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An advanced comprehensive statistical physical model revealing the effect of slickwater on methane adsorption in shale

Shuo Duan^a, Yong-Jian Zhang^a, Xiang-Yang Ling^a, Peng-Fei Shen^{a,b,*}, Ling-Zao Zeng^{c,d}, Ze-Yu Li^{c,d,*}^a School of Mining and Geomatics Engineering, Hebei University of Engineering, Handan, 056038, Hebei, China^b Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou, 510640, Guangdong, China^c Zhejiang Provincial Key Laboratory of Organic Pollution Process and Control, Zhejiang Ecological Civilization Academy, Huzhou, 313300, Zhejiang, China^d State Key Laboratory of Soil Pollution Control and Safety, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou, 310058, Zhejiang, China

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ABSTRACT

The impact of slickwater on methane adsorption in shale reservoirs is a critical factor in hydraulic fracturing design and production prediction, but its quantitative evaluation is a common problem facing current research. In this work, an advanced integrated model was established to combine multi-scale shale characterization with statistical physics modeling to reveal its underlying mechanisms. Two typical shale samples from the Bohai Bay Basin were taken in situ and treated with different concentrations of slickwater. The evolution of elemental and mineral composition, surface chemistry, and pore structure of shale samples before and after processing was compared using multi-scale characterization techniques. An advanced statistical physical adsorption model was established to analyze the CH₄ adsorption characteristics of raw and treated shale. The results indicated that shale treated with slickwater reduced the clay mineral content, specific surface area, and micropore volume, but increased the average pore size. The methane adsorption capacity of shale treated with slickwater was significantly reduced, and CH₄ molecules were adsorbed on the shale surface in a mixed parallel or vertical manner. In addition, in the shale samples treated with slippery water, the spontaneous decrease in CH₄ adsorption and the increase in disorder resulted in a reduction in the number of low-energy and high-energy sites available for CH₄ adsorption on the shale surface. These findings establish a quantitative, mechanistic framework for evaluating slickwater–shale interactions, providing critical theoretical support for enhancing shale gas recovery strategies.

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1. Introduction

As global energy demand continues to grow and the transition toward a low-carbon energy system, unconventional natural gas—notably shale gas—has assumed increasingly strategic importance (Kuang et al., 2026; Nian et al., 2026; Qi et al., 2026). As the core technology for commercial shale gas extraction, the effectiveness of hydraulic fracturing greatly depends on the performance of fracturing fluids (Li et al., 2025a). These fluids play a crucial role in

fracture creation and sand transport, yet their prolonged retention in reservoirs after injection leads to complex physicochemical interactions with shale (Awejori et al., 2024). This may permanently alter reservoir properties, affecting gas adsorption and flow, and ultimately affecting recovery rates (Yu et al., 2024). Therefore, a detailed investigation of the interaction mechanisms between fracturing fluids and shale is crucial for accurately evaluating the effectiveness of fracturing, optimizing fracturing fluid systems, and predicting the long-term production capacity of shale gas wells.

Among the numerous fracturing fluid systems, slickwater has emerged as the dominant type in shale gas extraction owing to its prominent advantages, including low price, simple formulation, high recovery rate, and minimal impairment to fracture flow capacity (Li et al., 2024a, 2024b, 2025b). In comparison to

* Corresponding authors.

E-mail addresses: shenpengfei@hebeu.edu.cn (P.-F. Shen), lizeyudarryu@zju.edu.cn (Z.-Y. Li).

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conventional fracturing fluids, such as cross-linked gels, slickwater achieves low friction by incorporating friction reducers, thereby facilitating the formation of more intricate fracture networks (Liu et al., 2021a, 2021b, 2024). In comparison with oil-based fracturing fluids, slickwater exhibits superior environmental compatibility. These advantages have led to its widespread application in coalbed methane enhancement, tight oil development, and shale gas reservoir stimulation (Liu et al., 2023a). However, slickwater injection also implies interaction with reservoir rocks, and its potential impacts cannot be ignored. Research indicates that the low viscosity of slickwater enables it to penetrate nanopores efficiently (Liu et al., 2021a, 2021b, 2023a, 2024). The hydration effects of sodium chloride have been observed to induce swelling and migration of clay minerals, such as illite and montmorillonite, which can result in pore blockage in the substrate (Liu et al., 2023b). Concurrently, the dissolution of minerals, such as carbonates, may result in the expansion of pores or the formation of new flow pathways. This modification of the pore structure is dual and complex (Li et al., 2024a, 2024b). The primary component of shale gas is methane. Although slickwater is widely used as a hydraulic fracturing fluid in shale gas development, understanding the potential mechanisms by which it affects methane adsorption behavior is crucial for hydraulic fracturing operations in shale gas extraction. Previous studies have shown that the CH₄ adsorption capacity of shale is subject to change following treatment with slickwater (Liu et al., 2021b); however, the underlying mechanisms and regulatory processes remain unclear. Consequently, it is imperative to investigate the effects of slickwater on shale constituents, microstructure, and CH₄ adsorption characteristics.

Slickwater contact with shale has been demonstrated to alter the constituents and microporous structure of the shale (Liu et al., 2021a, 2021b, 2023a, 2023b, 2024). In the last few years, a significant number of researchers have investigated the effects of slickwater on shale structure. Sun et al. (2018a) conducted a study on the impact of slickwater on shale mineral composition, pore structure, and methane adsorption capacity. It was found that dissolution of carbonate minerals created dissolution pores, reducing the surface area while increasing the pore size. This resulted in a notable reduction in CH₄ adsorption amount. Li et al. (2025b) systematically compared changes in pore information and mineral composition before and after exposure to slickwater of varying viscosities. The experimental findings demonstrated that as the viscosity of the water increased, no significant dissolution pores were formed on the shale matrix surface, existing fracture widths exhibited negligible changes, and no new hydration fractures appeared. Li et al. (2024a, 2024b) conducted a series of experimental studies on the effects of slickwater on shale pore structure and CH₄ adsorption properties. It was determined that the presence of slickwater resulted in the occlusion of pore throats, leading to the partial closure of open or semi-open pores. This reduction in accessible surface area and pore volume hinders methane adsorption, desorption, and diffusion processes. Liu et al. (2021a, 2021b, 2023a, 2024) conducted a series of studies investigating the influence of slickwater treatment on CH₄ adsorption and desorption in shale. The findings demonstrated that the application of slickwater treatment led to a substantial reduction in CH₄ adsorption capacity, while concurrently enhancing methane desorption efficiency. The investigation by Liu et al. (2023b) revealed that after fracturing fluid treatment, shale wettability distribution became more uniform, with fracturing fluids causing 6.4%–42.0% damage to shale porosity. Despite extensive research by scholars on the effects of slickwater on shale structure and CH₄ adsorption, their primary focus has been on how slickwater induces changes in micro-pore structure, resulting in reduced methane adsorption. Comprehensive studies that

holistically consider the influence of slickwater on mineral composition, surface chemistry, and pore information remain scarce.

To achieve a comprehensive understanding of the effects of slickwater on methane adsorption characteristics and the interactions between methane and shale surfaces, analyzing adsorption equilibrium data is crucial. This data is pivotal for elucidating the mechanisms by which slickwater influences methane adsorption (Duan et al., 2026). Equilibrium adsorption data is generally described using isothermal adsorption models (Duan et al., 2022). Although conventional adsorption models, such as Langmuir, Freundlich, and supercritical Dobinin-Radushevsky (SDR) model, are widely applied, the parameters derived from these models frequently lack physical significance (Duan et al., 2020). This limitation in their explanatory capacity hinders the ability to elucidate the microscopic mechanisms underlying adsorption processes and complicates the description of heterogeneous changes in shale surfaces following treatment with slickwater. Conversely, statistical physics models are well-suited for elucidating adsorption mechanisms. These models offer a more elaborate view, contributing to a deeper understanding of the adsorption process (Duan et al., 2025). These models are capable of determining the number of molecules attached to each site and site density, while also calculating the adsorption energies (Knani et al., 2025). Furthermore, they predict the geometric structure of molecular adsorption and thermodynamic changes, linking macroscopic adsorption quantities to microscopic adsorption states (Bouzid et al., 2025). This provides a robust theoretical basis for explaining complex phenomena such as competitive adsorption and surface heterogeneity (Duan et al., 2025). Given the advantages of statistical physics modeling, there is an escalating focus on analyzing shale gas adsorption behavior from a statistical physics view. For instance, Duan et al. (2020) employed statistical physics models to analyze methane adsorption on shale in Sichuan Basin. A significant number of researches have been dedicated to the subject of gas adsorption mechanisms on porous materials using statistical physics methods (Duan et al., 2025). Statistical physics models have been demonstrated to be particularly well-suited for analyzing alterations in shale surface characteristics following slickwater treatment, with the potential to control methane adsorption. However, studies employing statistical physics methods to elucidate the effects of slickwater on CH₄ adsorption in shale are scarce in the literature.

Thermodynamic parameters can reveal the energy alterations associated with CH₄ adsorption on shale from a thermodynamic viewpoint (Duan et al., 2022, 2026). Numbers of studies have employed the isosteric adsorption heat and adsorption entropy of CH₄ on shale to elucidate its adsorption behavior (Duan et al., 2016, 2020, 2026). The site energy distribution (SED) model is a theoretical method for analyzing adsorption mechanisms from an energy perspective. It is beneficial for studying adsorbents with uneven surface energy distribution (Duan et al., 2025, 2026). Integrating the SED model with adsorption models yields a distribution function reflecting the strength of surface sites on the adsorbent. While this model is widely applied in environmental fields, such as pollutant adsorption, its utilization in shale gas adsorption remains relatively restricted. Duan et al. (2020) applied the SED theory, based on statistical physics models, to investigate methane adsorption mechanisms on Sichuan Basin shale and to analyze surface energy heterogeneities. The interactions between shale and methane were found to be altered after slickwater treatment. Integrating statistical physics models with adsorption thermodynamics and SED theory to study methane adsorption on shale could significantly enhance the fundamental understanding of how slickwater affects shale gas and methane adsorption (Duan

et al., 2026). However, current literature on statistical physics models for investigating the mechanism by which slickwater affects shale gas adsorption remains relatively scarce.

The primary objective of this study is to systematically elucidate the microscopic mechanisms by which slickwater influences shale constituents, microstructure, and CH₄ adsorption characteristics, based on shale characteristics and statistical-physical modeling. In order to analyze changes in elemental composition, mineral content, pore structure, surface morphology, and functional groups before and after slickwater treatment, a range of techniques were employed, including XRD, XRF, SEM, FTIR, and N₂ adsorption at 77 K. Subsequently, equilibrium adsorption experiments for CH₄ were conducted on the shale before and after slickwater treatment at 308, 328, and 348 K. The data were analyzed using two classic and three statistical physics adsorption models. Nonlinear regression was applied to determine the most suitable model for describing the adsorption isotherms. Subsequently, the adsorption mechanism of methane was analyzed from a microscopic perspective. This analysis was based on stereographic and energy parameters derived from a statistical-physical model. The thermodynamic parameters—entropy (S_a), Gibbs free energy (G_a), and internal energy (E_{int})—were computed and elucidated. Finally, the study conducted an in-depth analysis of how slickwater alters the site energy distribution, thereby elucidating the intrinsic mechanism by which slickwater influences methane adsorption from a site energy perspective. Furthermore, by integrating changes in shale surface physicochemical characteristics with the statistical-physical model, the influence mechanism of slickwater on shale gas adsorption was explored, along with its implications for shale gas exploitation. These findings provide deeper theoretical support for the effective development of shale gas.

2. Materials and methods

2.1. Preparation of slickwater and shale samples

2.1.1. Preparation of slickwater

Due to the wide variety of additives and chemical reagents required for slickwater, incorporating all additive variables would inevitably entail an onerous workload. Consequently, only prime additives are regarded when formulating slickwater (Huang, 2020). After a comprehensive literature review, polyacrylamide was selected as the friction reducer, and KCl was selected as the anti-swelling agent (Huang et al., 2021). The concentrations of each additive are detailed in Table 1. In actual fracturing operations, the concentration of slickwater is adjusted based on factors such as geological conditions, fracturing process requirements, and construction costs. The three concentration gradients selected for this experiment cover the typical range of slickwater concentrations encountered in practical fracturing operations. They provide a comprehensive reflection of how slickwater at different concentrations affects shale properties and methane adsorption,

thereby enhancing the practical guidance value of the experimental results for engineering applications (Huang et al., 2021). The preparation method is outlined below: First, purified water was added to a 45 °C constant-temperature beaker and stirred thoroughly. Next, a measured quantity of potassium chloride was weighed and transferred into the beaker. Subsequently, an appropriate amount of polyacrylamide was added, and the solution was stirred until completely dissolved. Finally, the mixture was permitted to stand until the bubbles in the fracturing fluid gradually rose to the surface and dissipated. Upon completion, the fracturing fluid was sealed and stored in a constant-temperature chamber for subsequent utilization. The viscosities of the 0.1, 0.3, and 0.5 wt% slickwater solutions were 7.2, 15.6, and 48.9 mPa·s, respectively, in agreement with literature reports (Huang et al., 2021). After 16 h of testing, no remarkable reduction in fluid viscosity was observed, validating its stabilization (Huang et al., 2021).

2.1.2. Sample preparation

The raw shales selected originate from the Taiyuan Formation, a marine-terrestrial transitional facies in the Bohai Bay Basin, comprising two distinct types. These samples were collected from the Huanghua Depression in the Tangshan area, at depths ranging from 600 to 1000 m. The Bohai Bay Basin is one of the regions with an abundance of gas fields. The Taiyuan Formation shales, which belong to the Carboniferous-Permian sequence, exhibit favorable hydrocarbon potential (Duan et al., 2026; Zhao et al., 2024). Samples S0 and S1 were selected for this study due to their significant differences in terms of organic matter content, mineral composition and pore structure. Sample S0 has an organic matter content of 3.5%, which is lower than that of sample S1 (3.9%). In terms of mineral composition, clay minerals account for 26.75% of sample S0 and 30.43% of sample S1, while quartz accounts for 30.11% of sample S0 and 20.21% of sample S1. These differences may be related to mineral transformation and precipitation during the diagenetic process. Regarding pore structure, sample S0 contains micropores with an average size of 7.74 nm, whereas sample S1 contains no micropores and has an average pore size of 20.55 nm. These differences encompass the primary variations in the characteristics of shale samples within the study area. As illustrated in Fig. 1, the process flow for treating shale with slickwater is as follows. Firstly, the raw shale was crushed and ground to a particle size of 0.18–0.25 mm. This particle size ensures that slickwater fully wets the particle surfaces to quantify chemical adsorbent adsorption, while also preserving the shale's nanoporous structure to accurately reflect methane adsorption behavior (Liu et al., 2021a, 2021b). The obtained powder was then divided into 50 g batches. Each shale sample was then added to 500 g of slickwater at varying concentrations and immersed for five days under specified conditions: A constant pressure of 10 MPa supplied by helium gas and a controlled temperature of 45 °C. This ensured complete and uniform permeation of slickwater into the shale. The pressure set for this experiment was 10 MPa, which falls within the typical pressure range for actual shale gas well fracturing operations. This setting effectively simulates the pressure environment experienced by the fluid during the downhole fracturing process, ensuring that the experimental results align with actual engineering conditions in terms of pressure (Huang, 2020). The experimental temperature was set at 45 °C, a value selected to reflect actual formation temperatures. In the development of shale gas reservoirs in the Bohai Basin, formation temperatures generally fall within this range; this temperature condition helps accurately reflect the effect of slickwater fracturing fluid on shale under real formation temperature conditions (Abdelaal et al., 2021; Sun et al., 2018b). The five-day

Table 1
The composition of slickwater and mass fraction of additives

Group No.	Additive composition and mass fraction		Fracturing fluid
	Friction reducer (polyacrylamide, PAM)	Anti-swelling agent (KCl)	
1	0.1%	1.0%	0.1 wt% slickwater
2	0.3%		0.3 wt% slickwater
3	0.5%		0.5 wt% slickwater

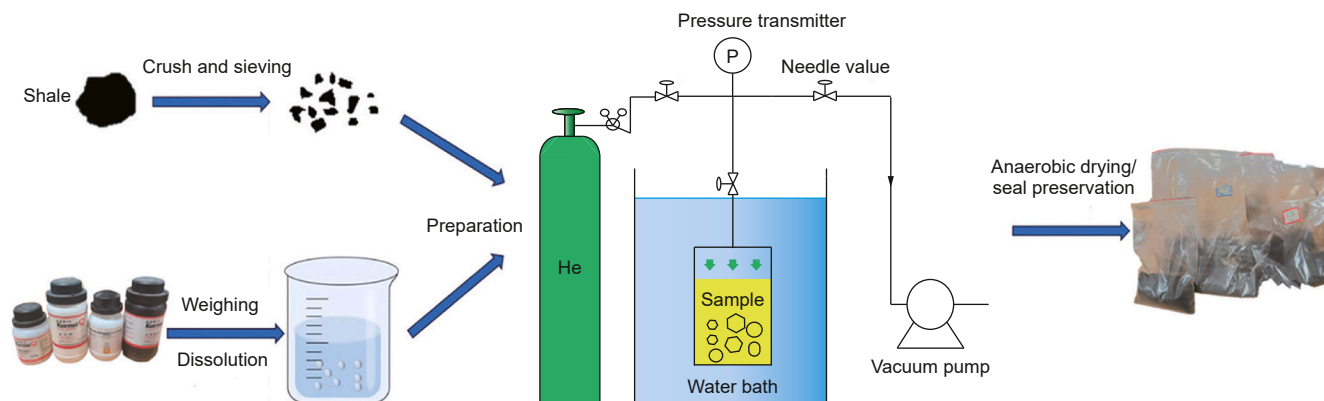


Fig. 1. Flowchart of shale sample preparation.

treatment period is considered the critical duration for the fracturing fluid to fully act upon the shale, thereby stabilizing its structure (Huang, 2020; Abdelaal et al., 2021; Hu et al., 2020; Sun et al., 2018b).

During the fracturing process, fracturing fluid begins to flow back after being injected into the shale reservoir. At this stage, the process involves expelling formation water from the well. Residual fracturing fluid in the reservoir may be eliminated through water during the flowback phase. Therefore, it is imperative to simulate the flushing effectiveness of fluids on slickwater residues during the drainage stage. The specific method is outlined below: The addition of clean water to a beaker is followed by stirring to achieve a dilution of the residual slickwater, thereby simulating the flushing effect. Following this, the upper turbid liquid layer is decanted. Subsequently, each beaker is placed in an oven and dried at 60 °C for 12 h, thus obtaining the respective samples. The raw shales are labeled S0 and S1, respectively, and the treated shales are named HS0 and HS1. The resulting treated shale with varying concentrations was named x -HS0/HS1, where x represents the slickwater concentrations. For instance, 0.1-HS0 denotes S0 that has been treated with 0.1 wt% slickwater. To minimize the impact of variations in sample composition on experimental outcomes, both raw samples underwent uniform pretreatment. During the fracturing fluid processing stage, identical concentrations and volumes of slickwater were applied to both samples under consistent experimental conditions. This ensured uniform interactive environments between the slickwater and each sample, enhancing experimental comparability.

2.2. Characterization of shale

Elemental analysis was conducted via X-ray fluorescence (XRF) spectroscopy (ARL Perform'X 4200, Thermo Scientific). Mineralogical characterization was carried out using X-ray diffraction (XRD) analysis on a Rigaku D/Max-2200 diffractometer. Fourier transform infrared (FT-IR) spectroscopy was performed with a Nicolet Avatar-370 spectrometer, with samples prepared as shale/KBr pellets. The surface morphology was investigated by scanning electron microscopy (SEM, Hitachi SU-8220, 10 kV).

