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Fractal Characteristics of Micro- and Mesopores in the Longmaxi Shale

Xiaoqi Wang ^{1,2,3}, Yanming Zhu ^{1,2,*} and Yang Wang ^{1,2}

¹ Key Laboratory of Coalbed Methane Resources and Reservoir Formation on Process, Ministry of Education, China University of Mining and Technology, Xuzhou 221008, China; tb17010016b2@cumt.edu.cn (X.W.); 15162189046@163.com (Y.W.)

² School of Resources and Geosciences, China University of Mining and Technology, Xuzhou 221116, China

³ The EMS Energy Institute and Leone Family Department of Energy and Mineral Engineering, The Pennsylvania State University, University Park, PA 16802, USA

* Correspondence: ymzhucumt@126.com

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Abstract: To better understand the variability and heterogeneity of pore size distributions (PSDs) in the Longmaxi Shale, twelve shale samples were collected from the Xiaoxi and Fendong section, Sichuan Province, South China. Multifractal analysis was employed to study PSDs of mesopores (2–50 nm) and micropores (<2 nm) based on low-pressure N₂/CO₂ adsorption (LP-N₂/CO₂GA). The results show that the PSDs of mesopores and micropores exhibit a multifractal behavior. The multifractal parameters can be divided into the parameters of heterogeneity (D_{-10} – D_{10} , D_0 – D_{10} and D_{-10} – D_0) and the parameters of singularity (D_1 and H). For both the mesopores and micropores, decreasing the singularity of the pore size distribution contributes to larger heterogeneous parameters. However, micropores and mesopores also vary widely in terms of the pore heterogeneity and its controlling factors. Shale with a higher total organic carbon (TOC) content may have a larger volume of micropores and more heterogeneous mesopores. Rough surface and less concentrated pore size distribution hinder the transport of adsorbent in mesopores. The transport properties of micropores are not affected by the pore fractal dimension.

Keywords: fractal characteristics; multifractal; micropores and mesopores; longmaxi shale; CO₂ and N₂ adsorption; Heterogeneity

1. Introduction

Black shale, as a nonconventional reservoir, has typical low porosity and low permeability characteristics [1–5]. The nanoscale pores in the shale constitute a complex pore network [6–9]. In particular, the micropores (pore diameter <2 nm) and mesopores (2–50 nm) have the characteristics of a large specific surface area and high degree of heterogeneity, thereby increasing the complexity of the accumulation and migration mechanism of shale gas [10–14]. The difficulty in the characterization of shale reservoirs is the quantitative description of micropore and mesopore structures. A variety of experiments have been used to study the pore structure, including scanning electron microscopy (SEM) [15–17], atomic force microscopy (AFM) [18,19], small-angle X-ray (SAXS) [20,21], small-angle/ultra-small-angle neutron scattering (SANS/USANS) [22–26], nuclear magnetic resonance (NMR) [27–30], high-pressure mercury intrusion (HMIP) [31–34] and low-temperature liquid nitrogen/carbon dioxide adsorption (LP-N₂/CO₂GA) [23–25,31,35]. Among these, LP-N₂/CO₂GA analysis has been proven to be an effective method in characterizing the pore size distribution of micropores and mesopores [23–25,31]. Furthermore, nanoscale pores in shale can be regarded as having a complex fractal geometry. Fractal theory provides a new quantitative method for quantitatively

characterizing the heterogeneity of nanoscale pores in shale [36–40]. Several methods have been used to measure fractal dimensions, such as image analysis [41,42], the fractal Frenkel–Halsey–Hill (FHH) model [43–45], the fractal BET model [46–48], small angle X-ray scattering [48] and HMIP [49]. Among these, the fractal FHH model has been widely used to study pore heterogeneity [50,51].

It is noteworthy that the multifractal theory expands the application of fractal geometry and has been widely used in various fields in recent years [52–55]. In general, fractals are mainly used to describe irregular geometries or geometric sets, and the spatial distribution of measures can be quantitatively represented by multifractal research [52]. It was found that a multifractal approach has been successfully applied to parameterize the spatial heterogeneity of porous materials [55]. Several multifractal studies were conducted based on two-dimensional image analysis, including X-ray computed tomography (CT) data [54], optical microscopy [56] and environmental scanning electron microscopy (ESEM) images [57]. Recently, multifractal analysis of PSDs determined by Hg injection datasets has been performed [55]. However, they are less frequent with the multifractal analysis of marine shales.

