection point where monolayer adsorption switches to multilayer adsorption), Langmuir isotherm can properly match experimental data, which indicates that Langmuir isotherm is suitable for monolayer adsorption in shale and then justifies the analytical result that monolayer adsorption takes place in the process of nitrogen adsorption at low temperature for shale.

As a normal method to acquire surface area of shale, multipoint BET method testifies that BET equation can be applied to describe adsorption on shale at certain conditions (usually relative pressure below $0.4 P/P_o$). From curve

fitting result (Figure 3), BET is appropriate for low and medium relative pressure sections, which illustrates that BET adsorption isotherm can depict experimental data before the presence of capillary condensation. This also reveals that multilayer adsorption exists in the process of nitrogen adsorption isotherm for shale.

As shown in Figure 4, Freundlich isotherm fits the medium-high relative pressure section of nitrogen adsorption on shale, especially relative pressure section after occurrence of capillary condensation.

FIGURE 4: Application of Freundlich isotherm to liquefied nitrogen adsorption isotherm for shale for medium-high relative pressure section.

On behalf of potentials of the three equations representing adsorption in different relative pressure sections, the new adsorption equation for shale needs to contain features of Langmuir isotherm, BET isotherm, and Freundlich isotherm.

4. Result

BET and Freundlich adsorption isotherms can be changed to functions which consider relative pressure as an independent variable. Thereafter, Langmuir adsorption isotherm is a case of BET adsorption isotherm, in which the pressure is much lower than saturated vapor pressure.

Rearranging BET adsorption isotherm equation one gets

$$V = \frac{V_m c P_r}{-(c-1)P_r^2 + (c-2)P_r + 1}. \quad (4)$$

Substituting P_r into (3) gives

$$m = k P_r^{1/n} P_0^{1/n}. \quad (5)$$

Freundlich adsorption isotherm describes the relationship between pressure and mass of adsorbate adsorbed on surface of adsorbent per unit of mass. In order to express adsorption capacity in same dimension, (5) is converted to

$$V = \frac{k P_r^{1/n} P_0^{1/n}}{\rho g}. \quad (6)$$

Under experimental conditions, saturated vapor pressure and density of adsorbate are constants. Therefore, setting $k P_0^{1/n} / \rho g = k'$, then (6) becomes

$$V = k' P_r^{1/n}. \quad (7)$$

From (1) and (2), the coefficient and exponent of pressure in Langmuir and BET adsorption isotherm (V_m, b, c) correspond to physical and chemical parameters of monolayer and multilayer adsorption. We apply the function with a

form of BET adsorption isotherm and combine Freundlich adsorption isotherm which can describe characteristic of liquid adsorption to build up shale adsorption isotherm. The coefficient and exponent of relative pressure are variable fitting parameters in the new shale adsorption isotherm expressed as follows:

$$V = \frac{A P_r^M}{(1-B) P_r^N + (B-2) P_r^K + 1}. \quad (8)$$

A, B are undetermined coefficients; M, N, K are undetermined exponent.

5. Discussion

5.1. Physical and Chemical Meaning of Variables in Shale Adsorption Isotherm Equation. From above discussion, coefficient and exponent in the new shale adsorption isotherm equation are related to physical and chemical meanings of coefficients and exponents of Langmuir, BET, and Freundlich adsorption isotherms.

Variable A in (8) can be given as

$$A = V_m c P_0^M. \quad (9)$$

Thus, A is related to maximum amount of monolayer adsorption (V_m), adsorption heat according to formula of c which will be detailed below, saturated vapor pressure at experimental temperature (P_0), and exponent M .

Variable B in (8) is

$$B = c. \quad (10)$$

Since the physical and chemical meaning of variable B in adsorption isotherm equals coefficient c in BET isotherm [57], c is expressed as follows based on BET theoretical derivation [58]:

$$c = \frac{a_1 g e^{((E_1 - E_L)/RT)}}{b_1}. \quad (11)$$

B is related to heat of adsorption (E_1, E_L) and experimental temperature (T).

Thermodynamically, the expression of exponent n in Freundlich adsorption isotherm is [59, 60]

$$n = -\frac{\Delta H_m}{RT}. \quad (12)$$

Compared with exponents of relative pressure in (8), coefficients M, N , and K are relevant to experimental temperature, which indicates that the enthalpy ΔH_m represents the strength of adsorption effect.

After clarifying the physical and chemical meaning of variables in (8), the range of these variables should be determined.

In (9), V_m, c, P_0^M are all positives, and then A should be positive ($A > 0$).

In BET theory, it is assumed that the strength of interaction between adsorbate at first adsorbed layer and adsorbent

is much bigger than the strength between adsorbates at subsequent layers. Thus, set heat of adsorption between subsequent adsorbates as E_L . Then, E_1 represents the heat of adsorption between adsorbate at first layer and adsorbent, and $E_1 > E_L$. Thus, c must be larger than 0, and then we can obtain $B > 0$.

In terms of adsorption isotherm system:

$$\Delta H_m = H_2 - H_1 = (U_2 + P_2 V_2) - (U_1 + P_1 V_1). \quad (13)$$

At given temperature, based on ideal gas law, $P_1 V_1 = P_2 V_2$ can be obtained. Thus, in the whole system, change in adsorption enthalpy is equal to change in internal energy; namely, $\Delta H_m = \Delta U$. The adsorption is a process of heat release, $\Delta U < 0$, so $\Delta H_m < 0$ and all variables M , N , K are positive.

For each shale sample, these parameters can be calculated by the new shale adsorption isotherm based on experimental data.