The pore structure information of the shale was characterized by N_2 adsorption-desorption isotherm data measured at 77 K, which was produced using the BSD-PM2 by Beishide. The specific surface area (S_{BET}) was computed using the Brunauer-Emmett-Teller (BET) model. The microporous volume (V_{mic}) was analyzed using the t -plot method, while the mesoporous volume (V_{mes}) was obtained using the Barrett-Joyner-Halenda (BJH) model. Pore size

distribution (PSD) characteristics were analyzed quantitatively using density functional theory (DFT) methods.

2.3. Methane adsorption experiment

Methane adsorption experiments were conducted using the volumetric apparatus depicted in Fig. 2. A pressure transmitter (PAA-33X, accuracy: 0.05% BSL, Keller AG, Switzerland) was employed to collect real-time system pressure data, while a constant-temperature circulating water bath maintained temperature fluctuations within ± 0.1 K. Prior to the experiment, the adsorption cell underwent 12 h of vacuum treatment at 373 K to remove adsorbed impurities. The void volume was determined using a helium calibration method. Gas densities were calculated using the SRK equation for CH_4 and the BWR equation for helium (Setzmann and Wagner, 1991; Mccarty and Arp, 1990). Both methane and helium used in the experiments achieved a purity of 99.995%, with specific operational procedures following references (Duan et al., 2020, 2026). Each pressure-adsorption experiment lasts at least 12 h, and adsorption equilibrium is considered to have been reached when the pressure change remains less than 0.001 MPa for two consecutive hours. CH_4 adsorption data on raw shales had been validated in our past studies (Duan et al., 2026). To validate the repeatability of experimental results within the uncertainty range, this study conducted three replicate CH_4 adsorption measurements on the shale samples. The repeatability of the process was quantified by calculating the standard deviation. The results suggest that the measurement error for CH_4 adsorption on shale was consistently controlled within 4.5%, thereby confirming the reliability and accuracy of the experimental apparatus and testing methodology employed in CH_4 shale adsorption experiments (Duan et al., 2020, 2022, 2026).

3. Results and discussion

3.1. Effect of slickwater on characterization of shale

3.1.1. Element content and mineral composition analysis

Table 2 illustrates the elemental contents of samples prior to and after slickwater treatment. Following the treatment, a significant decrease in Si content was observed within the shale. Specifically, the Si content in the S0 sample decreased from 30.46% to 29.33%, while that in the S1 sample decreased from 21.77% to 18.96%. This suggests the possibility of chemical reactions between slickwater and Si-containing minerals, such as clay. Furthermore, a decline in the Al, Fe, Mg, and S content was observed, indicating chemical interactions between the slickwater and mineral

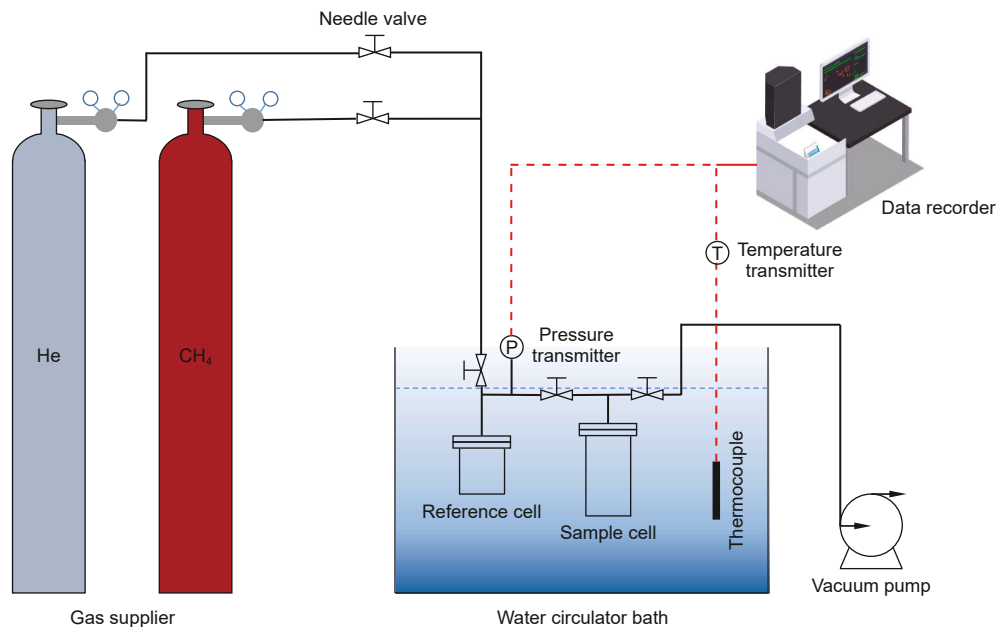


Fig. 2. Adsorption experiment system for CH₄ on shale.

Table 2
Main elements content (mass%) of pre-treatment and treated shale samples.

Sample	Si	Al	Fe	Mg	K	S	Ti	Ca	Sr	Mn
S0	31.14	10.56	3.00	1.42	2.91	0.92	0.36	0.72	0.04	0.01
0.1-HS0	30.46	10.34	2.79	1.38	3.17	0.915	0.351	0.654	0.0349	0.0173
0.3-HS0	30.52	10.32	2.67	1.39	3.14	0.914	0.351	0.675	0.035	0.0177
0.5-HS0	29.33	10.13	2.70	1.39	2.99	0.911	0.345	0.745	0.0377	0.0176
S1	21.77	8.13	16.54	1.79	1.28	10.29	0.30	2.06	0.03	0.03
0.1-HS1	18.88	7.72	16.35	1.41	1.53	10.17	0.326	1.48	0.0303	0.0270
0.3-HS1	18.90	7.83	16.11	1.51	1.56	10.19	0.329	1.54	0.321	0.0282
0.5-HS1	18.96	7.75	16.15	1.51	1.52	10.15	0.331	1.55	0.0319	0.0298

components of the shale, which resulted in the dissolution of specific minerals (Li et al., 2024a). In contrast, samples that were subjected to the treatment exhibited an increase in K content. This outcome was primarily attributable to the incorporation of potassium chloride as an anti-expansion agent during slickwater preparation (Chen et al., 2019), thereby introducing trace amounts of K⁺ ions into the solution and concomitantly elevating K levels. In general, the elemental variations among treated shales with

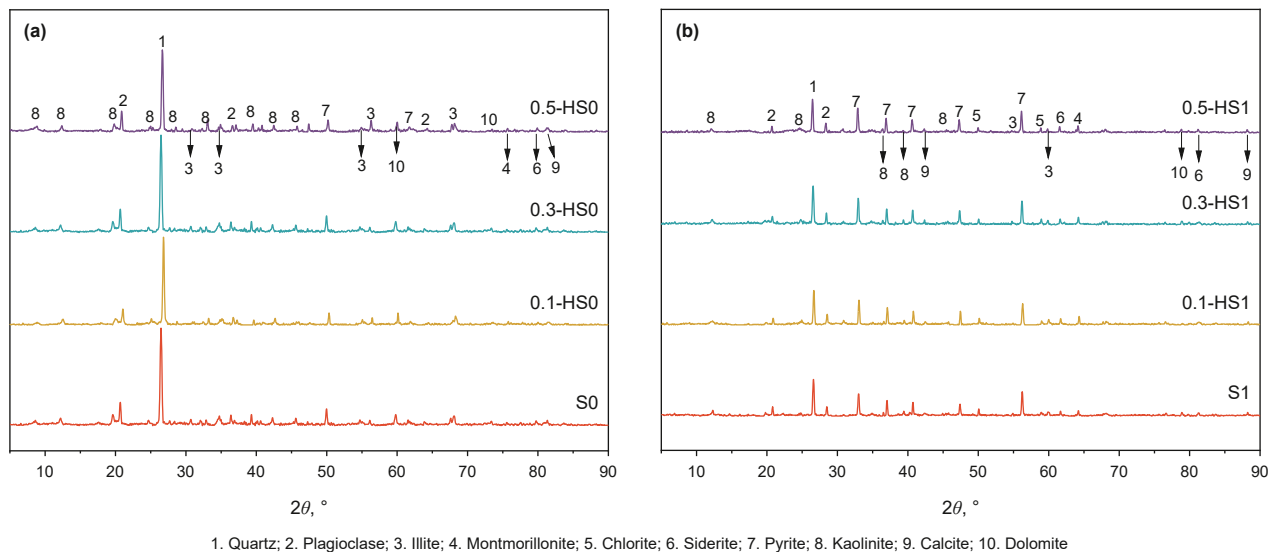


Fig. 3. XRD pattern of untreated and clean fracturing fluid treated shale samples. (a) S0, 0.1-HS0, 0.3-HS0, and 0.5-HS0, (b) S1, 0.1-HS1, 0.3-HS1, and 0.5-HS1.

different slickwater concentrations remained negligible, which can be primarily attributed to the inherent heterogeneity of the shale matrix.

The XRD patterns of shale samples prior to and following the treatment are illustrated in Fig. 3. A comparative analysis reveals that the mineral components did not undergo significant changes post-treatment, with only minor fluctuations in the intensity of the diffraction peaks. This finding suggests that the slickwater exerts a minimal effect on the mineralogical composition of shale. Although clay minerals may exhibit swelling effects due to water absorption and carbonate minerals may possess potential chemical reactivity, these processes did not result in changes to the mineral composition. Instead, the results obtained were minor adjustments to the relative abundances of various minerals (Huang et al., 2024). As illustrated in Table 3, the mineral content was calculated using semi-quantitative XRD peak area analysis. Following slickwater treatment, quartz content remained unchanged, while clay minerals (particularly illite and montmorillonite) exhibited reduced abundance. Additionally, minor decreases were observed in certain carbonate minerals (e.g., dolomite and calcite). This phenomenon is primarily attributable to the higher stability and reduced reactivity of quartz in contact with slickwater. The decline in other minerals was attributable to the generation of trace H^+ ions through the hydrolysis reactions of slickwater's friction reducers (Huang, 2020). Subsequently, these H^+ ions reacted with clay minerals and carbonate minerals. As the slickwater concentration increased, the illite content in S0 shale decreased from 7.68% to 6.94%, while the kaolinite content decreased from 12.87% to 11.98%. In S1 shale, illite content exhibited a decrease from 10.94% to 10.62%, kaolinite content decreased from 16.11% to 15.33%, and clay mineral content exhibited a more substantial decline. Sun et al. observed that H^+ released from the hydrolysis of friction reducers in slickwater caused a decrease in carbonate minerals (such as calcite and dolomite) (Sun et al., 2018a). As the slickwater concentration increased, the content of friction reducers increased accordingly, leading to increased H^+ production from hydrolysis reactions (Li et al., 2025b). The fracturing fluid undergoes a chemical reaction with clay minerals and carbonate minerals, reducing the content of specific mineral components and increasing the shale pore width. This alteration in pore structure has the potential to enhance the diffusion capacity of CH_4 within the shale, thereby creating favorable conditions for the efficient extraction of shale gas.

3.1.2. Surface topography and functional groups analysis

The formation of micro-pores within shale plays a crucial role in the storage and diffusion of shale gas. There are three main types of microscopic pores: organic pores, intergranular pores, and dissolution pores. Figs. 4 and 5 illustrate SEM images of raw and treated shale. The surficial morphologies of the shale exhibit

significant heterogeneity, characterized by notable variations in pore type and size, as well as substantial surface anisotropy. It is evident that sample S1 displays a multitude of particles on its surface, accompanied by conspicuous intergranular pores. This observation suggests the possibility of elevated porosity. These intergranular pores have the potential to increase shale porosity, thereby facilitating the storage and migration of shale gas (Gu et al., 2012; Yang, 2020). It is hypothesized that sample S0 contains a significant number of macropores, with a predominance of macropores, though a minor presence of micropores is also observed. Following treatment with polyacrylamide-containing slickwater, crystalline residues appeared locally on the shale surfaces. This observation can be ascribed to the dissolution of minerals within the shale by the slickwater, leading to the enlargement of pores. Concurrently, dissolved minerals adhered to the shale surfaces, forming crystalline residues that also blocked some smaller pores. However, the alterations observed on the shale surfaces after treatment with varying concentrations of slickwater were not significant.

The present study employed FTIR to analyze the evolution of functional groups on shale surfaces before and after slickwater treatment. As demonstrated in Fig. 6, the FTIR spectra of treated shale are presented. The shale exhibits the strongest characteristic absorption peaks at 1091.56 and 1033.71 cm^{-1} , respectively, attributable to the stretching vibration of silicon-oxygen tetrahedra (Si–O) (Duan et al., 2026; Gu et al., 2012). Furthermore, significant absorption peaks were detected in the bands around 3600–3700, 1450–1650, 680–800, and 430–550 cm^{-1} . Specifically, the characteristic peaks observed at 3600 and 3700 cm^{-1} correspond to the stretching vibrations of hydroxyl (–OH) groups. The absorption peak observed in the 1450–1650 cm^{-1} range is attributed to the bending vibrations of Si–O bonds. The absorption peaks detected at 800–780 cm^{-1} and 470 cm^{-1} are associated with quartz and clay minerals. Additionally, the absorption peaks observed in the 1625.77–1446.42 cm^{-1} band can be attributed to Si–O bond bending vibrations (Duan et al., 2026). A comparative analysis indicates that shale samples treated with slickwater exhibit similar distributions of characteristic absorption peaks to the original samples, but the intensities of each peak have changed. Among the samples examined, the shale sample treated with a 0.5 wt% concentration of slickwater exhibited the lowest peak intensity. This finding indicates that while slickwater treatment does not modify the fundamental types of functional groups on the shale surface, it can effectively regulate the relative content of these surface functional groups.

3.1.3. Pore structure

The N_2 ad-/desorption isotherms are demonstrated in Fig. 7. The hysteresis loop shape of acquired isotherms reveals the microscopic structure of the pores. According to the IUPAC classification of hysteresis loops, sample S0 exhibits an H2-type

Table 3
Mineral contents (mass%) of untreated and treated shale samples.

Sample	Quartz	Plagioclase	Illite	Montmorillonite	Chlorite	Siderite	Pyrite	Kaolinite	Calcite	Dolomite	Clay
S0	30.11	5.29	9.02	4.19	0	5.56	8.69	13.54	7.01	6.18	26.75
0.1-HS0	29.83	5.21	7.68	3.98	0.00	5.47	8.23	12.87	6.02	6.10	24.53
0.3-HS0	29.78	5.27	7.26	3.94	0.00	5.35	8.27	12.41	6.04	6.08	23.61
0.5-HS0	29.79	5.25	6.94	3.96	0.00	5.40	8.08	11.98	5.96	6.04	22.88
S1	20.21	5.16	10.91	1.8	2.14	11.99	18.7	15.58	6.37	7.13	30.43
0.1-HS1	20.60	4.92	10.94	1.46	1.66	11.83	18.87	16.11	6.21	6.86	30.17
0.3-HS1	20.43	4.89	10.73	1.43	1.66	11.70	18.51	15.35	5.62	6.82	29.17
0.5-HS1	20.09	4.70	10.62	1.33	1.62	11.62	18.38	15.33	5.99	6.72	28.90

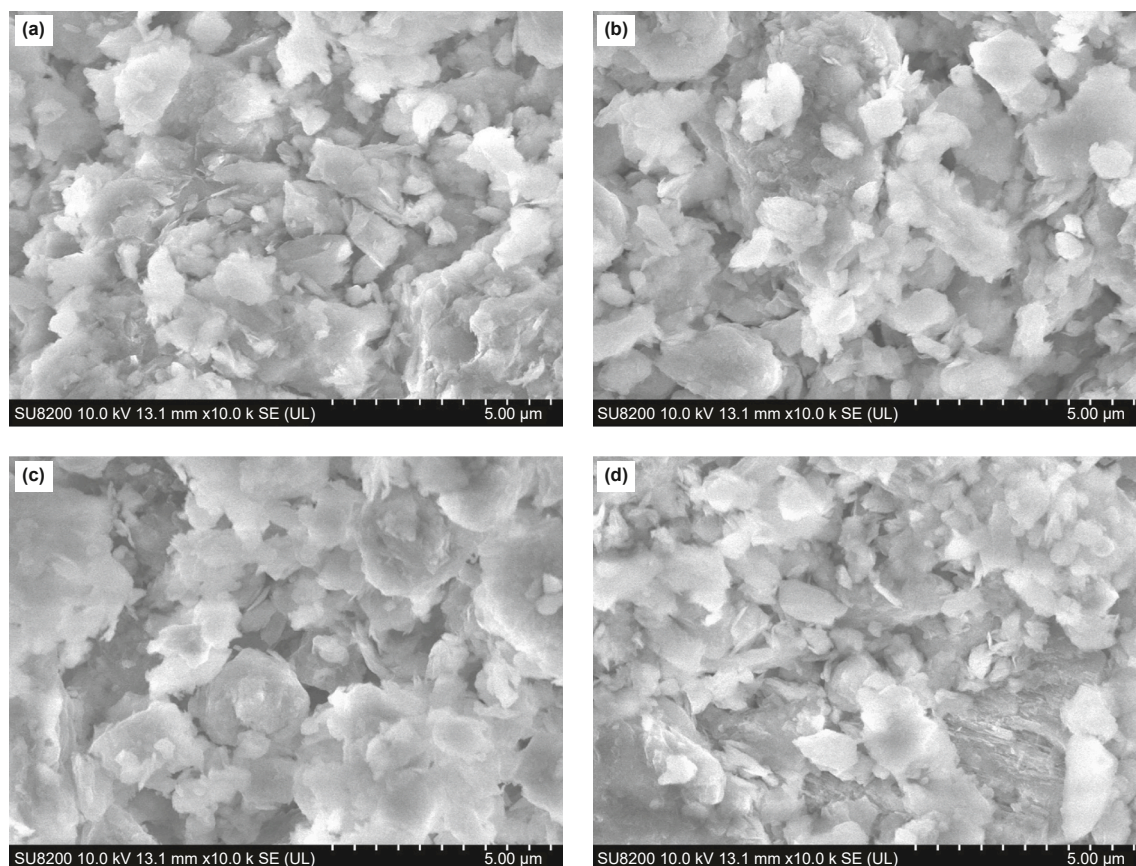


Fig. 4. SEM image of sample S0 before and after fracturing fluid treatment: (a) Raw sample, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

hysteresis loop, indicating the presence of composite pores in S0, including narrow-neck pores and partially open interconnected pores (Gu and Xian, 2015). Conversely, the S1 sample displays an H3-type hysteresis loop, suggesting the presence of a complex internal pore structure, characterized by slit-like mesopores or macropores.

Following slickwater treatment, the N_2 adsorption/desorption curves exhibited no significant changes, suggesting that the treatment had no substantial impact on the pore morphology. The sample S0 was found to be predominantly composed of bottle-neck pores, with a concomitant presence of partially open interconnected pores. In contrast, sample S1 is predominantly characterized by slit-type mesopores or macropores (Duan et al., 2026). Following slickwater treatment, the hysteresis loop area exhibited a slight decrease, indicating a reduced proportion of narrow-neck pores and impaired pore connectivity. This phenomenon was attributed to the dissolution of some inorganic materials within the pores (Duan et al., 2026). Additionally, the high viscosity of the reverse-flush cleaning process impeded the expulsion of residual fracturing fluid from the pores, thereby further contributing to alterations in shale porosity. Concurrently, adsorption/desorption isotherms exhibited a downward trend after slickwater treatment, indicating a reduction in adsorption amount.