In this study, we mainly carried out fractal analyses on the Lower Silurian Longmaxi shale based on the data of LP-N₂/CO₂GA experiments. The relationships between the fractal parameters and adsorbent transport rate are also discussed.

2. Materials and Methods

For this investigation, twelve shale samples were collected from the Longmaxi Formation in the Xiaoxi and Fendong section, Sichuan Province, South China. The total organic carbon (TOC) content analysis and X-ray diffraction (XRD) were applied to analyze the material composition. In addition, a low-pressure N₂/CO₂ adsorption experiment (LP-N₂/CO₂GA) was employed to analyze the pore structure parameters, including the BET-specific surface area (SSA), micropore volume (PV1), mesopore volume (PV2) and pore size distribution (PSD). Furthermore, multifractal analysis was performed based on the PSD data measured from LP-N₂/CO₂GA experiments. Finally, the Frenkel–Halsey–Hill (FHH) and volume-surface area (V-S) fractal models were used to study their relationship with multifractals.

2.1. Experiments

The total organic carbon content (TOC) analysis was conducted by using a multi EA 4000 elemental analyzer (Analytik Jena AG, Jena, Germany). The highest temperature of this instrument can reach 1500 °C, and accuracy is ± 0.01 ppm. X-ray diffraction (XRD) analysis was performed using X'Pert3 Powder. Both analyses were conducted at the Jiangsu Provincial Mineral Design Institute, China.

The LP-N₂/CO₂GA experiment was conducted using an Autosorb-IQ-MP apparatus at the China University of Mining and Technology. Samples were degassed and dried before the experiments. The LP-N₂GA experiment was performed at temperature of 77.35 K, and the LP-CO₂GA experiment was conducted at temperature of 273 K. The Brunauer–Emmett–Teller (BET) multilayer adsorption equation was applied to obtain the specific surface area [58]. PSD were calculated using the density functional theory [59].

2.2. Multifractal Analysis

A number of scholars have carried out multifractal analysis based on pore size distribution data of mercury intrusion experiments, and the generalized dimension spectrum is used to characterize the heterogeneity of pore structures [60]. In this study, the generalized dimension spectrum was calculated based on pore size distribution data of N₂ and CO₂ adsorption experiments. The calculation steps are summarized as follows [55]:

The key to the multifractal analysis of the pore size distribution is to define a pore volume probability on multiple sizes scales. First, the aperture range is taken as interval J . According to the dichotomy principle, the interval J of length r is divided into $N(r)$ boxes with scale r , so that the smallest

subinterval contains the measured value. The probability distribution $\rho_i(r)$ of the pore volume in each box is defined as:

$$\rho_i(r) = M_i(r) / M \quad (1)$$

where $M_i(r)$ is the total amount of the study volume in lattice i , and M is the total amount of the study volume in the entire study space. Then, the assignment function $\chi_q(r)$ can be defined as:

$$\chi_q(r) = \sum_{i=1}^{N(r)} \rho_i^q(r) \quad (2)$$

where $N(r)$ is the total number of lattice units with side length r , and q is the order of the distribution function ($-\infty \leq q \leq \infty$).

If $q > 0$, the larger $\rho_i(r)$ interval will have a greater contribution to $\chi_q(r)$, which can reflect the fractal characteristics of the hole-dense region. When $q < 0$, the region with a small $\rho_i(r)$ value will have a large contribution to $\chi_q(r)$, which can reflect the fractal characteristics of the sparse region. Thus, a single fractal can be extended to a variety of singular degrees of fractal so that the internal structure of the fractal can be fully presented. If $\rho_i(r)$ obeys the multifractal pattern, the distribution function has a simple power-law relationship to the grid cell size r :

$$\chi_q(r) = \sum_{i=1}^{N(r)} \rho_i^q(r) \quad (3)$$

where $\tau(q)$ is the power exponent of the q -order moment. If the studied measure satisfies the multifractal pattern, when a q value is given, a line between $\chi_q(r)$ and r will be formed on a double logarithmic plot. The slope of each line gives a $\tau(q)$ value.