5.2. Specialization of Shale Adsorption Isotherm. When $M = N = 1$; $A = V_m b$; $B = b$, (8) can be simplified to (1) which is Langmuir adsorption isotherm.

When $M = K = 1$; $N = 2$, (8) can be simplified to

$$V = \frac{AP_r}{(1-B)P_r^2 + (B-2)P_r + 1}. \quad (14)$$

At the right hand side of equation, multiply both numerator and denominator by saturated vapor pressure P_0 as

$$V = \frac{AP}{(1-B)P_r^2 P_0 + (B-2)P_r P_0 + P_0}. \quad (15)$$

The term $(B-2)P_r P_0$ can be written as $(B-1)P_r P_0 - P_r P_0$. Equation (15) can be converted to

$$V = \frac{AP}{(P_0 - P)[1 + (B-1)(P/P_0)]}. \quad (16)$$

Then, $A = V_m * c$; $B = c$, and (16) converts to BET adsorption isotherm as (2).

In (8), if $M \gg 1$; $K \gg 1$, $A = k' P_0^M$, $M = 1/n$, reduces to (7).

By multiplying density of adsorbate (ρ) on both sides of (7) one gets

$$m = k' P^{1/n} \rho. \quad (17)$$

Setting $k' \rho = k$, then (17) can be simplified to Freundlich adsorption isotherm as (3).

5.3. Application of New Adsorption Equation. According to the new shale adsorption isotherm equation and the range of variables, we applied Matlab to perform curve fitting of relative pressure versus amount of adsorption for 80 shale samples. The results of 6 samples are selected randomly and displayed in Figure 5, and the other fitting results are shown in Table 1. It appears that average value of R^2 is 0.9782, maximum value of R^2 is 0.9999, minimum value

of R^2 is 0.7652, and the percentage of shale samples for which the value of R^2 is larger than 0.9 is 96.25%. It indicates that the new generated shale adsorption isotherm can represent a complete process of adsorption including monolayer adsorption, multilayer adsorption, and capillary condensation processes compared with Langmuir, BET, and Freundlich adsorption isotherms individually. In particular, it demonstrates better performance on depicting nitrogen adsorption isotherm at low temperature.

5.4. Coefficient B and the Shape of Adsorption Curve. Taking into account the physical and chemical meaning of coefficient B in the new generated shale adsorption isotherm, it represents coefficient c in BET isotherm (11). According to the research by Kondou et al. [61], the value of c in BET isotherm is related to heat of adsorption. The value of c is bigger, and the heat of adsorption is larger, which indicates that strength of interaction for adsorption is larger and adsorption curve increases more rapidly in low-pressure section shown in Figure 6(a). Focusing on the value of B in shale adsorption isotherm and the shape of adsorption isotherm curve, we figure out that the curve becomes gradually convex as the value of B increases, as shown in Figure 6(b). This illustrates that the generated shale adsorption isotherm can express the difference of heat of adsorption released between different shale samples. Furthermore, the changes in the shape of the curve are relevant to changes in heat of adsorption.

6. Conclusion

(1) The new shale adsorption isotherm is built up based on Langmuir adsorption isotherm, BET isotherm, and Freundlich isotherm, which can offer description for shale adsorption isotherm including monolayer adsorption, multilayer adsorption, and capillary condensation processes. The new shale adsorption isotherm can be converted to Langmuir, BET, and Freundlich isotherms by giving certain values to variables.

(2) The variables in new shale adsorption isotherm are related to coefficients and exponents in Langmuir, BET, and Freundlich adsorption isotherms. The physical and chemical meanings of parameters are figured out and ranges for each parameter are determined, which is used to restrict value of variables in the adsorption isotherm when doing regression analysis to match data from shale samples adsorption experiment.

(3) Based on new shale adsorption isotherm and variable range, curve fitting of relative pressure versus amount of adsorption has been performed. The adsorption isotherms with ability to illustrate the process of monolayer adsorption, multilayer adsorption, and capillary condensation for 80 shale samples from Ordos Basin and Sichuan Basin are obtained. The results of curve fitting are highly accurate.

(4) Variable B in shale adsorption isotherm is related to shape of adsorption curve due to adsorption heat. Variables in shale adsorption isotherm are related to shape of adsorption curve and parameter of heat of adsorption. Adsorption isotherm curve becomes gradually convex as the value of B

FIGURE 5: Curve fitting for adsorption isotherm.

FIGURE 6: Change in shape of adsorption curve versus change in value of B .

increases. Computation according to physical and chemical meaning of coefficient B on heat of adsorption between adsorbate at first layer and adsorbent demonstrates that diversity exists among the heat of adsorption from different shale samples.

Nomenclature

V :	Adsorption volume (cc/g)
P :	Equilibrium pressure (MPa)
V_m :	Saturated adsorption volume (cc/g)
b :	Coefficient
P_0 :	Saturated vapor pressure at certain temperature (MPa)
c :	Coefficient
m :	Adsorption mass (g/g)
k :	Coefficient
n :	Coefficient (Mpa)
Pr :	The ration of equilibrium pressure P and saturated vapor pressure P_0 (1)
ΔH_m :	Adsorption enthalpy (J)
R :	Molar gas constant (J/(mol·K))
T :	Temperature (K)
ρ_g :	Gas density (g/ml)
A :	Variable
B :	Variable
M :	Variable
N :	Variable
K :	Variable
a_1 :	Constant
b_1 :	Constant
g :	Constant
E_1 :	Heat of adsorption between adsorbate at first layer and adsorbent (kJ/mol)
E_L :	Heat of adsorption between adsorbate at n layer and adsorbate at $n + 1$ layer ($n \geq 1$) (kJ/mol).

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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