The pore parameters were obtained via low-temperature N_2 isotherms, as demonstrated in Table 4. The pore size distribution (PSD) is depicted in Fig. 8, revealing that mesopores constitute the largest proportion. This finding suggests that mesopores occupy a greater proportion than other pores in the shale samples. The abundance of mesopores facilitates gas migration within the shale (Qin et al., 2021). Following slickwater

treatment, a decrease in the S_{BET} of shale S0 was observed, while an initial increase followed by a subsequent decrease was evident in shale S1. Both samples exhibited a trend of initial increase followed by a decrease in pore volume. This phenomenon can be attributed to the combined effects of fluid dissolution and residual blockage (Marcon et al., 2017). Slickwater may dissolve clay and carbonate minerals, thereby increasing pore volume. When slickwater continues to act on the rock, some of the dissolved minerals precipitate and subsequently fill existing pores, reducing pore connectivity and decreasing effective pore volume, which in turn affects fluid flow pathways. The V_{mic} and V_{mic}/V_t values of both shale samples decreased significantly, likely due to micropores being more susceptible to corrosion and blockage. The S0 sample, which consists of a higher percentage of micropores, exhibited a more pronounced effect. Following the implementation of slickwater treatment, micropores in shale S1 were found to be non-existent, with mesopores now occupying the majority of pore space. An increase in average pore size was observed in both S0 and S1 samples following slickwater application.

The PSD exhibited a continuous range of pores from 1 to 100 nm in diameter, with substantial variations in distribution observed between samples. Following slickwater treatment, the pore volume corresponding to small pores decreased in the S0 sample, while it increased in the S1 sample. This finding suggests that the erosive effects of slickwater on shale pores may vary. Pore evolution is the result of the combined effects of mineral dissolution and precipitation; this dynamic process of mineral dissolution and precipitation collectively shapes the final pore structure characteristics of shale.

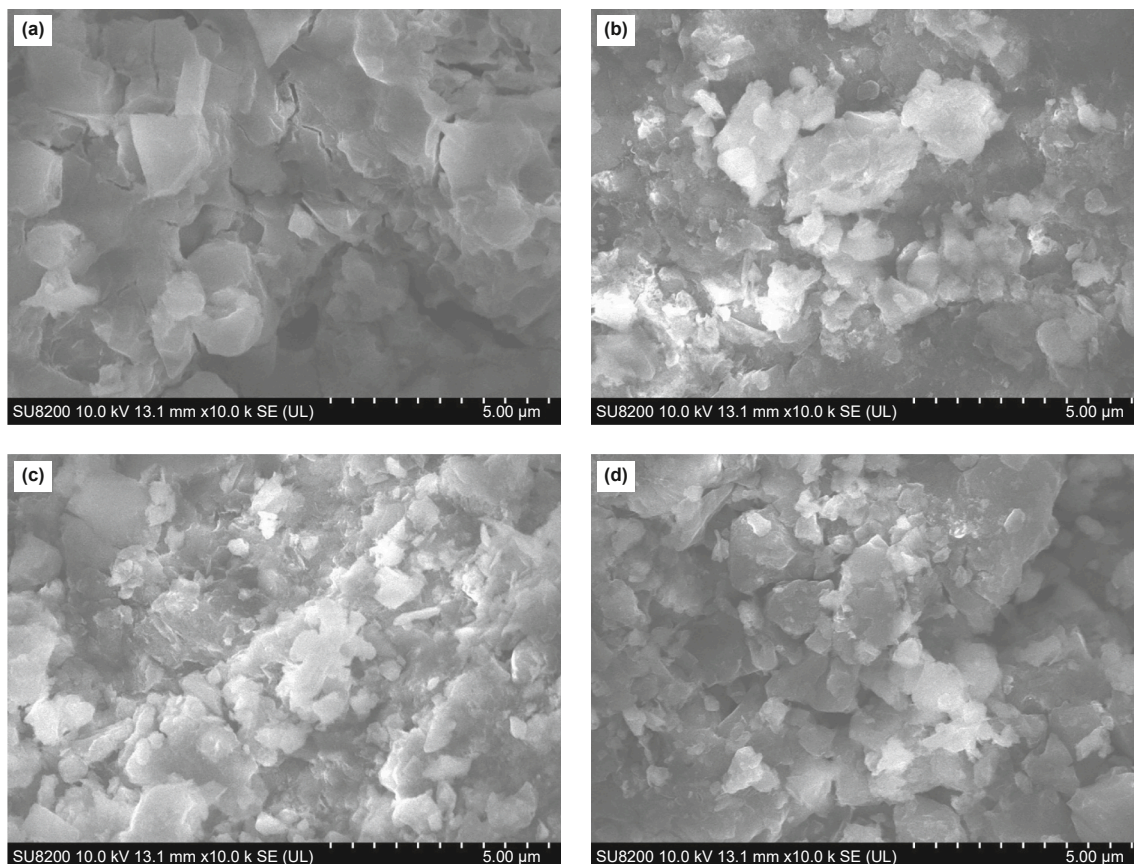


Fig. 5. SEM image of sample S1 before and after fracturing fluid treatment: (a) Raw sample, (b) 0.1-HS1, (c) 0.1-HS1, (d) 0.1-HS1.

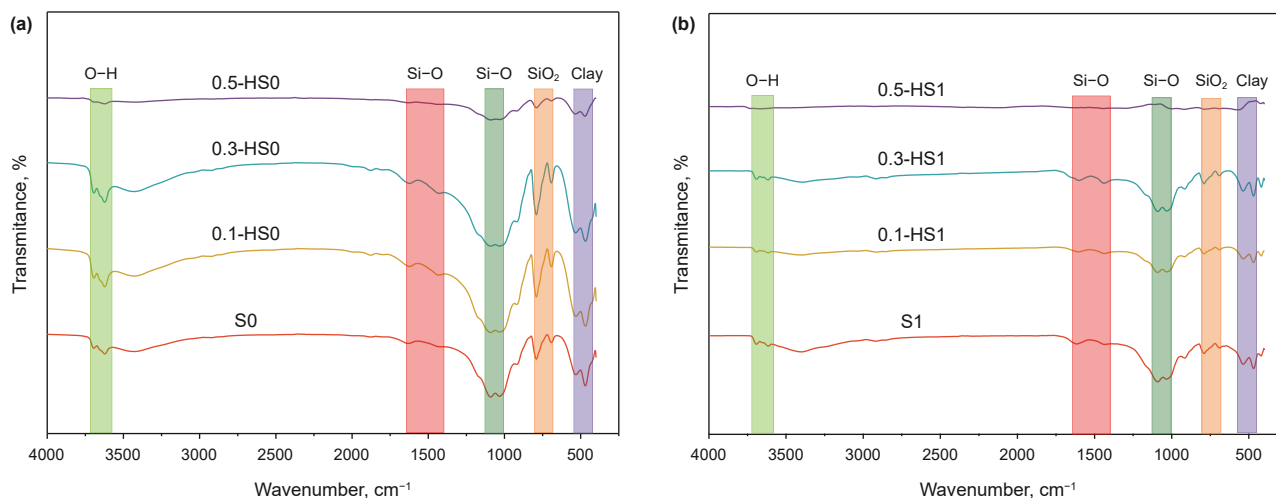


Fig. 6. FTIR spectra of shale samples before and after slickwater treatment: (a) S0, (b) S1.

3.2. Analysis of adsorption isotherm using statistical physics models

3.2.1. Methane adsorption on slickwater treated shale

The adsorption isotherms of CH₄, spanning the temperature range of 308 to 348 K, are illustrated in Figs. 9 and 10. The adsorption amount of CH₄ shows a consistent increase with pressure, displaying a notable acceleration in the low-pressure region (0 to 4 MPa). This indicates that pressure is the primary

determinant of adsorption performance during the initial loading phase (Duan et al., 2016). As the system transitions to higher-pressure conditions, the adsorption rate enhancement noticeably slows, suggesting reduced pressure sensitivity at raised pressures. From the standpoint of adsorption equilibrium and kinetics, the microstructure initially supplies abundant accessible sites for CH₄ (Duan et al., 2026; Sun et al., 2018a). However, with continued pressure increase, these active sites gradually saturate, ultimately reaching an equilibrium state. The remaining available sites

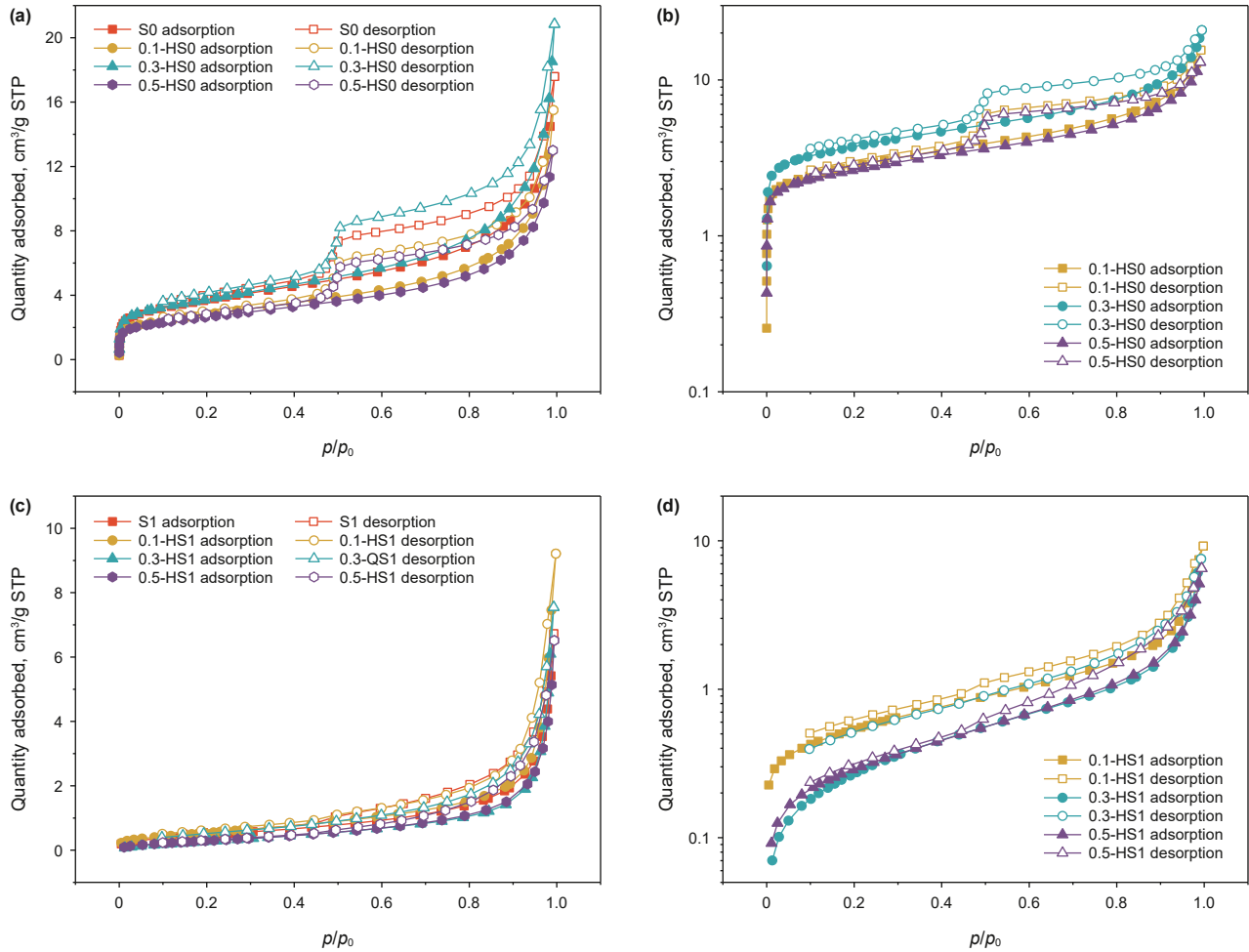


Fig. 7. Low temperature nitrogen adsorption/desorption isotherm of shale: (a) Raw and treated shale S0, (b) treated shale S0, (c) raw and treated shale S1, (d) treated shale S1.

Table 4

The pore structure parameters of the shale samples before and after slickwater treatment by low temperature N₂ adsorption

Shale samples	S_{BET} , m ² ·g ⁻¹	V_t , cm ³ ·g ⁻¹	V_{mic} , cm ³ ·g ⁻¹	V_{mes} , cm ³ ·g ⁻¹	V_{mic}/V_t , %	V_{mes}/V_t , %	D_{ave} , nm
S0	12.8756	0.0249	0.0041	0.0205	16.47	82.33	7.7356
0.1-HS0	9.8328	0.0229	0.0006	0.0220	2.62	96.07	9.3158
0.3-HS0	9.0433	0.0292	0.0010	0.0278	3.42	95.21	8.9548
0.5-HS0	9.1739	0.0197	0.0007	0.0186	3.55	94.42	8.5896
S1	1.8299	0.0094	0.0006	0.0084	6.38	89.36	20.5496
0.1-HS1	2.0837	0.0121	0	0.0119	0	98.35	23.2279
0.3-HS1	1.1897	0.0110	0	0.0109	0	99.09	23.2104
0.5-HS1	1.1101	0.0105	0	0.0104	0	99.05	23.1917

become the limiting factor. Consequently, the adsorption capacity approaches asymptotic stability, and the adsorption kinetics gradually decelerate. The CH₄ adsorption capacity results obtained in this study are consistent with those reported for shale samples in previous research (Li et al., 2024a, 2024c; Tang et al., 2024), indicating that the fundamental adsorption mechanisms are standard across different shale formations.

Since the adsorption amount measured by the manometric approach corresponds to excess adsorption (q_{exc}), the deviation from absolute adsorption (q_{abs}) is minimal under low-pressure but exhibits a substantial increase at high-pressure. This pressure-dependent variation is attributable to the experimental system

of the volumetric method, which inherently incorporates a free gas phase volume (Duan et al., 2022). Therefore, the measured excess adsorption does not accurately reflect the actual number of methane molecules adsorbed onto pore surfaces. It is therefore imperative that the excess adsorption be converted to absolute adsorption using the Gibbs adsorption equation in order to accurately predict CH₄ adsorption behavior in shale (Qin et al., 2021).

$$q_{exc} = q_{abs} \left(1 - \frac{\rho_g}{\rho_{ads}} \right) \quad (1)$$

where q_{exc} and q_{abs} represent the excess and absolute adsorption capacity, respectively; ρ_g denotes the gas density, ρ_{ads} represents the adsorption phase density.

The morphological characteristics of isotherms encapsulate crucial physicochemical information about the adsorption, providing key guidance for model selection and data interpretation (Duan et al., 2025). The CH₄ adsorption isotherms demonstrated in Fig. 9 indicate that methane exhibits a saturation trend at high pressures, with all isotherms conforming to the characteristics of Type I isotherms as delineated by IUPAC (Gu and Xian, 2015). The monolayer adsorption model effectively describes adsorption processes exhibiting this isotherm type (Gu and Xian, 2015). Accordingly, this study selected two traditional models and three statistical physics-based monolayer models (see Table 5 for details) to systematically analyze the adsorption process of CH₄ in shale. The parameters for the classical models are defined as

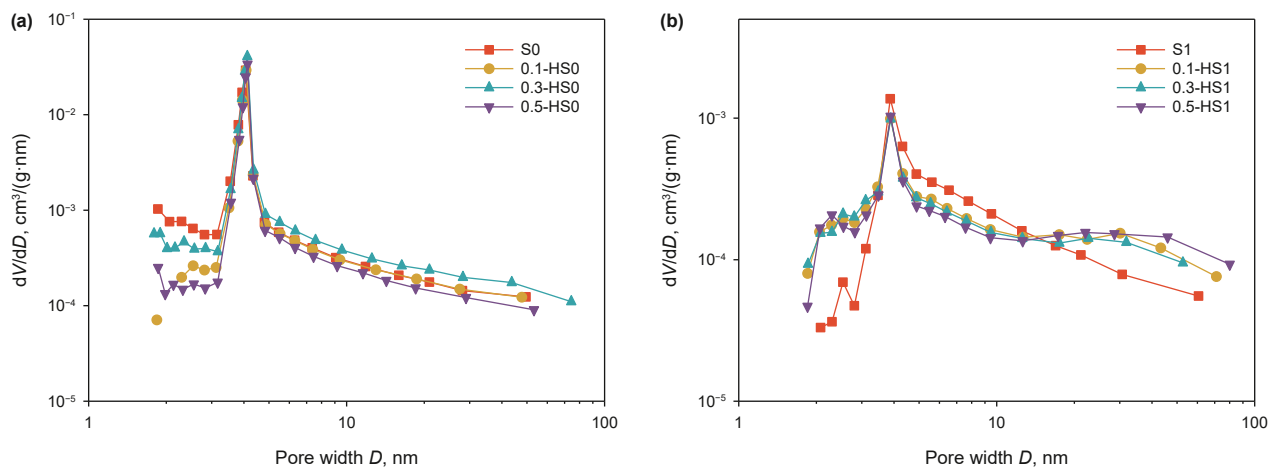


Fig. 8. Pore size distribution of shale: (a) S0, (b) S1.

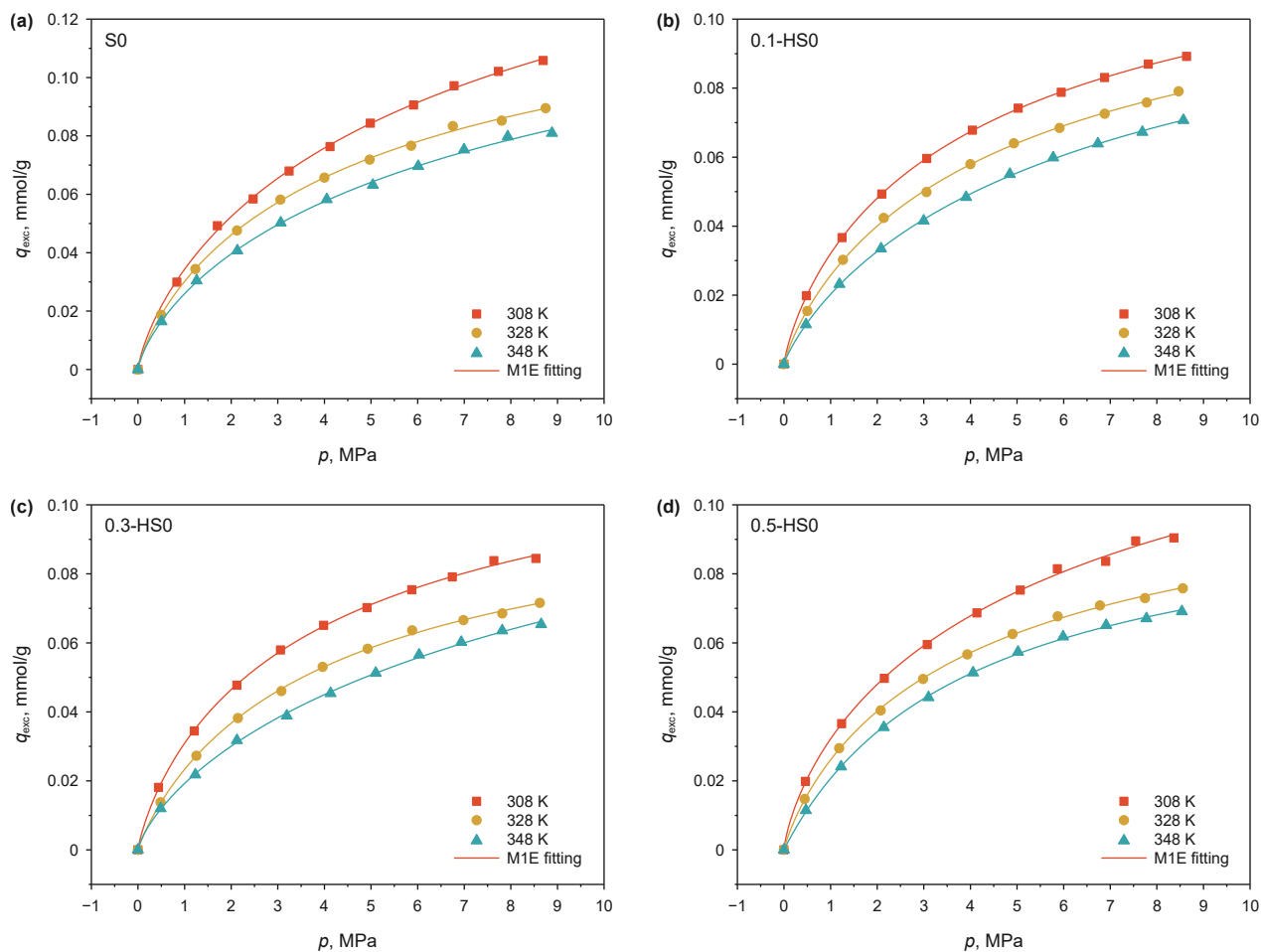


Fig. 9. Adsorption isotherm and fitting by M1E model for shale samples before and after slickwater treatment: (a) S0, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

follows: k_F and n_F are the Freundlich adsorption constant and exponent, respectively; q_L and b_L are the maximum adsorption capacity and equilibrium constant in the Langmuir model, respectively. Statistical physics model parameters include: q_m as the monolayer saturation adsorption capacity, n as the number of molecules per site, N_m as the adsorption site density, and $p_{1/2}$ as the half-saturation pressure. For the two-site model, n_1 and n_2

represent the number of molecules occupying the first and second sites, respectively, with p_1 and p_2 as their corresponding half-saturation pressures. N_{m1} and N_{m2} denote the density parameters for the two types of adsorption sites.