When q is not equal to 1, D_q can be obtained from the power exponent $\tau(q)$ of the q -order moment:

$$D_q = \frac{\tau(q)}{1 - q} \quad (4)$$

When $q = 1$, D_1 can be expressed as:

$$D_1 = \lim_{r \rightarrow 0} \frac{\sum_{i=1}^{N(r)} \rho_i(r) \log \rho_i(r)}{\log(r)} \quad (5)$$

The D_q values correspond to the information dimension D_1 and the associated dimension D_2 respectively, when the q value is equal to 1 or 2. The q - $D(q)$ curve constitutes the generalized dimension spectrum of the pore size distribution. The generalized dimension spectrum has five characteristic parameters ($D_1, H, D_{-10}-D_0, D_0-D_{10}$ and $D_{-10}-D_{10}$), which can quantitatively characterize the heterogeneity of the pore size distribution from different angles. The information dimension D_1 is a measure of the uniformity of the pore size distribution. The larger the D_1 , the greater the uniformity of the pore size distribution. The D_1 values of mesopores and micropores are abbreviated as D_{1N} and D_{1C} . Most of the pores are distributed in a number of pore ranges [60]. H is the Hurst index, which is calculated as:

$$H = \frac{D_2 + 1}{2} \quad (6)$$

H can be used as the characterization parameter of porosity autocorrelation, and its value range is within the interval (0.5,1). When H is closer to 1, it indicates that the autocorrelation of the pore size distribution is stronger [52,53]. The H values of mesopores and micropores are abbreviated as H_N and H_C . $D_{-10}-D_0$, D_0-D_{10} and $D_{-10}-D_{10}$ represent the left branch, the right branch and the full spectrum width of the q - $D(q)$ curve, respectively. For the convenience of expression, the above three

spectral width parameters were expressed as D_{NN} , D_{PN} and D_{TN} for mesopores and D_{NC} , D_{PC} and D_{TC} for micropores, respectively. In general, pore heterogeneity increases with wider multifractal spectrum [52,53,55,60].

2.3. FHH and V-S Fractal Model

The FHH fractal model can be expressed by [61–63]:

$$\ln(V/V_0) = C + A \cdot \ln(p_0/p) \quad (7)$$

where V is the nitrogen adsorption volume, V_0 represent the monolayer adsorption volume, p_0 is the saturated vapor pressure and A and C are fitting coefficients. The FHH fractal dimension is $A + 3$. In this study, the FHH fractal dimension was divided into D_{N1} ($p_0/p < 0.5$) and D_{N2} ($p_0/p > 0.5$).

The V-S model can be expressed by [64,65]:

$$\ln(V) = \frac{3}{D_C} \ln S + k \quad (8)$$

where V is adsorption volume, cm^3/g , S is the cumulative specific surface area, m^2/g , and D_C is the V-S fractal dimension of the micropores.

3. Results

3.1. TOC and XRD Analysis

The TOC content and mineral composition are presented in Table 1. The TOC content of the two sections ranges from 1.2% to 9.9% (average = 4.4%), and the dominant mineralogical composition are quartz, clay and calcite. Among these, quartz, ranging from 32% to 83% (average = 53%), displays the highest concentration. Clay ranges from 10% to 42% (average = 21%) and calcite ranges from 0% to 26% (average = 15%).

Table 1. Total organic carbon (TOC) and X-ray diffraction (XRD) analysis results of shale samples.

Sample No.	TOC (%)	Mineralogical Compositions (%)						
		Quartz	Orthoclase	Plagioclase	Calcite	Dolomite	Pyrite	Clay
X-4	8.26	37.00	4.00	12.00	22.00	8.00	-	17.00
X-5	9.93	77.00	3.00	4.00	-	-	-	16.00
X-7	5.81	44.00	2.20	1.00	13.40	5.10	2.30	32.00
X-9	1.62	36.80	1.10	6.40	6.70	5.20	1.60	42.20
X-10	1.19	51.00	6.00	17.00	-	-	-	26.00
X-14	1.64	34.00	10.00	10.00	20.00	-	-	26.00
X-15	1.34	32.00	6.00	10.00	26.00	-	-	26.00
F-4	4.95	76.10	0.50	2.70	5.80	3.80	0.90	10.20
F-6	4.60	52.40	0.50	3.10	16.00	7.80	4.30	15.90
F-8	5.26	42.50	0.50	4.10	18.40	14.90	3.60	16.00
F-14	4.20	62.00	-	5.00	6.00	13.00	-	14.00
F-15	3.60	83.00	-	1.00	-	-	-	16.00

3.2. N_2 and CO_2 Adsorption

Following the Brunauer, Deming, Deming and Teller classification [27], the adsorption isotherms of N_2 and CO_2 are type II and type I, respectively (Figures 1 and 2). Samples with a high TOC content tended to have higher N_2 and CO_2 adsorption capacities. The pore volume of mesopores (PV1) ranged from 0.006 to 0.022 mL/g (average = 0.015 mL/g). Meanwhile, the micropores had a smaller pore volume (PV2) relative to the mesopores, with a range from 0.0016 to 0.0085 mL/g (average = 0.0057 mL/g). Compared to the existing data from the same region [66], the relative error of these two parameters was found to be within 25% (Figure 3). PV1 had no correlation with the shale composition. However,

there was a weak positive correlation between PV2 and the content of TOC ($R^2 = 0.3$) and a certain negative correlation with the clay content ($R^2 = 0.4$).