This study quantitatively evaluated five candidate models using statistical metrics such as root-sum-squares (RSS), coefficient of determination (R^2), and Akaike information criterion

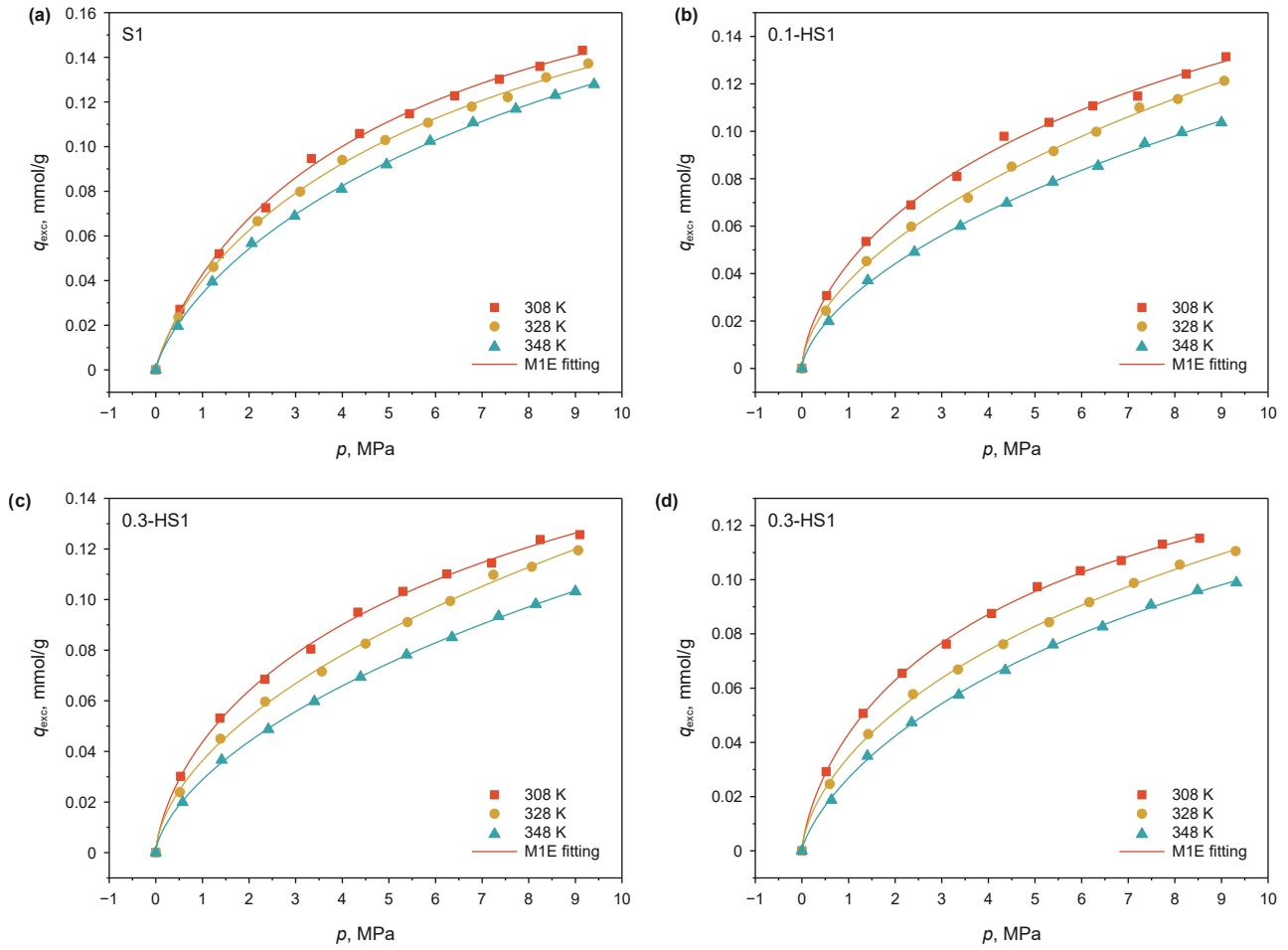


Fig. 10. Adsorption isotherm and fitting by M1E model for shale samples before and after slickwater treatment: (a) S1, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

Table 5

Adsorption models used for experiment data fitting

Model	Equation	Extension of equation	Parameters	References
Freundlich	$q = k_F p^{1/n_F}$	$q_{exc} = k_F p^{1/n_F} \left(1 - \frac{\rho_g}{\rho_{ads}}\right)$	k_F, n_F, ρ_{ads}	Duong (1998)
Langmuir	$q = \frac{q_L b_L p}{1 + b_L p}$	$q_{exc} = \frac{q_L b_L p}{1 + b_L p} \left(1 - \frac{\rho_g}{\rho_{ads}}\right)$	q_L, b_L, ρ_{ads}	Duong (1998)
Monolayer model (ME)	$q = \frac{q_m}{1 + \frac{p_{1/2}}{p}}$	$q_{exc} = \frac{q_m}{1 + \frac{p_{1/2}}{p}} \left(1 - \frac{\rho_g}{\rho_{ads}}\right)$	$q_m, p_{1/2}, \rho_{ads}$	Duan et al. (2020)
Monolayer model with one energy (M1E)	$q = \frac{n N_m}{1 + \left(\frac{p_{1/2}}{p}\right)^n}$	$q_{exc} = \frac{n N_m}{1 + \left(\frac{p_{1/2}}{p}\right)^n} \left(1 - \frac{\rho_g}{\rho_{ads}}\right)$	$n, N_m, p_{1/2}, \rho_{ads}$	Duan et al. (2025)
Monolayer model with two energies (M2E)	$q = \frac{n_1 N_{m1}}{1 + \left(\frac{p_1}{p}\right)^{n_1}} + \frac{n_2 N_{m2}}{1 + \left(\frac{p_2}{p}\right)^{n_2}}$	$q_{exc} = \left(\frac{n_1 N_{m1}}{1 + \left(\frac{p_1}{p}\right)^{n_1}} + \frac{n_2 N_{m2}}{1 + \left(\frac{p_2}{p}\right)^{n_2}} \right) \left(1 - \frac{\rho_g}{\rho_{ads}}\right)$	$n_1, n_2, N_{m1}, N_{m2}, p_1, p_2, \rho_{ads}$	Mokhati et al. (2024)

(AIC), based on experimental observational data. These metrics were employed to assess model performance. Generally, the most suitable model from experimental data is selected based on the highest R^2 value and the lowest RSS and AIC values (Duan et al., 2022, 2024b).

$$R^2 = \frac{\sum (q_{exp} - \bar{q}_{cal})^2}{\sum (q_{exp} - \bar{q}_{cal})^2 + \sum (q_{cal} - \bar{q}_{cal})^2} \quad (2)$$

$$RSS = \sum_{i=1}^N (q_{cal} - q_{exp})^2 \quad (3)$$

$$AIC = N \ln \left(\frac{RSS}{N} \right) + 2M + \frac{2M(M+1)}{N-M-1} \quad (4)$$

where q_{exp} and q_{cal} represents the adsorption capacity from experiments and model, respectively. $\bar{q}_{cal}$ denotes the average amount of model. N denotes the experiment count. M is number of variable parameters in the model.

Table 6
Fitting parameters of M1E model.

Gas	T, K	N_m , mmol/g	n	$p_{1/2}$, MPa	ρ_{ads} , mg/cm ³
S0	308	0.2078	0.9059	5.6731	0.8127
	328	0.2101	0.8171	6.6460	0.7930
	348	0.2203	0.7276	7.7506	0.7754
0.1-HS0	308	0.2134	0.8051	6.2713	0.7120
	328	0.2048	0.7608	7.1510	0.6912
	348	0.1954	0.7198	8.0719	0.6726
0.3-HS0	308	0.2192	0.7842	6.9066	0.6845
	328	0.1959	0.7445	7.6412	0.6654
	348	0.1880	0.7023	8.3997	0.6404
0.5-HS0	308	0.2239	0.7971	6.5891	0.7036
	328	0.2049	0.7491	7.3164	0.6843
	348	0.2023	0.7102	8.2949	0.6671
S1	308	0.3122	0.8710	6.9364	0.8412
	328	0.3187	0.8215	7.6460	0.8173
	348	0.3196	0.7668	8.3506	0.7994
0.1-HS1	308	0.3148	0.8119	7.6162	0.7861
	328	0.3092	0.7634	8.1565	0.7612
	348	0.2826	0.7182	8.6605	0.7402
0.3-HS1	308	0.3209	0.8087	7.9612	0.7719
	328	0.3118	0.7572	8.3369	0.7436
	348	0.2862	0.7101	8.8742	0.7037
0.5-HS1	308	0.3287	0.7635	8.3948	0.7356
	328	0.3103	0.7145	8.7291	0.7073
	348	0.2929	0.6723	9.2274	0.6784

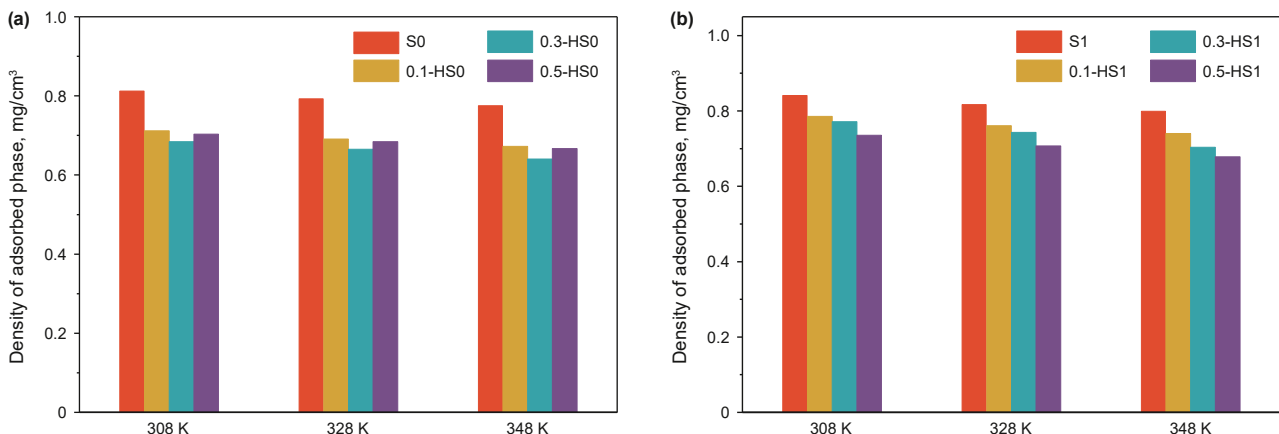
This study employed a nonlinear iterative algorithm to evaluate the fit between the models and experimental data. The results are detailed in Table S1, which lists the values of the R^2 , RSS, and AIC for the five models. Analysis indicates that the R^2 values for all five models are incredibly close to 1, and that the differences in RSS values are comparatively negligible. This finding confirms the effectiveness of these five models in describing the experimental data. The core principle of the AIC criterion is to balance the complexity and fitting accuracy of the model, effectively averting overfitting issues that can be caused solely by statistical significance (Duan et al., 2016). In this study, the M1E model exhibited the minimum AIC value, along with the best R^2 and RSS values, strongly substantiating its effectiveness in depicting the observed data. Furthermore, all four parameters of the M1E model have clear physical significance: q_m directly reflects the maximum adsorption capacity, n reveals the occupancy characteristics of adsorption sites; N_m quantifies the number of active sites on the shale surface; and $p_{1/2}$ is related to the strength of the interaction between CH₄ and shale. In contrast, the parameters of traditional models are mostly empirical fit values and lack support from

specific physical mechanisms. Therefore, the M1E model not only offers higher fitting accuracy but also provides a more reliable theoretical basis for analyzing adsorption mechanisms. The fitting outcomes of the M1E model are presented in Figs. 9 and 10, while the fitted parameters are detailed in Table 6.

As demonstrated in Fig. 11 and Table 6, the adsorption phase density (ρ_{ads}) of CH₄ ranged from 0.6654 to 0.8412 g/cm³, with all measured values exceeding the density of liquid CH₄ at its boiling point (−161 °C, 0.1 MPa) of 0.424 g/cm³. Higher ρ_{ads} values of methane have also been reported in other shale adsorption studies (Gasparik et al., 2014; Hu et al., 2015; Tian et al., 2016). Gasparik et al. (2014) reported that the methane ρ_{ads} in the Haynesville shale could reach 0.79 g/cm³. Hu et al. employed a ρ_{ads} value as high as 1.051 g/cm³ in their study of the Wufeng-Longmaxi Formation shales in Sichuan Basin (Hu et al., 2015); while Tian et al. (2016) reported a ρ_{ads} as high as 1.027 g/cm³ in their study of the Ordovician shales in Sichuan Basin. These relatively overestimated ρ_{ads} values result from the expansion effect of shale during adsorption (Duan et al., 2020). The ρ_{ads} values decrease with rising temperature, due to the weakening of interaction forces between methane and shale at elevated temperatures, reducing the number of adsorbed CH₄ molecules and consequently decreasing the adsorption capacity. Notably, the ρ_{ads} consistently show a decreasing trend in shale treated with slickwater. This phenomenon indicates that slickwater treatment significantly impacts the interaction forces between CH₄ and shale.

3.2.2. Effect of slickwater on methane adsorption

Figs. 12 and 13 display CH₄ adsorption isotherms on treated shale at the same temperature. The impact of slickwater treatment on the CH₄ adsorption was significant. Within the pressure range below 2 MPa, the change in methane adsorption capacity for treated shale was relatively minor compared to that of raw shale. When the pressure is raised, a significant reduction in CH₄ adsorption is observed in both treated shale samples. This finding suggests that the presence of slickwater significantly inhibits the adsorption of CH₄ (Liu et al., 2021b). This result aligns with the findings reported in the relevant literature (Li et al., 2024a, 2024b). For sample S0, a decrease in methane adsorption capacity is initially observed, followed by an increase as the slickwater concentration increases. This observation is ascribed to the slight effect of low-concentration (0.1 wt%) slickwater permeation on the shale's pore structure and surface chemistry, resulting in a negligible effect on methane adsorption (Duan et al., 2026). However, when the fracturing fluid

**Fig. 11.** Density of adsorbed phase for CH₄ calculated by M1E model.

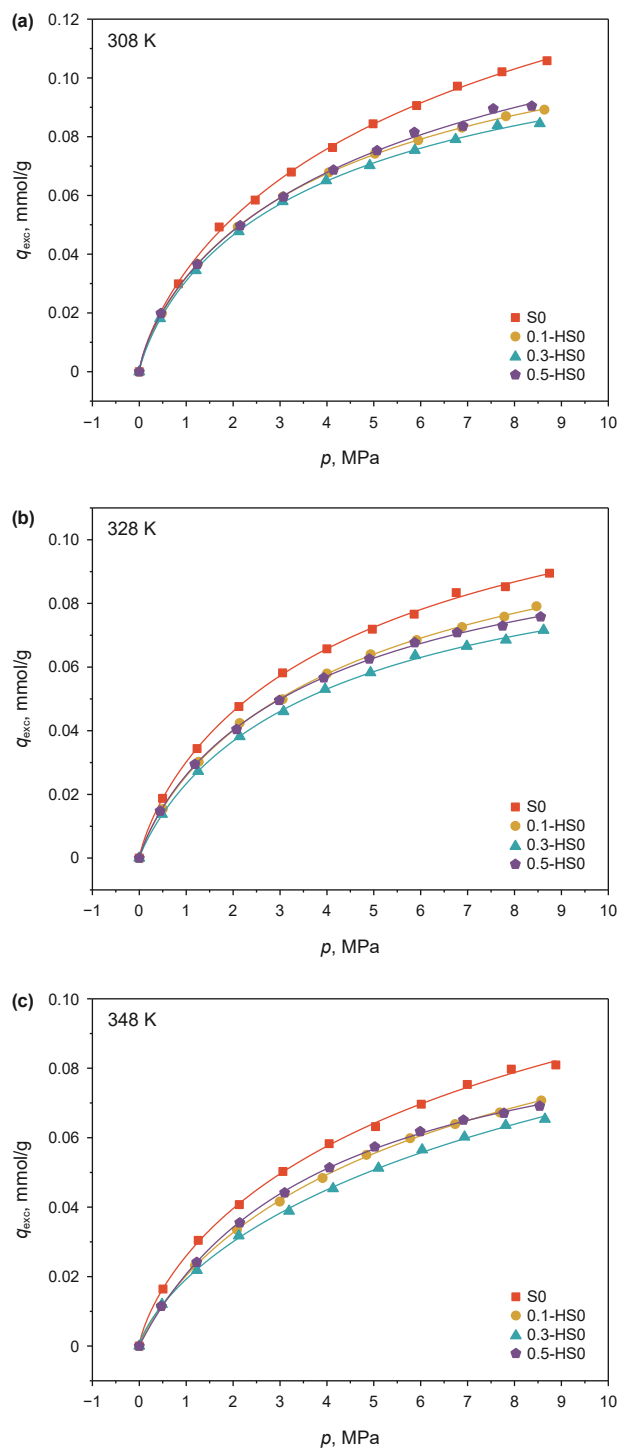


Fig. 12. Adsorption isotherms of treated shale samples S0: (a) 308 K, (b) 328 K, (c) 348 K.

concentration increased to 0.5 wt%, the surface area of the S0 sample expanded, enhancing the methane adsorption capacity. For the sample S1, methane adsorption exhibited a slight decrease with varying slickwater concentrations, though this change was not significant. This was primarily due to the comparatively reduced surface area and pore volume of the sample S1. Residual particles adhering to the pore surfaces occupied and disrupted most methane adsorption sites, thereby

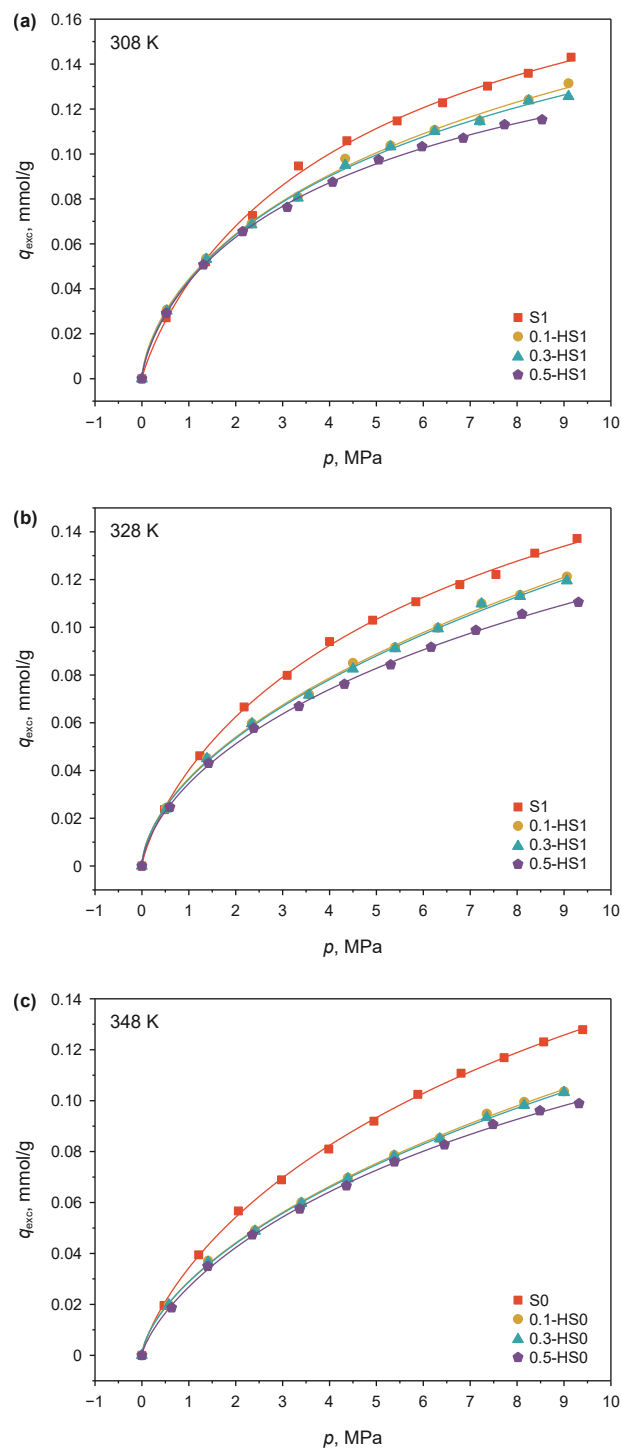


Fig. 13. Adsorption isotherms of treated shale samples S1: (a) 308 K, (b) 328 K, (c) 348 K.

weakening the effect of slickwater concentration on methane adsorption capacity.

This study systematically compared and analyzed the properties of shale treated with slickwater and its CH_4 adsorption characteristics with previous research, and relevant data detailed in Table 7. The analysis suggests that the data acquired from slickwater-treated shale in this study are highly consistent with existing literature reports. Further analysis reveals significant

Table 7
Comparison of change in clay, pore structure and adsorption for shale after fracturing fluid treatment from literature.

Shale	Properties before treatment		Fracturing fluid	Properties after treatment		Changes in adsorption of CH ₄	References
	Clay, wt%	Pore information ^a		Clay, wt%	Pore information		
Taiyuan Formation shale S0, Bohai Bay Basin	26.75	S_{BET} 12.876 m ² /g; V_t 0.025 cm ³ /g; D_{ap} 7.736 nm	Slickwater (0.1–0.5 wt% friction reducer (polyacrylamide, PAM), and 1.0 wt% anti-swelling agent (KCl))	22.88 – 24.53	S_{BET} 9.043–9.833 m ² /g; V_t 0.020 – 0.0029 cm ³ /g; D_{ap} 8.590–9.316 nm	Reduced from 0.112 to 0.095 mmol/g at 9 MPa, 308 K	This study
Taiyuan Formation shale S1, Bohai Bay Basin	30.43	S_{BET} 1.830 m ² /g; V_t 0.009 cm ³ /g; D_{ap} 20.550 nm	Slickwater (0.1–0.5 wt% friction reducer (polyacrylamide, PAM), and 1.0 wt% anti-swelling agent (KCl))	28.90 – 30.17	S_{BET} 1.110 – 2.084 m ² /g; V_t 0.012 cm ³ /g; D_{ap} 23.192–23.228 nm	Reduced from 0.151 to 0.098 mmol/g at 9 MPa, 308 K	This study
Longmaxi Formation shale, Sichuan Basin	16	S_{BET} 13.67 m ² /g; V_t 0.0249 cm ³ /g; D_{ap} 4.29 nm	Slickwater (0.2 wt% friction reducer, 1 wt% clay control agent, 0.15 wt% cleanup agent and 0.05 wt% demulsifier)	19	S_{BET} 8.29 m ² /g; V_t 0.00991 cm ³ /g; D_{ap} 4.78 nm	Reduced from 1.15 to 0.85 mmol/g at 10 MPa, 303 K	Sun et al. (2018a)
Longmaxi Formation shale, Sichuan Basin		S_{BET} 13.931 m ² /g;	Slickwater (0.7% polyacrylamide (drag reducer), 1% potassium chloride (anti-swelling agent))		S_{BET} 9.545 m ² /g;	Reduced from 0.201 to 0.134 mmol/g at 18 MPa, 333 K	Li et al. (2024a)
Taiyuan Formation shale, Bohai Bay Basin	26.75	S_{BET} 12.8756 m ² /g; V_t 0.01465 cm ³ /g; D_{ap} 7.7356 nm	Clean fracturing fluids (1–5 wt% cetyl trimethyl ammonium bromide, 0.6 wt% sodium salicylate, 1.5 wt% KCl)	23.14 – 24.81	S_{BET} 0.498–0.756 m ² /g; V_t 0.004 – 0.0069 cm ³ /g; D_{ap} 32.1221 – 32.6290 nm	Reduced from 0.125 to 0.098 mmol/g at 9 MPa, 308 K	Duan et al. (2026)
Yanzitan village shale, Yiyang city, Hunan	14		Fracturing fluids (main cations: Na ⁺ , K ⁺ , Mg ²⁺ , and Ca ⁺ ; main anions: COOH ⁻ , Cl ⁻ , NO ₃ ⁻ , and SO ₄ ⁻)	11.808			Tan et al. (2022)
Longmaxi Formation shale, Sichuan Basin	17	The pore size was between 3 and 29 nm	Alkali solution (NaOH)	31.52	The pore size was between 1.5 and 77 nm		Shao et al. (2023)
Wufeng formation shale, Sichuan basin	29.6	S_{BET} 17.5784 m ² /g; V_t 0.025 cm ³ /g; D_{ap} 6.93 nm	Supercritical CO ₂ -water (exposure conditions: 15 MPa, 338 K)	27.8	S_{BET} 13.9623 m ² /g; V_t 0.02665 cm ³ /g; D_{ap} 7.92 nm	Reduced from 0.069 to 0.058 mmol/g at 10 MPa, 338 K	Yang et al. (2022)
Longmaxi Formation shale, Sichuan Basin		S_{BET} 30.961 m ² /g; V_t 0.016 cm ³ /g	Supercritical CO ₂ -water (exposure conditions: 20 MPa, 343 K)		S_{BET} 22.539 m ² /g; V_t 0.015 cm ³ /g	Reduced from 0.082 to 0.051 mmol/g at 10 MPa, 303.15 K	Qin et al. (2023)
CS1# Shale, Qaidam Basin	74.8	S_{BET} 6.462 m ² /g; V_t 0.0113 cm ³ /g	Supercritical CO ₂ -water (exposure conditions: 10 MPa, 323 K)	65.4	S_{BET} 12.900 m ² /g; V_t 0.0141 cm ³ /g		Luo et al. (2019)
FS1# shale, Ordos Basin	55.3	S_{BET} 2.719 m ² /g; V_t 0.0117 cm ³ /g	Supercritical CO ₂ -water (exposure conditions: 10 MPa, 323 K)	50.7	S_{BET} 3.403 m ² /g; V_t 0.0131 cm ³ /g		Luo et al. (2019)

^a S_{BET} represents surface area, V_t represents pore volume, D_{ap} denotes average pore diameter.

differences in the regulatory effects of various fracturing fluids on shale properties: Fracturing systems, such as slickwater, clean fracturing fluids, and supercritical CO₂, can effectively reduce the clay mineral content in shale (Sun et al., 2018a; Tan et al., 2022; Shao et al., 2023; Yang et al., 2022). However, treatment with a NaOH solution leads to the increase in clay content (Shao et al., 2023). Following treatment with various fracturing fluids or supercritical CO₂, the pore parameters decreased to varying degrees, while the average pore size exhibited an increasing trend. These alterations in composition and microstructure directly led to reduced methane adsorption capacity (Li et al., 2024a). From desorption kinetics perspective, this phenomenon facilitates accelerated CH₄ desorption, a process that is advantageous for the exploitation of shale gas (Duan et al., 2026). Nonetheless, it is important to note that residual fracturing fluid deposits within shale pores restrict gas diffusion pathways. Corresponding changes in pore volume confirm the negative impact of these deposits on methane diffusion processes.

3.3. Analysis of the physicochemical interpretation of the adsorption model parameters

3.3.1. Stereographic parameters

The stoichiometric coefficient (n) offers insights into the adsorption orientation of CH₄ molecules on shale surfaces (i.e., parallel or perpendicular), which can be employed to elucidate the adsorption mechanism of CH₄ (Raffah et al., 2024; Aouaini et al., 2022). Specifically, there are three scenarios (Mokhati et al., 2024; Sellaoui et al., 2024): when the n value is less than 0.5, two or more sites share a single adsorbed methane molecule through a multi-docking mechanism, demonstrating parallel orientation. When $0.5 < n < 1$, CH₄ molecules exhibit coexisting parallel and perpendicular adsorption orientations at the shale interface, characterized by distinct geometric configurations. When $n \geq 1$, active sites on the shale surface can accommodate one or more adsorbed molecules, indicating the presence of perpendicular orientation and a multi-molecular adsorption mechanism (Mokhati et al., 2024).

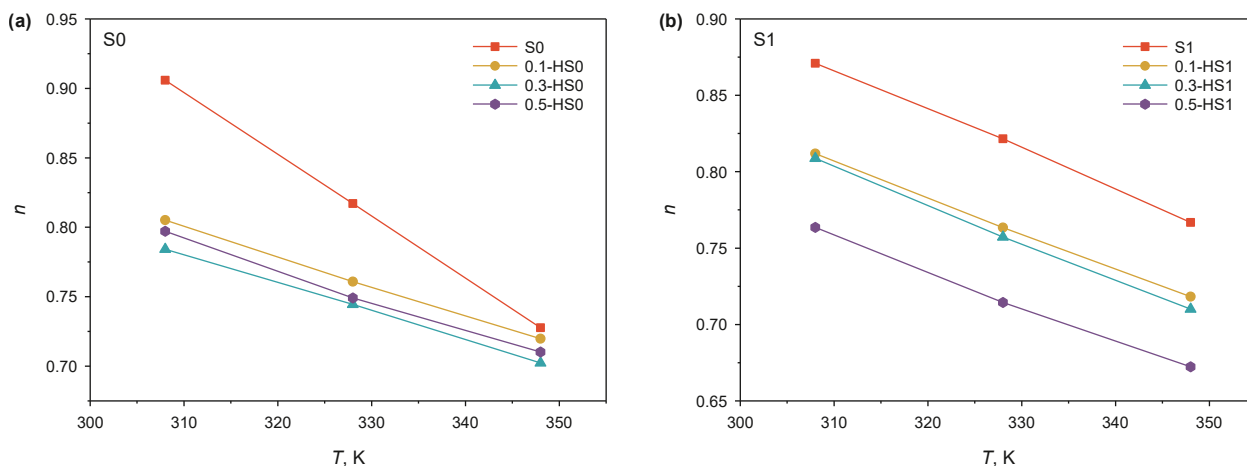


Fig. 14. Number of molecules per site (n) for treated shale samples: (a) S0, (b) S1.

The n -values with respect to temperature are demonstrated in Fig. 14. The n values for both samples are lower than 1 but higher than 0.5. This suggests that a mixed multi-molecular attachment mode occurs during adsorption, with some molecules attaching in parallel positions and others attaching perpendicularly (Mokhati et al., 2024). As shown in Fig. 15, if n is lower than 1, it means that one CH_4 molecule is bonded and adhered to $1/n$ sites (Raffah et al., 2024). Taking the S0 shale at 308 K as an example, $n = 0.9059$. This indicates that CH_4 molecules may either adsorb simultaneously at two sites on surface with a probability (y), or adsorb at one site with a probability ($1-y$). Solving the equation $y \times 0.5 + (1-y) \times 1 = 0.9059$ reveals that about 18.8% of molecules are simultaneously attached at

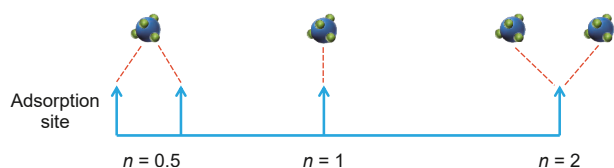


Fig. 15. Possible CH_4 adsorption attachment on the shale surface: parallel ($n < 0.5$), mixed ($0.5 < n < 1$) or perpendicular ($n \geq 1$).

two sites, while 81.2% are anchored at only one site. The n value decreases with increasing temperature, reflecting that the adsorption behavior is endothermic. As the temperature rises, the interactions between CH_4 and the active sites weaken, reducing the number of gas molecules adhering to the shale surface and consequently decreasing the n value (Aouaini et al., 2022). Fig. 16 displays the calculated proportions of methane molecules anchored on shale surfaces. As the temperature rises, the proportion of CH_4 molecules simultaneously anchored at two sites gradually rises. This is primarily attributed to the weakened interactions between methane and shale at elevated temperatures, requiring CH_4 molecules to utilize more active sites for anchoring (Duan et al., 2020).

Following the application of slickwater, the n -values decreased uniformly. This decline stems from slickwater diminishing the adsorption capacity of CH_4 . Consequently, the number of CH_4 molecules on the shale surface decreased, and the number of molecules attached to individual adsorption sites correspondingly declined (Duan et al., 2020). For S0 shale, the n value exhibited a decrease, followed by a slight increase with increasing slickwater concentration, thereby aligning with the trend of slickwater concentration affecting CH_4 adsorption capacity. For S1 shale, the n -value undergoes a decline in proportion to the rise in slickwater concentration. This phenomenon can be attributed to the reduction in interaction forces between CH_4 and shale caused by

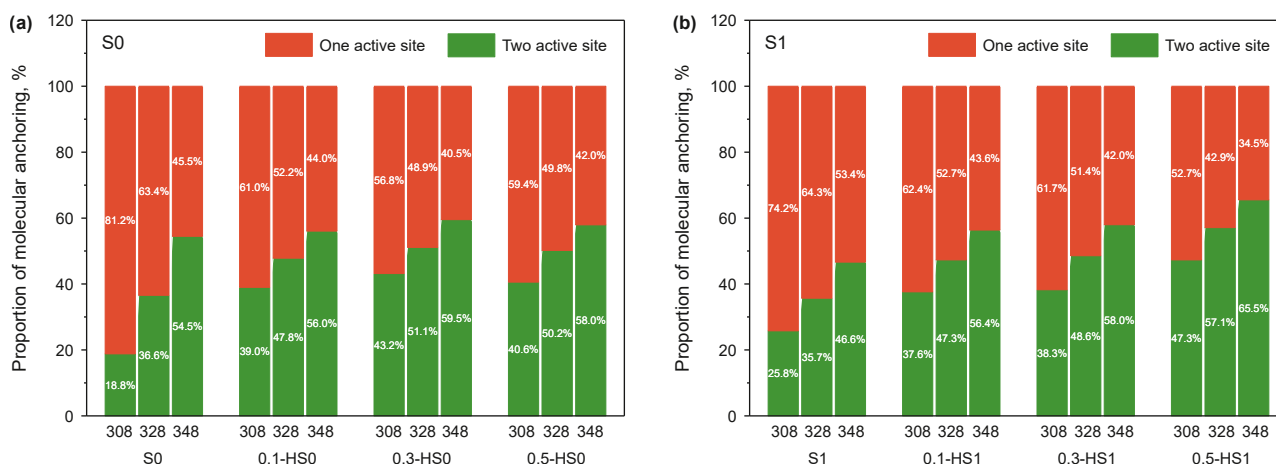


Fig. 16. Proportion of molecular anchoring by one active site or two active site.

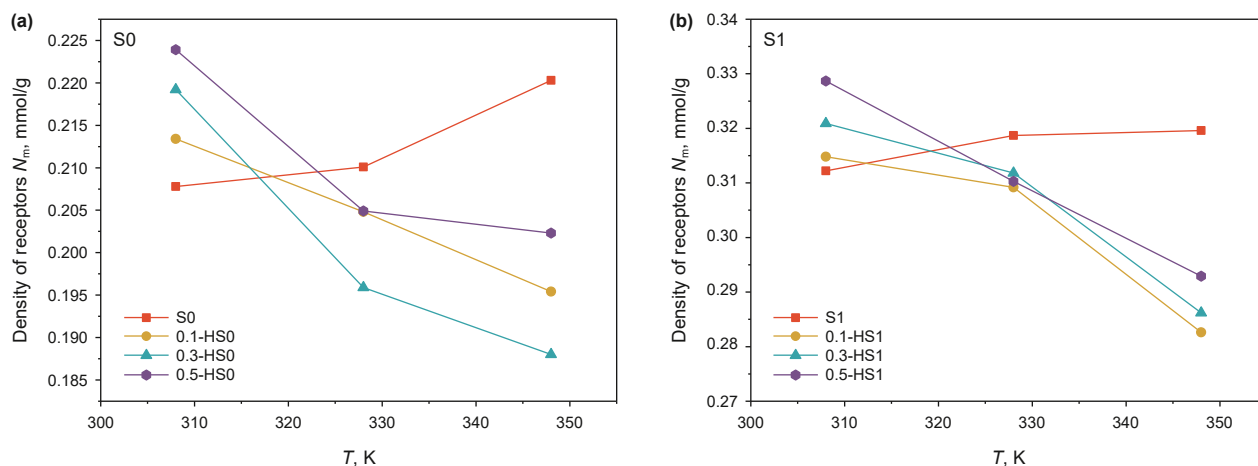


Fig. 17. Density of receptors (N_m) for shale samples treated with different slickwater: (a) S0, (b) S1.