Figure 1. N_2 adsorption-desorption isotherms of the Longmaxi Shale samples.

Figure 2. CO_2 adsorption isotherms of the Longmaxi Shale samples.

Figure 3. Pore volume (a) and Brunauer–Emmett–Teller (BET)-specific surface area (b) of the Longmaxi Shale samples.

SSA ranged from 15.9 to 26.9 m²/g (average = 20.1 m²/g), and it was substantially consistent with the results of Yang et al. [66]. Meanwhile, the SSA had a positive correlation with the TOC content ($R^2 = 0.5$) and quartz content ($R^2 = 0.3$). The pore volume distributions of the mesopores and macropores are illustrated in Figure 4, suggesting a unimodal PSD in the mesopore range and a multimodal PSD in the micropore range. In general, most samples had a broad peak between 10 and 100 nm and a sharp peak between 0.4 and 0.7 nm.

Figure 4. Pore size distribution of micropores and mesopores.

3.3. Multifractal Parameters

The plot of $\log[\chi(q, \epsilon)]$ versus $\log(\epsilon)$ is often used to determine whether the observed data have multifractal features [67]. Linear relationships could be observed between $\log[\chi(q, \epsilon)]$ and $\log(\epsilon)$ in all the samples (Figures 5 and 6), suggesting that the PSDs of micropores and mesopores in shale had multifractal characteristics. In general, the Dq spectra displayed a monotonically decreasing function of q with an anti-S curve (Figures 7 and 8). Although the shapes of the Dq spectra were roughly similar, there were differences in the parameters of the Dq spectra (Table 2). Thus, it was necessary to analyze the correlation of each characteristic parameter. The correlation coefficients of the shale material composition data, pore parameters and fractal parameters are presented in Figure 9. A better correlation was found between the multifractal parameters of mesopores. Specifically, there was a positive correlation between D_{1N} and D_{HN} , and these two parameters were negatively correlated with D_{NN} , D_{PN} and D_{TN} . However, the correlation between multifractal parameters of the micropores was more complex compared to the mesopores. Similar to the mesopores, D_{1C} was positively correlated with H_C , and D_{NC} was also positively related to D_{TC} . However, unlike the mesopores, D_{PC} had no correlation with D_{TC} .

Figure 5. Plots of $\log[\chi(q, \epsilon)]$ versus $\log(\epsilon)$ for the pore size distributions (PSDs) of mesopores.

Figure 6. Plots of $\log[\chi(q, \epsilon)]$ versus $\log(\epsilon)$ for the PSDs of the micropores.

Figure 7. Plots of Dq versus q ($-10 < q < 10$) for the PSDs of the mesopores of samples from Xiaoxi (a) and Fendong section (b).

Figure 8. Plots of Dq versus q ($-10 < q < 10$) for the PSDs of the micropores of samples from Xiaoxi (a) and Fendong section (b).

Figure 9. Correlation coefficients of the shale material composition data, pore parameters and fractal parameters.

Table 2. Multi-fractal parameters of Longmaxi Formation shale.

Sample No.	Mesopores						Microporous						
	D_{1N}	H_N	D_{TN}	D_{PN}	D_{NN}	D_{N1}	D_{N2}	D_{1C}	H_C	D_{TC}	D_{PC}	D_{NC}	D_C
X-4	1.01	0.99	0.81	0.19	0.63	2.76	2.70	0.97	0.97	0.52	0.22	0.30	2.23
X-5	1.01	0.98	0.97	0.22	0.75	2.77	2.72	0.95	0.96	0.54	0.16	0.38	2.56
X-7	1.01	0.99	0.74	0.23	0.50	2.75	2.65	0.96	0.96	0.53	0.19	0.34	2.62
X-9	1.00	0.98	0.90	0.25	0.65	2.73	2.66	0.97	0.97	0.66	0.18	0.49	2.30
X-10	1.04	1.01	0.45	0.12	0.33	2.71	2.65	0.98	0.97	0.51	0.15	0.36	2.23
X-14	1.02	0.99	0.62	0.21	0.41	2.70	2.62	0.97	0.97	0.58	0.16	0.42	2.29
X-15	1.01	0.98	0.68	0.24	0.44	2.72	2.62	0.95	0.95	0.48	0.23	0.25	2.52
F-4	1.02	0.99	0.74	0.22	0.52	2.71	2.70	0.98	0.97	0.51	0.20	0.32	2.29
F-6	1.02	1.00	0.65	0.15	0.50	2.75	2.70	0.98	0.97	0.57	0.18	0.39	2.31
F-8	1.02	0.99	0.69	0.23	0.47	2.73	2.70	0.98	0.97	0.47	0.18	0.28	2.27
F-14	1.02	0.99	0.63	0.21	0.42	2.72	2.68	0.98	0.97	0.57	0.18	0.39	2.26
F-15	1.03	1.00	0.59	0.18	0.41	2.66	2.63	0.94	0.94	0.62	0.31	0.32	2.32

3.4. FHH and V-S Fractal Dimension

The fairly well-fitting results of formula 7 (with correlation coefficients of $R^2 > 0.97$, see Tables 3 and 4 and Figures 10 and 11) indicated that the mesopores in shale had FHH fractal characteristics. D_{N1} ranged from 2.66 to 2.77, with a mean of 2.72. D_{N2} was lower than that of D_{N1} and ranged from 2.62 to 2.72, with an average of 2.67. There was a positive correlation between D_{N1} and D_{N2} ($R^2 = 0.5$). These results were consistent with previous studies [68]. It is noteworthy that both D_{N1} and D_{N2} were negatively correlated with D_{1N} and H_N but were positively correlated with D_{TN} and D_{PN} (Figure 9).

Table 3. Fractal dimensions derived from the fractal Frenkel–Halsey–Hill (FHH) model.

Sample No.	$P/P_0 > 0.5$			$P/P_0 < 0.5$		
	Fitting Equation	R^2	D_1	Fitting Equation	R^2	D_2
X-4	$y = -0.239x + 2.097$	0.999	2.761	$y = -0.299x + 2.092$	0.996	2.701
X-5	$y = -0.233x + 2.049$	0.999	2.767	$y = -0.282x + 2.042$	0.997	2.718
X-7	$y = -0.254x + 2.151$	0.997	2.746	$y = -0.347x + 2.105$	0.998	2.653
X-9	$y = -0.273x + 1.705$	0.998	2.727	$y = -0.344x + 1.691$	0.998	2.656
X-10	$y = -0.295x + 1.734$	0.998	2.705	$y = -0.355x + 1.725$	0.999	2.645
X-14	$y = -0.304x + 1.729$	0.999	2.696	$y = -0.382x + 1.719$	0.998	2.618
X-15	$y = -0.282x + 1.690$	0.999	2.718	$y = -0.378x + 1.671$	0.996	2.622
F-4	$y = -0.289x + 2.177$	0.998	2.711	$y = -0.305x + 2.185$	0.998	2.695
F-6	$y = -0.248x + 1.816$	0.997	2.752	$y = -0.296x + 1.806$	0.997	2.704
F-8	$y = -0.275x + 1.656$	0.999	2.725	$y = -0.304x + 1.661$	0.998	2.696
F-14	$y = -0.285x + 1.889$	0.998	2.715	$y = -0.319x + 1.889$	0.996	2.681
F-15	$y = -0.336x + 1.990$	0.997	2.664	$y = -0.372x + 1.980$	0.999	2.628

Table 4. Fractal dimensions derived from the volume-surface area (V-S) model.

Sample No.	Fitting Equation	R^2	D	Sample No.	Fitting Equation	R^2	D
X-4	$y = 0.742x + 6.941$	0.979	2.229	X-15	$y = 0.840x + 7.159$	0.999	2.522
X-5	$y = 0.852x + 7.487$	0.998	2.556	F-4	$y = 0.762x + 7.037$	0.994	2.288
X-7	$y = 0.872x + 7.451$	0.999	2.617	F-6	$y = 0.770x + 6.978$	0.995	2.310
X-9	$y = 0.767x + 6.874$	0.996	2.304	F-8	$y = 0.757x + 6.979$	0.994	2.271
X-10	$y = 0.764x + 6.916$	0.995	2.227	F-14	$y = 0.752x + 6.872$	0.995	2.257
X-14	$y = 0.762x + 6.872$	0.995	2.286	F-15	$y = 0.772x + 7.013$	0.997	2.316

Figure 10. Plots of $\ln(V)$ versus $\ln(\ln(P/P_0))$ from the N_2 adsorption isotherms.