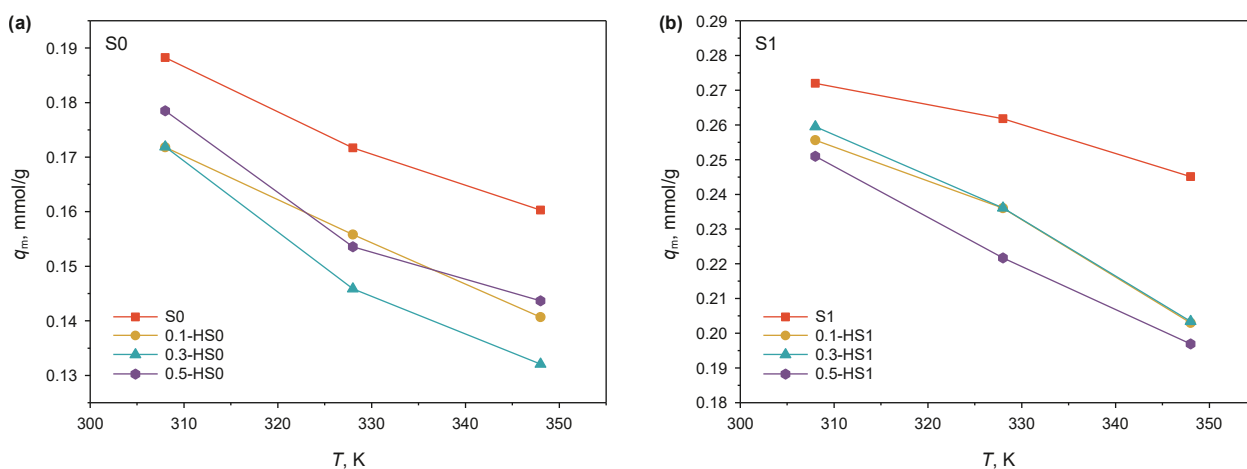


Fig. 18. Total adsorbed quantity (q_m) for treated shale samples: (a) S0, (b) S1.

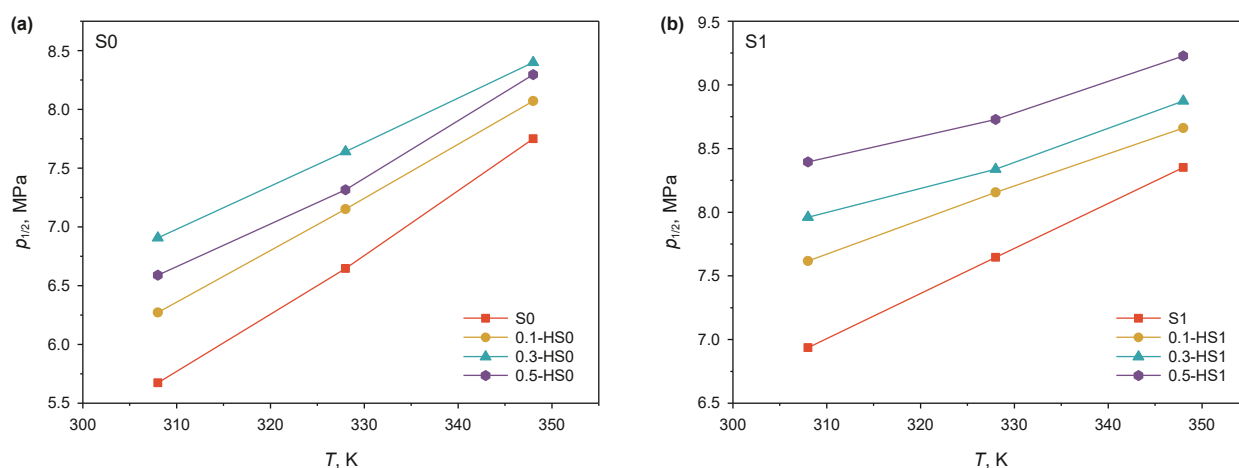


Fig. 19. Energetic parameter ($p_{1/2}$) for shale samples as a function of temperature: (a) S0, (b) S1.

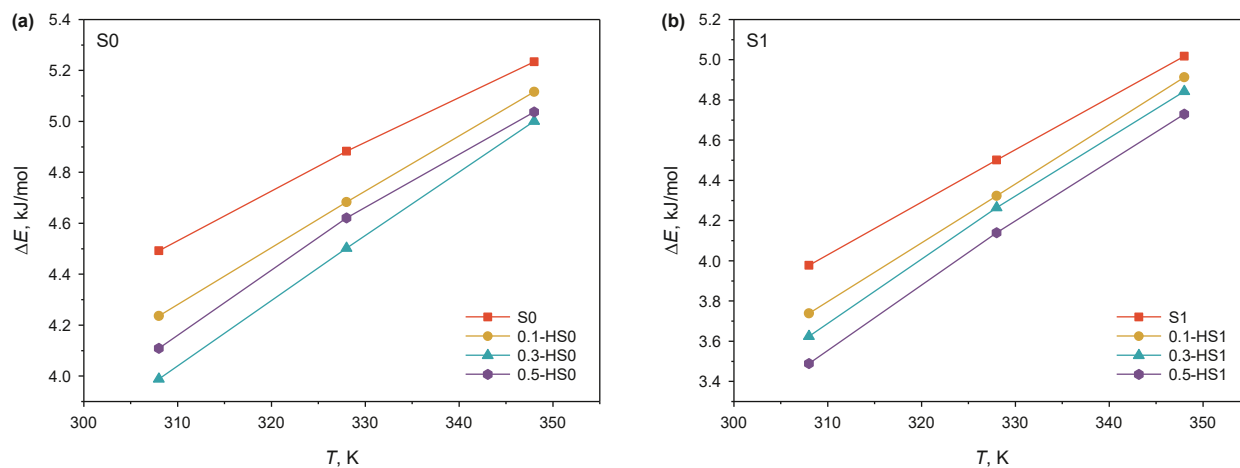


Fig. 20. Adsorption energies (ΔE) for shale samples as a function of temperature: (a) S0, (b) S1.

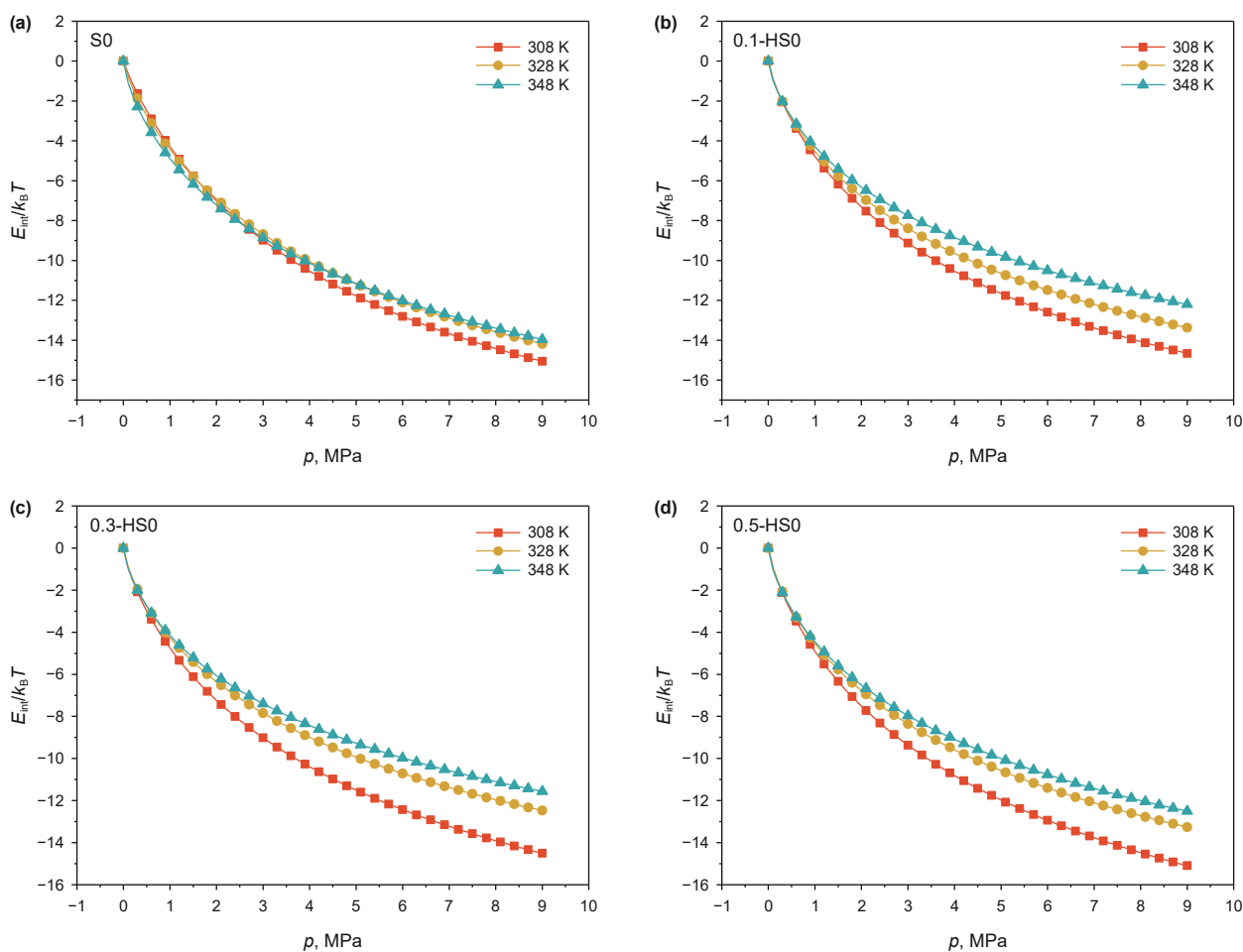


Fig. 21. Internal energy (E_{int}) for shale samples: (a) S0, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

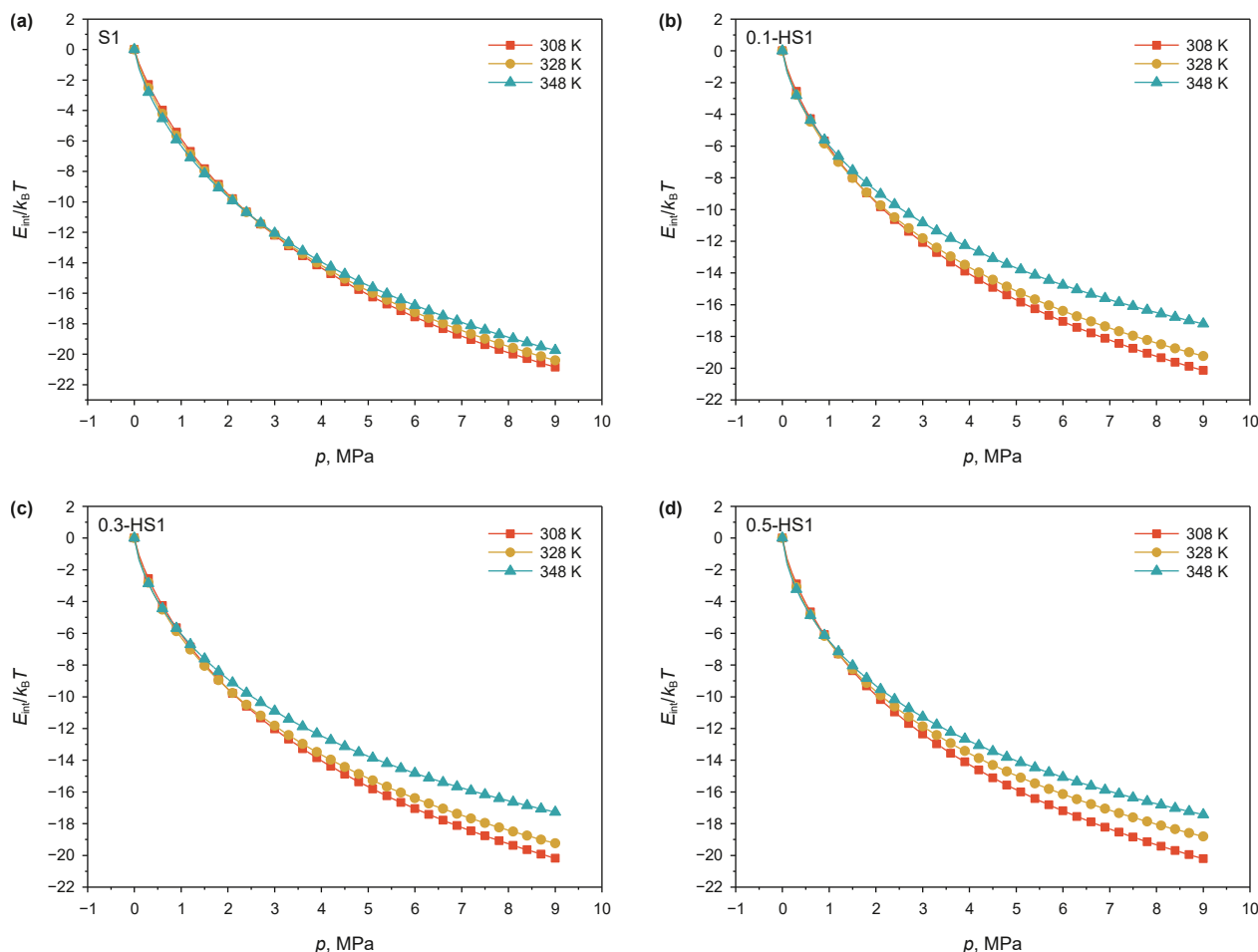


Fig. 22. Internal energy (E_{int}) for shale samples: (a) S1, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

slickwater residues, resulting in a decline in the number of CH_4 molecules per active site (Bouزيد et al., 2025). Moreover, the observed correlation between the slickwater concentration and the anchoring form of CH_4 molecules is consistent with the established n -value trend.

Fig. 17 shows the variation in methane receptor site density (N_m) with temperature. This parameter provides information on the number of adsorption sites required when adsorption reaches saturation (Bouزيد et al., 2025). The N_m values for both raw shales, S0 and S1, increase with rising temperature. This is in contrast to the temperature trend of the n value, attributed to a reduction in the number of methane molecules adsorbed per site. This process leads to the creation of additional available space on the adsorbent, thereby facilitating the formation of further binding sites and, consequently, enhancing receptor site density (Mokhati et al., 2024). In contrast, the receptor density N_m of treated shale demonstrates a monotonically decreasing trend, attributable to the effects of thermal agitation. The exothermic nature of adsorption stems from the disruption, destruction, or release of the binding energy of methane molecules as a consequence of thermal collisions (Knani et al., 2025). Additionally, the stereographic effect states that the magnitude of methane molecules increases with rising temperature, and these aggregated molecules interfere with adjacent receptors. Changes in receptor site density reflect variations in the available space per receptor for methane molecule adsorption, which in turn correlates with alterations in slickwater concentration.

The total adsorption capacity q_m represents the amount of CH_4 adsorbed onto shale at saturation, calculated as follows (da Silva Bruckmann et al., 2024):

$$q_m = nN_m \quad (5)$$

Fig. 18 demonstrates the q_m values of CH_4 with respect to temperature. The q_m values decrease as the temperature rises. This indicates that temperature influences the aggregation phenomenon of CH_4 molecules (Sun et al., 2018a). As the temperature rises, the binding strength between CH_4 and the shale diminishes, resulting in a decline in saturated adsorption amount. This behavior also correlates with trends in spatial parameters (n , N_m). The decline in n , coupled with the diminution or gradual escalation in N_m , signifies that the CH_4 adsorption sites within these shales reach saturation as temperature rises (Knani et al., 2025). Consequently, the number of molecules per site is a pivotal factor in determining the CH_4 adsorption capacity of shale. The saturated adsorption amount of CH_4 underwent a substantial decline following slickwater treatment, thereby indicating that slickwater treatment is detrimental to CH_4 adsorption.

Slickwater has been demonstrated to affect CH_4 adsorption behavior by altering shale composition and pore structure (Li et al., 2024a, 2024b). The relationship between the n and q_m on shale, as well as the clay content and S_{BET} , is demonstrated in Figs. S1 and S2. The parameter n has been observed to increase with rising clay content, as clay serves as the primary mineral providing CH_4

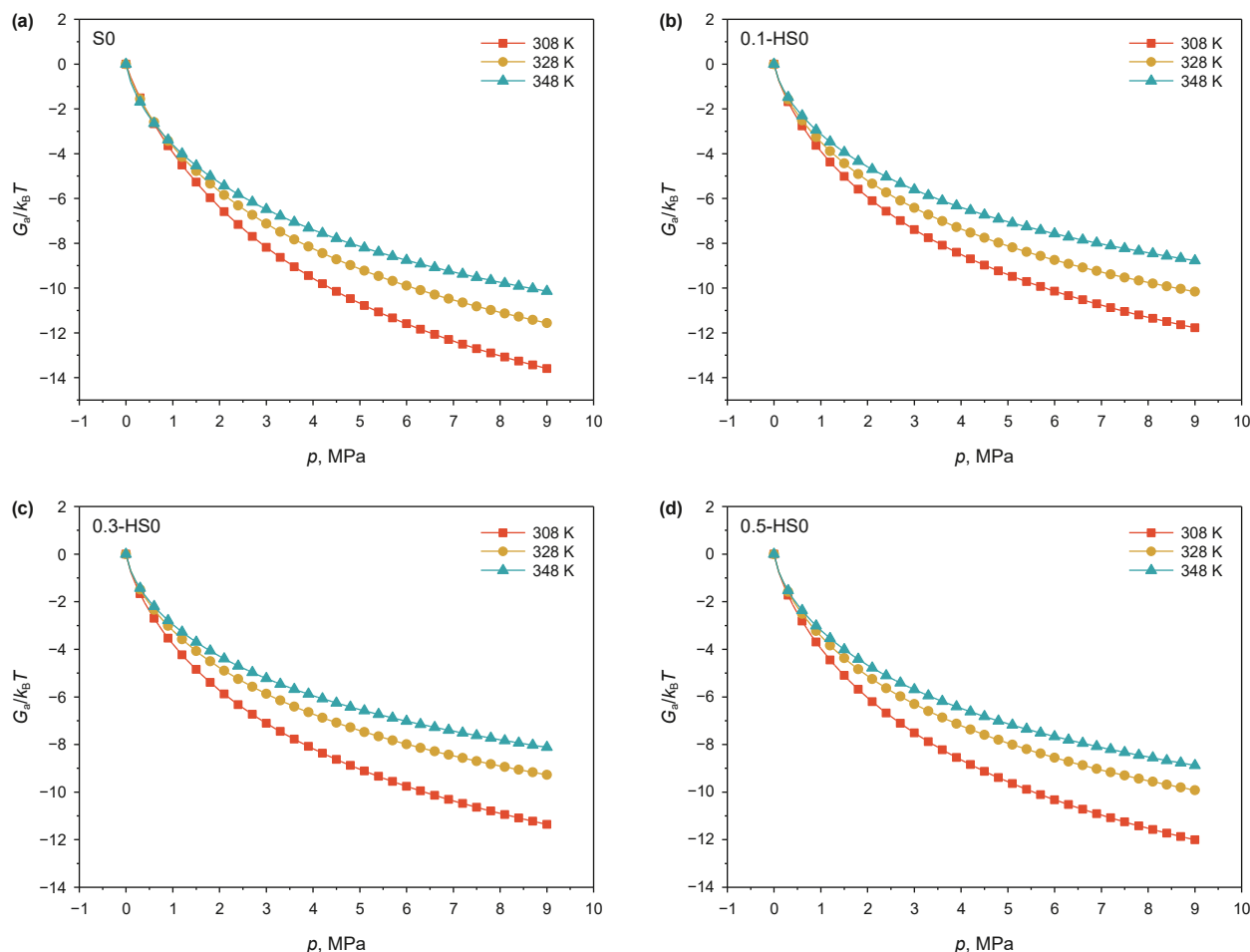


Fig. 23. Gibbs free energy (G_a) for shale samples: (a) S0, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

adsorption sites. An increased clay content provides more sites for CH_4 molecules to attach, thus increasing the number of adsorbed CH_4 molecules per site. Previous studies have indicated that shales with high clay content exhibit greater methane adsorption capacity (Duan et al., 2016). For shale S0, the q_m exhibited a transient decrease, followed by an increase with rising clay content. For shale S1, the q_m initially increased, then plateaued, and subsequently continued to rise with increasing clay content. This suggests that clay is not the sole factor influencing methane adsorption, and that other factors also play a significant role (Duan et al., 2026). As the S_{BET} of shale S0 increases, the parameter n also rises. In the case of shale S1, the parameter n increases initially before decreasing as S_{BET} rises. Similarly, for shale S0, the q_m initially rises and then falls as the S_{BET} increases. In the case of shale S1, the q_m increases continuously with an increase in S_{BET} . An increase in the S_{BET} leads to a greater number of adsorption sites available for methane molecules, thereby favoring CH_4 adsorption on shale. Shale is a rock characterized by complicated composition and microstructure. Slickwater alteration can cause varying degrees of alteration to the composition and pore structure of shale. Therefore, the influence of shale microstructure and composition on methane adsorption capacity depends on multiple factors.

3.3.2. Energetic interpretations

To gain a deeper understanding of the adsorption process and evaluate the strength of interactions between the CH_4 molecule and shale, the M1E model was utilized to determine adsorption

energy (Bouzi et al., 2025). This model calculates adsorption energy (ΔE) by using the pressure corresponding to the half-saturation point ($p_{1/2}$). The equation employed for calculating ΔE is as follows (Duan et al., 2020):

$$\Delta E = RT \cdot \ln \left(\frac{p_0}{p_{1/2}} \right) \quad (6)$$

where p_0 represents the saturated vapor pressure, and R represents the ideal gas constant ($8.314 \times 10^{-3} \text{ kJ}/(\text{K} \cdot \text{mol})$). The Clausius-Clapeyron model was utilized to determine the p_0 values when the temperature exceeds the critical temperature (Duan et al., 2025). The p_0 values at 308, 328, and 348 K are 36.25, 39.83, and 47.31 MPa for CH_4 , respectively.

As demonstrated in Fig. 19, the half-saturation pressure ($p_{1/2}$) varies with temperature, indicating an increase in $p_{1/2}$ with rising temperature. That is, the pressure required for methane adsorption to reach saturation increases as temperature rises. Fig. 20 presents the calculated results for the change in adsorption energy (ΔE). The range of ΔE is from 3.2 to 5.3 kJ/mol, all below 30 kJ/mol. This indicates that van der Waals forces and London dispersion forces, signifying a physical adsorption phenomenon, predominantly govern CH_4 adsorption on shale (Duan et al., 2020). van der Waals forces (4 to 10 kJ/mol) and hydrophobic bonding forces (approximately 5 kJ/mol) are common mechanisms for physical adsorption (Knani et al., 2025). Consequently, under high-temperature conditions, interactions between CH_4

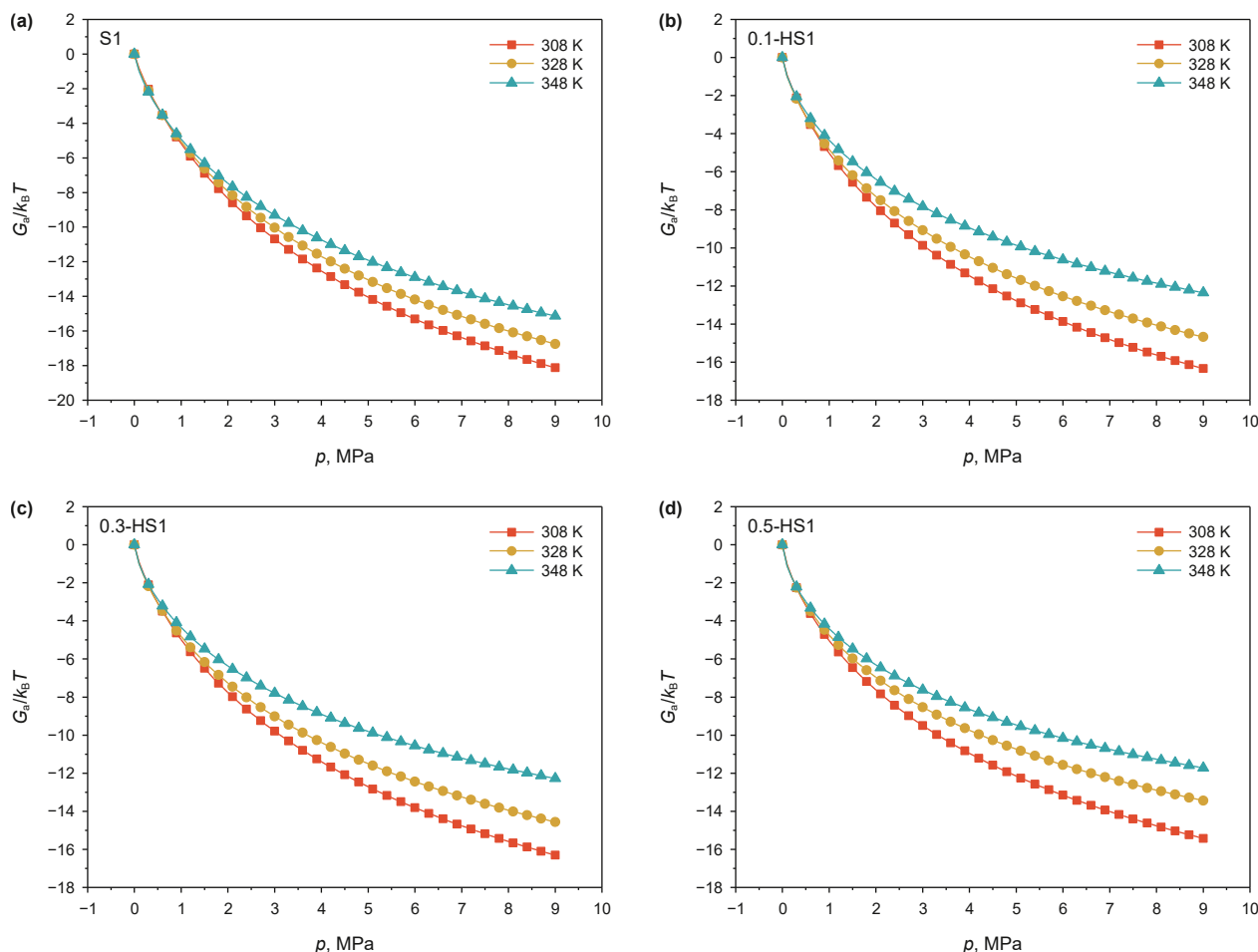


Fig. 24. Gibbs free energy (G_a) for shale samples: (a) S1, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

and shale involve both hydrophobic bonding forces and van der Waals forces (Bouzid et al., 2025). The adsorption energy is the energy required for methane molecules to adsorb onto the shale surface, as well as the interaction between methane and the shale surface. Following the slickwater treatment, a substantial decrease in the ΔE value was observed, thereby indicating a notable weakening of the forces between methane and shale. The trend of ΔE values for both samples with varying slickwater concentrations was consistent with the trend of adsorption amount changes.

Adsorption energy varies with temperature because temperature affects the strength of interactions between methane molecules and the shale surface (Bouzid et al., 2025). Increased temperature has been shown to enhance the mobility of methane molecules, which may consequently lead to alterations in their distribution on the shale surface and thereby affect adsorption energy intensity. In addition, the temperature-dependent variation in energy indicates that the interaction between CH_4 and shale undergoes changes as the temperature rises (Duan et al., 2025). For both shales, the ΔE values increase with rising temperature before and after slickwater treatment. This is primarily attributable to thermal expansion, which is caused by thermal agitation and increased gas molecule aggregation. As the temperature rises, the binding strength between the adsorbate and adsorbent may change owing to alterations in surface characteristics or molecular movement (Bouzid et al., 2025). The adsorption

process is not governed by a single type of interaction, but may encompass multiple factors or the combined action of several adsorption sites. It is essential to note that different adsorption sites possess distinct energy levels, resulting in varying responses to temperature changes.

3.4. Statistical thermodynamic evaluations

3.4.1. Thermodynamic function for methane adsorption on shale

The internal enthalpy (E_{int}) represents the total accumulated energy within the adsorption system, stemming from the molecular interaction between CH_4 and the shale surface, calculated as follows (Duan et al., 2020, 2024a):

$$E_{\text{int}} = -\frac{\partial \ln Z_g}{\partial \beta} + \frac{\mu}{\beta} \left(\frac{\partial \ln Z_g}{\partial \mu} \right) \quad (7)$$

$$\mu = k_B T \ln \frac{\beta p}{Z_g} \quad (8)$$

where Z_g denotes the partition function of CH_4 molecules, μ is the chemical potential of the adsorbed molecule, β is Boltzmann factor, and k_B is the Boltzmann constant. E_{int} can be acquired through M1E model and Eq. (7), and the formula can be expressed as follows (Duan et al., 2020):

$$\frac{E_{\text{int}}}{k_B T} = \ln \frac{\beta p}{Z_g} \left[\frac{N_m \left(\frac{p}{p_{1/2}} \right)^n}{1 + \left(\frac{p}{p_{1/2}} \right)^n} \right] - \frac{N_m \left(\frac{p}{p_{1/2}} \right)^n \ln \left(\frac{p}{p_{1/2}} \right)^n}{1 + \left(\frac{p}{p_{1/2}} \right)^n} \quad (9)$$

Figs. 21 and 22 demonstrate the variation in the E_{int} value for CH₄ on shale with increasing pressure. The shapes of the E_{int} curves demonstrate analogous characteristics at three temperatures, with all samples exhibiting negative E_{int} values. This finding indicates that CH₄ adsorption of shale exhibits exothermic characteristics, meaning that the adsorption system releases energy when capturing CH₄ molecules (Duan et al., 2020). As the pressure increases, the E_{int} value gradually decreases, indicating that CH₄ adsorption onto shale occurs spontaneously. Concurrently, the rate of decrease in E_{int} decelerates as pressure escalates, indicating that CH₄ adsorption onto shale approaches saturation with increasing pressure. In addition, the negative E_{int} value diminishes with rising temperature. This observation is ascribed to the superior adsorption of CH₄ on shale at low temperatures compared to high temperatures (Knani et al., 2025).

Gibbs free energy (G_a) has been identified as the core metric for measuring a system's spontaneity and is the key criterion for assessing the spontaneous tendency of a process (Duan et al., 2024a). Its value can be calculated using the following equation (Bouaziz et al., 2019):

$$G_a = \mu N_m n = \mu q \quad (10)$$

where μ represents the chemical potential linked to the adsorption site.

G_a can be derived from M1E model and Eq. (11), expressed as (Duan et al., 2020):

$$\frac{G_a}{k_B T} = \ln \frac{\beta p}{Z_g} \frac{n N_m}{1 + \left(\frac{p_{1/2}}{p} \right)^n} \quad (11)$$

As demonstrated in Figs. 23 and 24, the G_a of CH₄ is contingent on adsorption pressure. G_a exhibits negative values at all temperatures. This not only confirms the feasibility of CH₄ adsorption onto shale surfaces, but also indicates that this adsorption process is thermodynamically spontaneous (Knani et al., 2025). In low-pressure conditions, the level of gas begins at zero and gradually declines with rising pressure. This phenomenon suggests that high pressure is more conducive to CH₄ molecule adsorption onto shale (Duan et al., 2020). As the temperature rises, the absolute value of G_a decreases, indicating that thermal effects diminish the spontaneity of the adsorption process, rendering adsorption behavior less favorable at elevated temperatures (Duan et al., 2024a). The variation in G_a values further demonstrates that thermal perturbations reduce the spontaneous tendency for molecular capture, leading to a decreased adsorption capacity under high-

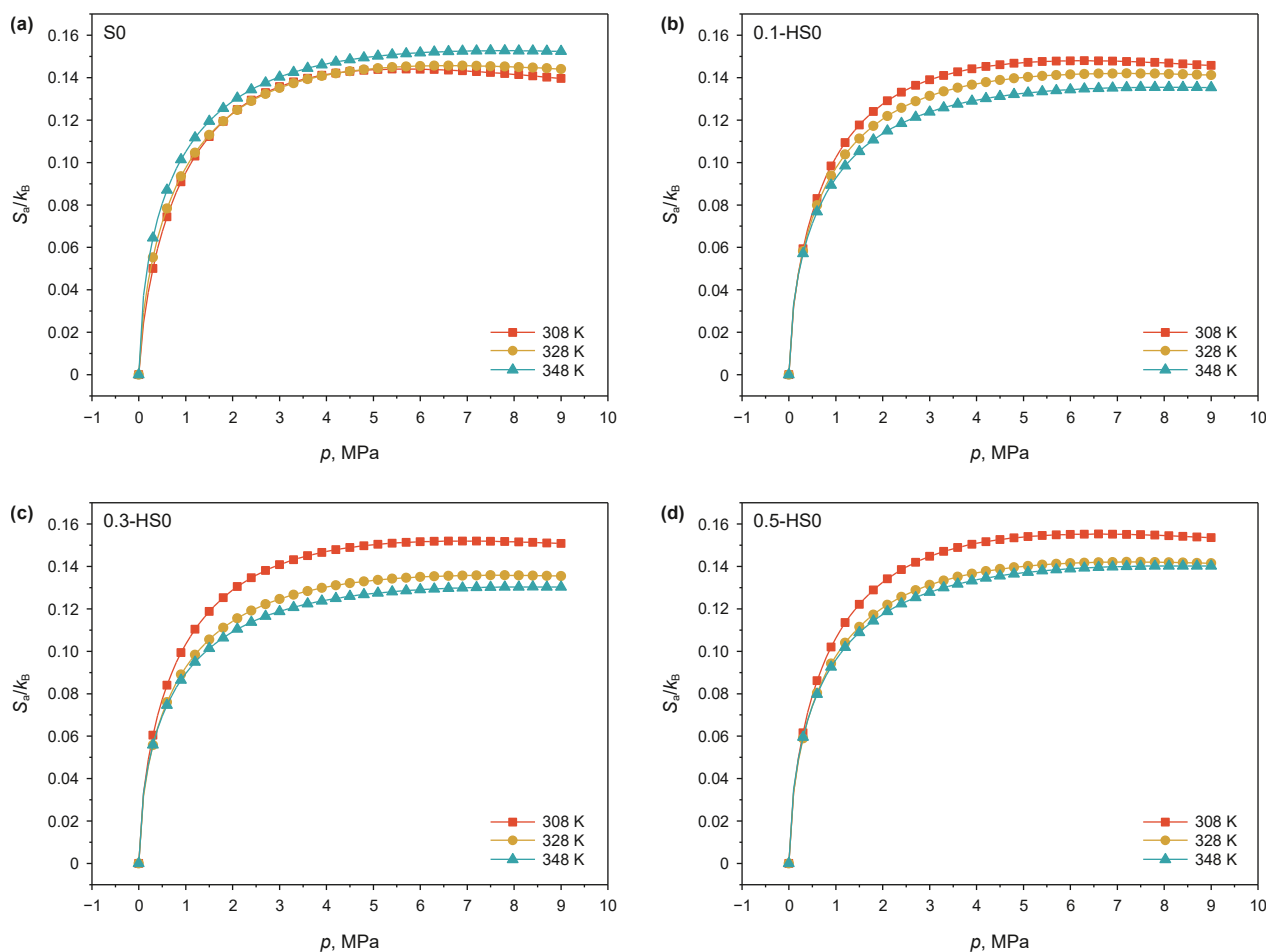


Fig. 25. Entropy (S_a) for shale samples: (a) S0, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

temperature conditions. Consequently, in the context of shale gas development, high-temperature environments are more conducive to the desorption process of shale gas.

Entropy serves as a key parameter for measuring the thermodynamic disorder or molecular rearrangement characteristics within an adsorption system. It fundamentally reflects the combined effects of various motion forms within adsorption sites, including vibration, rotation, conformational adjustments, and free migration of gas molecules (Duan et al., 2022). Adsorption entropy (S_a) can be quantitatively calculated using the following formula (Duan et al., 2020):

$$S_a = -\beta \cdot k_B \frac{\partial \ln Z_g}{\partial \beta} + k_B \ln Z_g \quad (12)$$

By combining the M1E model with Eq. (12), the expression for S_a is obtained:

$$\frac{S_a}{k_B} = N_m \ln \left[1 + \left(\frac{p}{p_{1/2}} \right)^n \right] - \frac{N_m \left(\frac{p}{p_{1/2}} \right)^n \ln \left(\frac{p}{p_{1/2}} \right)^n}{1 + \left(\frac{p}{p_{1/2}} \right)^n} \quad (13)$$

The variation of S_a with adsorption pressure is shown in Figs. 25 and 26 at different temperatures. All temperature curves demonstrate comparable two-stage properties: at lower

pressures, S_a rises swiftly as pressure rises. This phenomenon is ascribed to the abundance of unoccupied sites on the shale surface, which provides methane molecules with multiple adsorption options, leading to a significant increase in system disorder (Knani et al., 2025). When pressure reaches the half-saturation pressure ($p_{1/2}$), S_a reaches the peak. This finding is attributed to the intense competition among CH_4 molecules for the remaining vacant sites, thereby increasing system disorder. Concurrently, most sites become occupied, thereby significantly reducing the number of available sites. As pressure increases, CH_4 molecules face restricted site selection, reducing system disorder (Duan et al., 2020). Consequently, S_a exhibits a monotonically decreasing trend with increasing pressure. The calculation results indicate that the S_a values for the S0 and S1 samples are comparable at different temperatures. In the case of shale treated with slickwater, it is evident that the S_a value declines in proportion to rising temperature under constant pressure conditions. This observation indicates that the molecular disorder and migration activity within the low-temperature system are higher compared to other systems. This characteristic facilitates effective diffusion and interaction of adsorbate molecules on the adsorbent surface, consistent with the experimentally observed trend of increased adsorption capacity with decreasing temperature. In addition, the temperature dependence of adsorption entropy has been confirmed in CH_4 adsorption on zeolite (Duan et al., 2025).