Figure 11. Plots of $\ln(V)$ versus $\ln(S)$ from the CO_2 adsorption isotherms.

The V-S fractal dimension of micropores (D_C) varied from 2.23 to 2.62, with a mean of 2.72. D_C was negatively correlated with D_{1C} and H_C (Figure 9). In addition, there was no significant correlation between D_C and the other multifractal parameters of micropores. It is noteworthy that D_C had a weak positive correlation with D_{NI} (Figure 9).

4. Discussion

4.1. Pore Structure Parameters and Their Controlling Factors

Previous studies have found that the material composition of shale, including the organic matter and inorganic minerals, is an important factor in controlling the pore structure parameters [69,70]. The difference between the PV1-TOC and PV2-TOC covariance (Figure 12a) was consistent with those described by Wang et al. [66]. Some researchers have found that mesopores consisted of elliptical organic matter pores as well, as there were quite a few inorganic matter pores with various morphologies based on FE-SEM [71–74]. It is well documented that considerable micropores are formed within the macromolecular structure of organic matter [75]. This may be the reason why the micropore volume had a notable positive correlation with the TOC content.

Figure 12. Relationship between the TOC content and pore volume (a) and BET-specific surface area (b) of Longmaxi Formation shale.

Overall, the results of this study are consistent with previous research results indicating that organic matter pores had the largest contribution to the specific surface area (Figure 12b) [76,77]. The specific surface area of the mineral pores was smaller than that of the organic pores [78], which may have resulted in the absence of a positive correlation between the mineral composition and SSA. In addition, the weak positive correlation between SSA and PV1 or PV2 reflects that the micropores and mesopores contribute most of the specific surface area in shale. Therefore, organic pores with a pore size of smaller than 50 nm may provide the majority of the specific surface area of the shale.

4.2. Multifractal Characteristics of Micropores and Mesopores

The Dq spectrum in the anti-S shaped curve represents a heterogeneous distribution of pore sizes [60]. A larger Dq spectrum width suggests more heterogeneity in the PSDs [52]. The large difference of the multifractal parameters indicates a significant disparity in heterogeneity among the samples. D_{TN} increased with increasing TOC content (Figure 13a). However, there was no correlation between D_{TC} and TOC content (Figure 13b). The thermal evolution degree of the Longmaxi Shale had entered the over-maturation phase, causing the formation of a complex organic pore network [79–82]. Therefore, shale with a higher TOC content may have more heterogeneous mesopores. In the organic matter with a higher degree of thermal evolution, the molecular structure becomes ordered [83], so the

microporous structure, related to the macromolecular structure of organic matter, may not become complicated as the organic matter content increases.

Figure 13. Relationship between the TOC content and spectral width parameter of mesopores (a) and micropores (b).

The multifractal parameters for $q > 0$ corresponded to the dominance of a large concentration of the pore volume, and the parameters for $q < 0$ could be mainly affected by a small concentration of the pore volume [53,60,74]. As mentioned above, the PSDs of mesopores were unimodal. Consequently, the change in D_{PN} may have been due to various distributions of pore sizes larger than 10 nm, and the value of D_{NN} could be assigned to a pore size smaller than 10 nm. However, the PSDs of micropores have a multimodal distribution. Therefore, the change in both D_{PC} and D_{NC} may have been due to a pore volume distribution over multiple ranges of the pore size. Ultimately, the complexity of the multifractal features of micropores increased. It is noteworthy that D_{NN} was larger than D_{PN} , resulting in a notable positive correlation between D_{NN} and D_{TN} . This result is likely because mesopores with pore sizes smaller than 10 nm have a higher degree of heterogeneity. In addition, the TOC content was positively correlated with D_{NN} and had no correlation with D_{PN} . Accordingly, mesopores in the shale sample with a high TOC content showed a heterogeneous structure in the inner distribution of pores smaller than 10 nm. It is noteworthy that there was no correlation between D_{PC} , D_{NC} and D_{TC} of the micropores. Additionally, only the clay mineral content had a weak positive correlation with D_{NC} of the micropores. Considering that the micropores are mostly distributed in the molecular structure, it is presumed that the pores in the molecular structure of the clay had a greater heterogeneity compared to the pores in the molecules of the organic matter.

The information dimension (D_1) and the Hurst exponent (H) are also commonly used multifractal parameters [52,60]. D_1 is considered a measure of the concentration degree of PSD [52]. The smaller the values of D_1 , the more highly concentrated in the distribution of the pore volume [60]. H indicates the autocorrelation of the distribution of pore volume [54]. The nearer H approximates one, the stronger the existing autocorrelation PSD [54]. Whether considering micropores or mesopores, D_1 had a notable positive correlation with H , suggesting that the more concentrated the pore size distribution, the greater the autocorrelation of the micropores and mesopores (Figure 9c). It is noteworthy that both D_{1N} and H_N were negatively associated with D_{PN} , D_{NN} and D_{TN} for mesopores (Figure 14a), suggesting that as the singularity of the pore size distribution increased, the pore volume was more concentrated in a certain pore size range, and the heterogeneity of the pores decreased. However, only D_{PC} had a negative correlation with D_{1C} and H_C for the micropores (Figure 9). It is hypothesized that due to the multimodal distribution of the PSD in the micropores, the correlation between the singularity and the heterogeneity was weakened compared with the mesopores. Therefore, we can divide the multifractal parameters into the parameters of heterogeneity ($D_{-10}-D_{10}$, D_0-D_{10} and $D_{-10}-D_0$) and the parameters of singularity

(D_1 and H). The parameters are interrelated and have their own independence, which can be used to characterize the fractal regularity of the pore system [55]. Just as there is no correlation between the mesopore volume and micropore volume, the correlation between the multifractal parameters of the mesopores and micropores is not clear, indicating that there may be a large difference in pore types and heterogeneity of pore structures between the mesopores and micropores.

Figure 14. Plots of D_{N1} versus singularity parameters (a) and D_{N1} versus the spectral width parameters (b).

4.3. Association between Fractal Dimensions

A strongly positive correlation was found between the fraction dimension of mesopores (D_{N1} and D_{N2}) and the TOC content (Figures 9a and 15a), suggesting that a higher TOC content in shale may lead to a more complicated pore structure and result in greater FHH fractal dimensions. This conclusion is consistent with the recent studies concerning marine gas shale [39] and lacustrine shale [61]. However, there was no obvious relationship between the value of D_c and the shale composition (Figure 9b). The controlling factors of the micropore volume fractal dimension require further study.

Figure 15. Plots of D_{N1} versus D_{N2} (a) and D_c versus the spectral width parameters (b).

There was a close relationship between the multifractal parameters and FHH fractal dimensions for mesopores (Figure 14b). In particular, the FHH fractal dimension was consistent with the spectral width parameter of the multifractal parameters, so they are all measures of pore heterogeneity. The FHH fractal dimensions were in disagreement with D_{1N} and H_N , indicating that as the singularity of the pore size distribution increased, the pore volume was more concentrated in a certain pore size

range, and the heterogeneity of the pores decreased. For the micropores, D_C was not related to the spectral width parameter of the multifractal parameters but was negatively correlated with D_{1C} and H_C (Figure 15b). This result also suggests the opposite of the singularity and heterogeneity of the pore size distribution. The above studies showed that the fractal features of micropores are more complicated. Thus, more research on this topic needs to be conducted about the association between micropores and shale molecular structures.

4.4. The Relationship between Fractal Parameters and Shale Transport Properties

A previous study found that the multifractal parameters of tectonic coals are closely related to permeability [55]. A negative correlation between fractal dimension (FHH model) and permeability (measure by pulse-decay) was observed in an earlier study [39]. The relationships between permeability (K) and porosity (φ) and fractal dimensions (D) were also acquired based on the Kozeny–Carman equation [84]:

$$K = \frac{r^2}{8} \frac{\varphi}{\tau} \left[\frac{2\varphi}{3\tau(1-\varphi)} \right]^{\frac{2}{D-1}}$$

where r is the average radius and τ is tortuosity.

Due to the complex mesopore and micropore features of both tectonic coals and shales [23,25,55,70], shale fractal parameters may be related to the shale permeability or the diffusion coefficient. Here, we characterized the transport properties of shale based on the cumulative adsorption and corresponding equilibrium time measured by low-pressure N_2/CO_2 adsorption. Since the adsorption process is considered transient, the adsorption time is closely related to the transport rate of the adsorbate molecules in the connected pore system. Therefore, we characterized the transport rate of the adsorbent according to the ratio of the adsorption amount to corresponding equilibrium time (Table 5). The results show that for mesopores, the transport rate has a positive correlation with the information dimension D_{N1} , and a negative correlation with the FHH fractal dimension (D_{1N}) (Figure 16). Therefore, it is suggested that the adsorbent transport rate is higher with the decrease of the pore surface heterogeneity and the increase in the concentration of the pore size distribution inside the connected mesoporous system. There is no obvious correlation between transport rate and the structure parameters (including fractal dimension) of micropores. Controlling factors for fluid transport inside microporous pores need further study. As connectivity, tortuosity and constrictivity are classical parameters used to characterize the pore morphology, it might be possible to find a causal connection between these parameters to fractal characteristics for deepening the understanding of shale transport properties in future investigations.

Table 5. Adsorbent transport rate of Longmaxi shale based on low-pressure N_2/CO_2 adsorption (LP- N_2/CO_2 GA).

Sample No.	Transport Rate of N_2 ($cm^3/(g \cdot min)$)	Transport Rate of CO_2 ($cm^3/(g \cdot min)$)
X-4	0.037	0.009
X-5	0.034	0.017
X-7	0.029	0.008
X-9	0.037	0.003
X-10	0.059	0.009
X-14	0.049	0.003
X-15	0.047	0.004
F-4	0.052	0.005
F-6	0.033	0.008
F-8	0.031	0.009
F-14	0.042	0.005
F-15	0.071	0.020

Figure 16. Relationship between the fractal parameter and transport rate of the adsorbate of mesopores.

5. Conclusions

(1) The PSDs of mesopores are unimodal, whereas micropores have a multimodal distribution. Organic matter pores with a pore size smaller than 50 nm may provide the majority of the specific surface area of a shale and have strong heterogeneity.

(2) The multifractal parameters can be divided into the parameters of heterogeneity ($D_{-10}-D_{10}$, D_0-D_{10} and $D_{-10}-D_0$) and the parameters of singularity (D_1 and H). As the singularity of the pore size distribution increases, the pore volume is more concentrated in a certain pore size range, and the heterogeneity of the pores decreases. The roughness of the mesoporous surface has a positive correlation with the heterogeneity of its pore size distribution.

(3) A rough mesoporous surface hinders the transport of adsorbent. Mesopores with more concentrated pore size distribution have a higher adsorbate transport rate. The transport properties of micropores are not affected by the pore fractal dimension. The main controlling factors of the transport properties of micropores need further study.

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Abbreviations

TOC	Total organic carbon content, %	D_{TN}	D_{-10} – D_{10} of mesopores, dimensionless
Qtz	Quartz content, %	D_{PN}	D_0 – D_{10} of mesopores, dimensionless
Fsp	Feldspar content, %	D_{NN}	D_{-10} – D_0 of mesopores, dimensionless
Cb	Carbonate content, %	D_{1C}	Information dimension of micropores, dimensionless
Clay	Clay content, %	H_C	Hurst index of micropores, dimensionless
PV1	Mesopore pore volume, cm^3/g	D_{TC}	D_{-10} – D_{10} of micropores, dimensionless
PV2	Micropore pore volume, cm^3/g	D_{PC}	D_0 – D_{10} of micropores, dimensionless
SSA	BET specific surface area, m^2/g	D_{NC}	D_{-10} – D_0 of micropores, dimensionless
D_{1N}	Information dimension of mesopores, dimensionless	D_{N1}	FHH fractal dimension of mesopores, dimensionless
H_N	Hurst index of mesopores, dimensionless	D_{N2}	V-S fractal dimension of micropores, dimensionless
p_0	The saturated vapor pressure, MPa	D_C	Gas adsorption volume at the balance pressure, cm^3/g
A, C	Fitting parameters in Frenkel-Halsey-Hill fractal model	V	The gas volume of the monolayer adsorption, cm^3/g
p	Adsorbent pressure in adsorption experiments, MPa	V_0	The order of the distribution function
$N(r)$	Number of boxes in multifractal analysis	q	The order of the distribution function
$\rho_i(r)$	The probability distribution of the pore volume	$\tau(q)$	Power exponent of the q-order moment
φ	Porosity	$x_q(r)$	The assignment function in multifractal analysis
		τ	Tortuosity

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