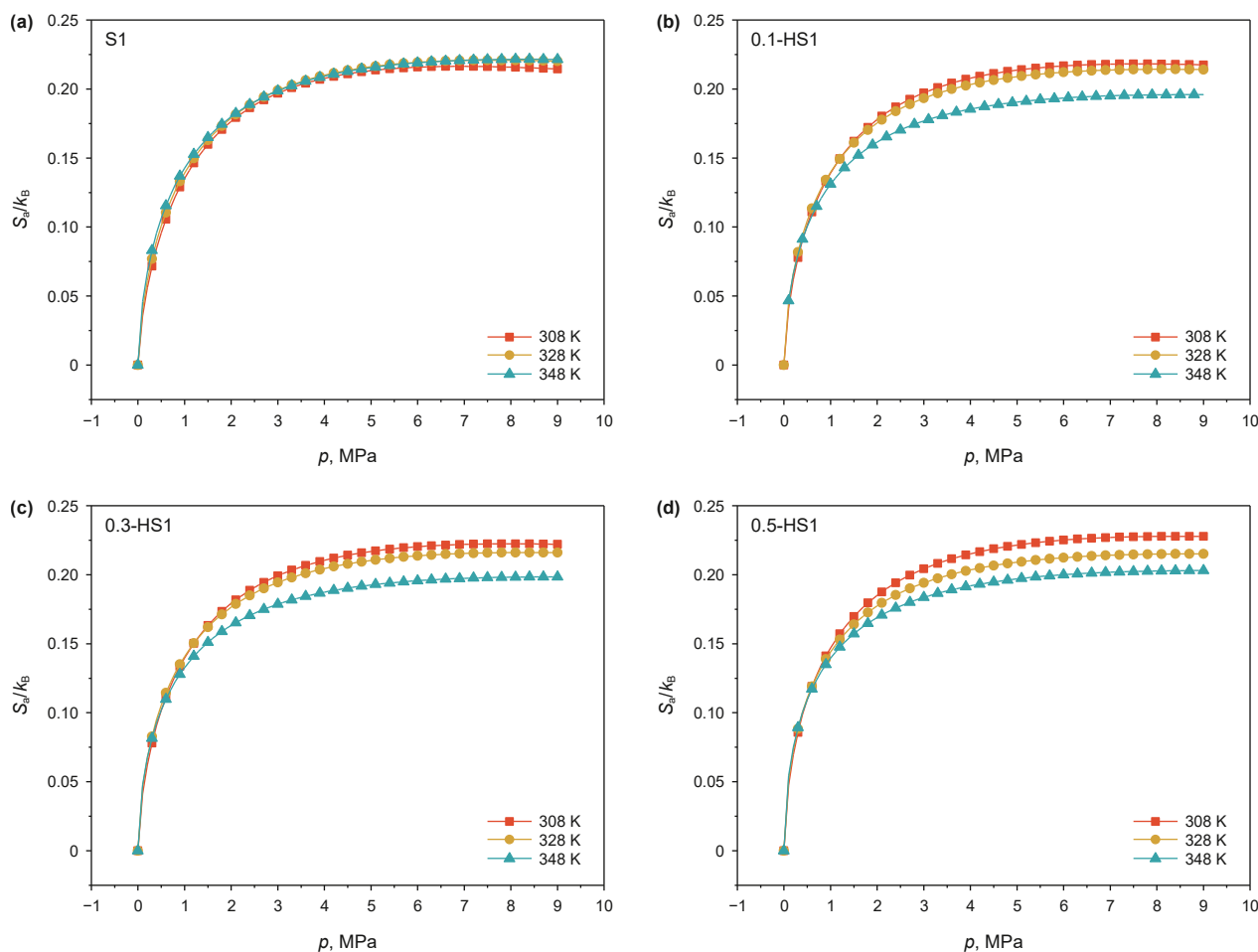


Fig. 26. Entropy (S_a) for shale samples: (a) S1, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

3.4.2. Effect of slickwater on thermodynamic parameters of methane

The comparison of thermodynamic parameters in treated shales at 308 K is demonstrated in Figs. 27 and 28; the other temperatures are showed in Figs. S3–S6. The curves of E_{int} for treated shales are similar in shape and closely aligned values. However, the negative E_{int} values on treated shale are smaller compared to those on raw shale, suggesting that CH_4 adsorption of raw shale is more spontaneous (Duan et al., 2020). This finding

implies that CH_4 adsorption of treated shale is less stable. Furthermore, the negative G_a value on raw shale is significantly higher, which further confirms the highest level of spontaneity of CH_4 adsorption on raw shale. For shale S0, the negative G_a value initially decreases and then increases with increasing slickwater concentration. For shale S1, a negative correlation exists between the G_a value and the slickwater concentration; this is aligned with the recognized association between CH_4 adsorption capacity and slickwater concentration. The S_a values demonstrate analogous

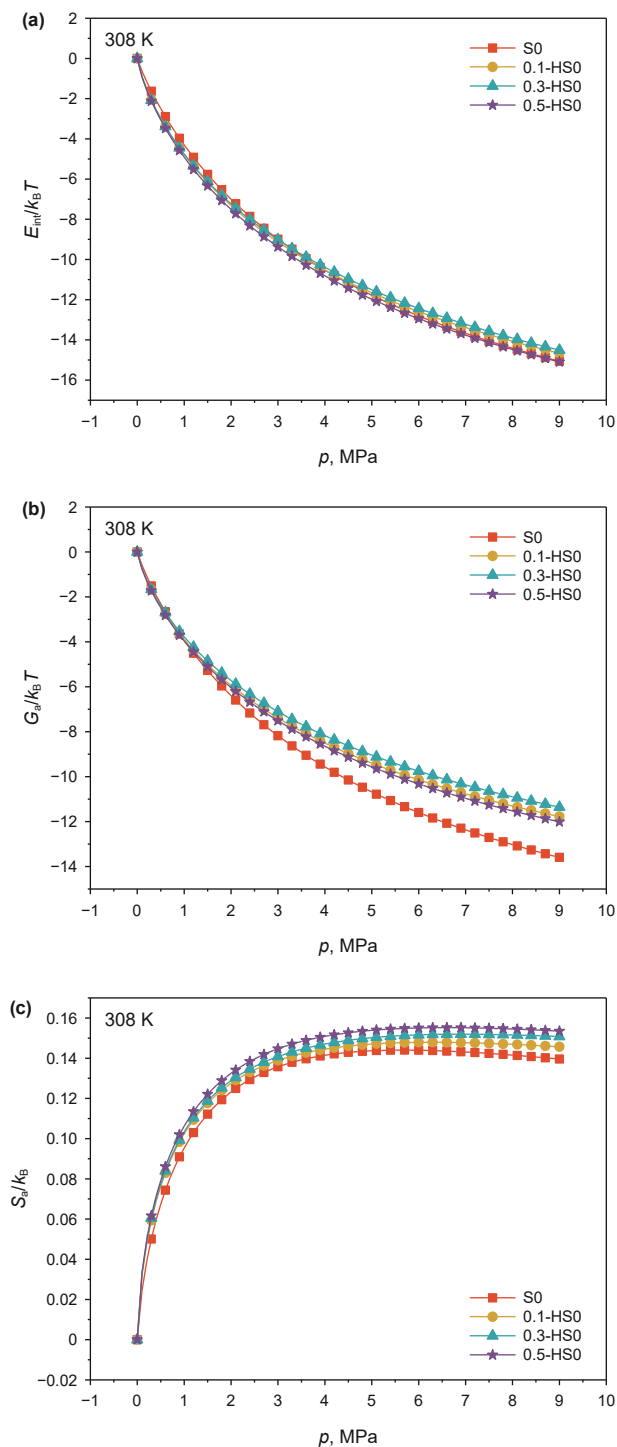


Fig. 27. Comparison of thermodynamic parameters for shale samples S0 at 308 K: (a) internal energy, (b) Gibbs free energy, (c) entropy.

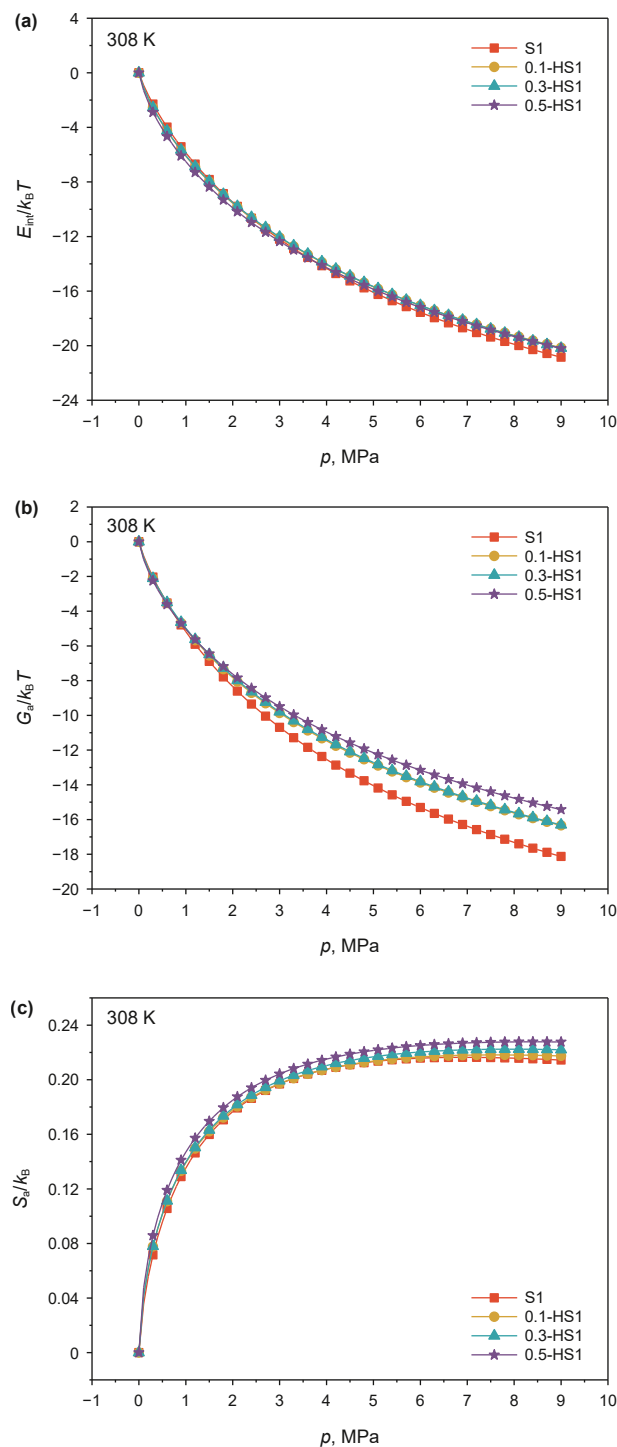


Fig. 28. Comparison of thermodynamic parameters for shale samples S1 at 308 K: (a) internal energy, (b) Gibbs free energy, (c) entropy.

trends across shales subjected to varying concentrations. The S_a value for treated shale is higher compared to raw shale, implying greater disorder during CH₄ adsorption on treated shale. The S_a value progressively increases with rising slickwater concentration, suggesting that as the slickwater concentration increases, the number of available active sites on the shale surface correspondingly expands.

3.5. Determination of site energy distribution (SED)

3.5.1. Site energy distribution of methane adsorption on shale

Site energy distribution (SED) theory is an investigative framework that examines the mechanisms of heterogeneous adsorption on adsorbent surfaces from an energy viewpoint (Bouazid et al., 2025). It provides the energy values of adsorption sites and their corresponding distribution functions, thereby characterizing the binding strength between the adsorbate and adsorption sites (Hu et al., 2025). Adopting Polanyi's potential energy theory and the M1E model as a foundation, this adsorption model can be delineated through the utilization of the site energy E^* , articulated as follows (Duan et al., 2020):

$$q_e(E^*) = \frac{N_m n}{1 + \left[\frac{p_{1/2}}{p_0} \exp\left(\frac{E^*}{RT}\right) \right]^n} \quad (14)$$

where $q_e(E^*)$ represents the adsorption amount.

By differentiating $q_e(E^*)$ with respect to E^* , the SED function $F(E^*)$ can be derived and calculated as follows (Duan et al., 2025):

$$F(E^*) = \frac{N_m n^2 \left[\frac{p_{1/2}}{p_0} \exp\left(\frac{E^*}{RT}\right) \right]^n}{RT \cdot \left\{ 1 + \left[\frac{p_{1/2}}{p_0} \exp\left(\frac{E^*}{RT}\right) \right]^n \right\}^2} \quad (15)$$

The maximum values of the SED function (E_m^* , $F(E_m^*)$) can be calculated:

$$E_m^* = RT \ln \left(\frac{p_0}{p_{1/2}} \right) \quad (16)$$

$$F(E_m^*) = \frac{N_m n^2}{4RT} \quad (17)$$

The adsorption site energy (E^*) as a function of adsorption amount is illustrated in Figs. 29 and 30. The E^* value gradually decreases with increasing adsorption amount. This phenomenon indicates that a limited number of high-energy sites exist on the shale surface, revealing the energy heterogeneity of the surface (Duan et al., 2024b). During adsorption, methane molecules under low-pressure conditions preferentially occupy high-energy sites. Subsequently, methane molecules diffuse to occupy sites with relatively lower energy. Furthermore, the slope of the relationship between E^* and q rises with increasing temperature, implying that

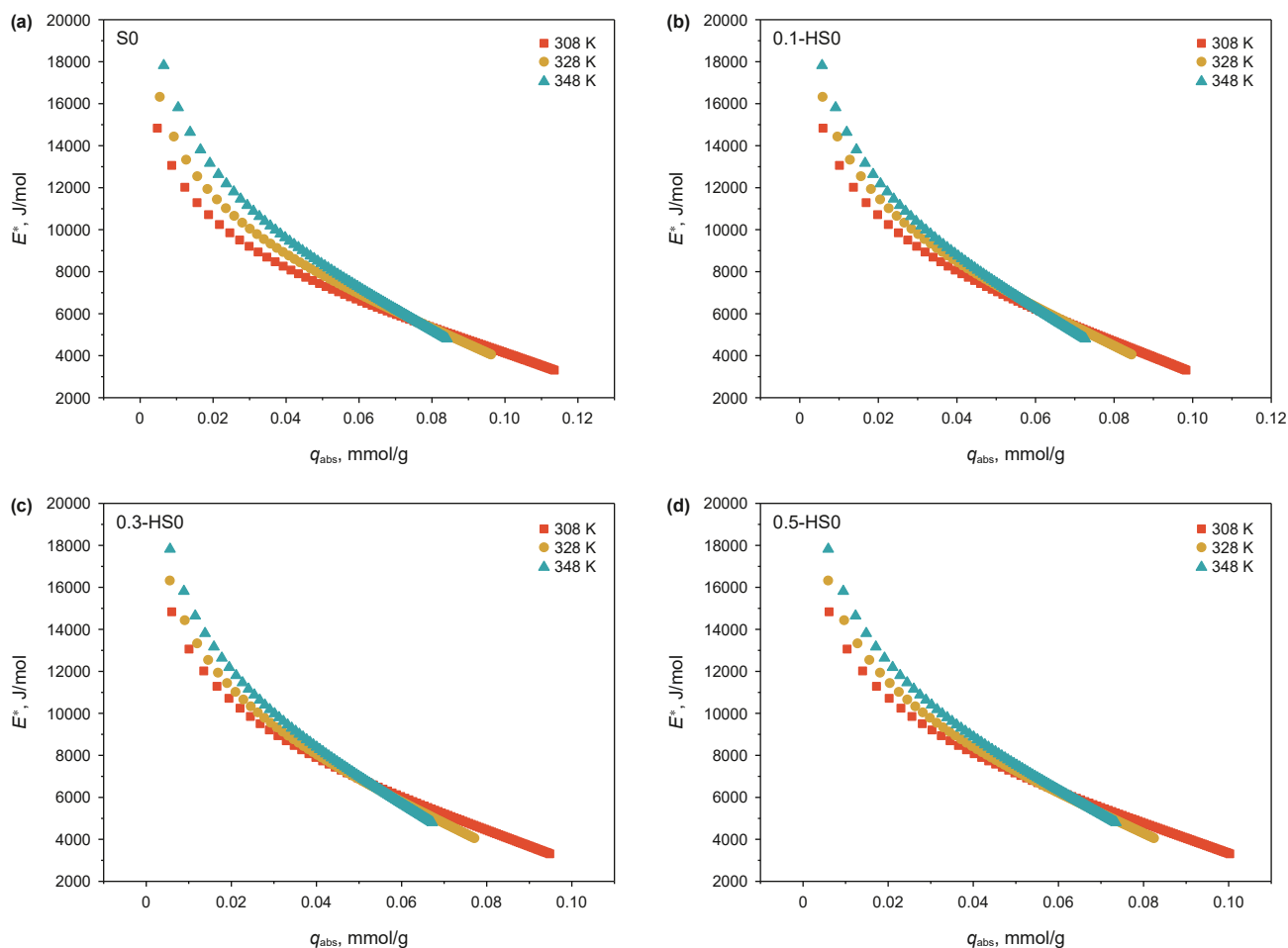


Fig. 29. The adsorption site energy (E^*) with adsorption capacity for sample S0 before and after slickwater treatment: (a) Raw sample, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

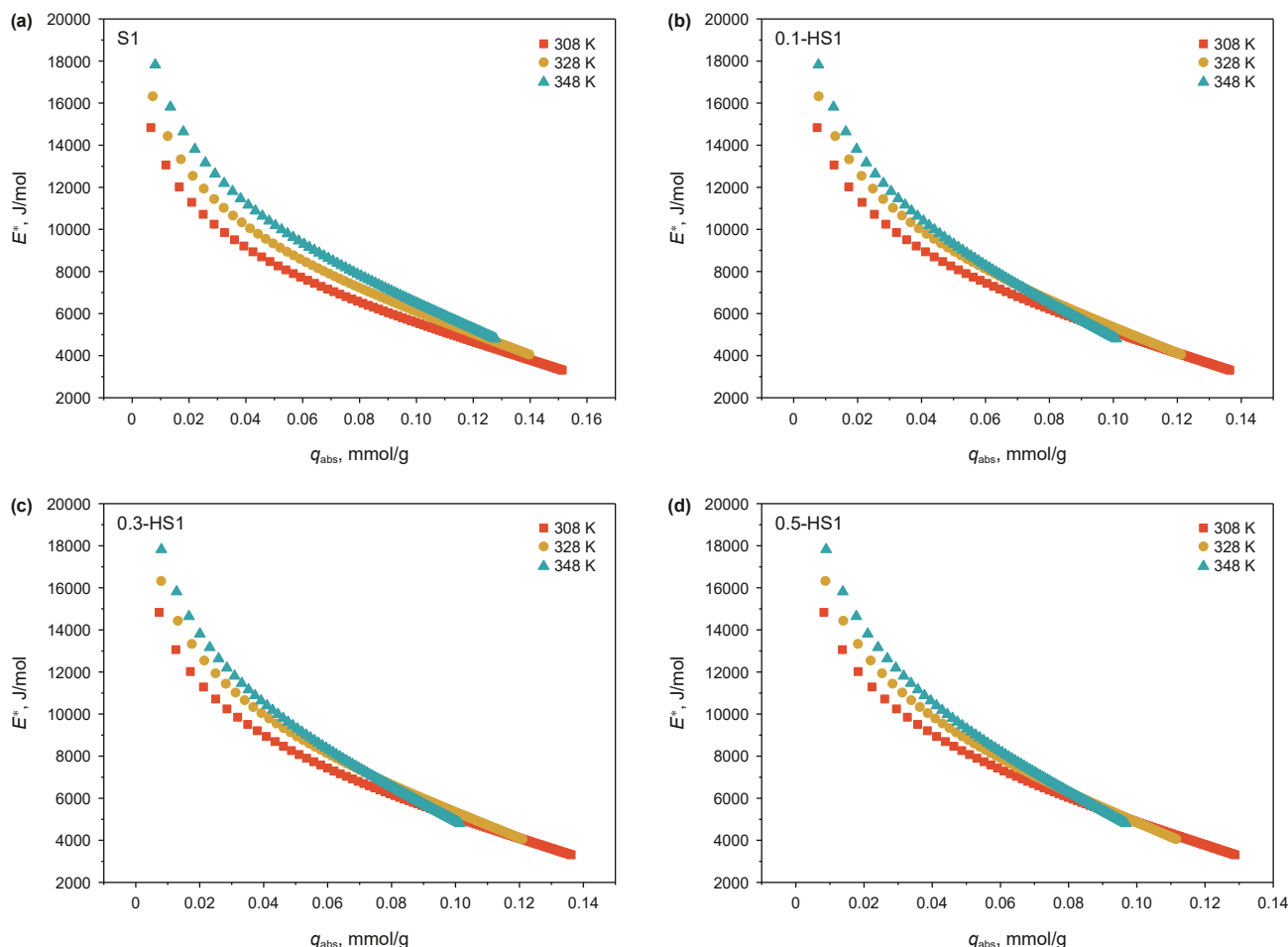


Fig. 30. The adsorption site energy (E^*) with adsorption capacity for sample S1 before and after slickwater treatment: (a) Raw sample, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

lower temperatures are more conducive to methane adsorption (Hu et al., 2025). Within the low adsorption amount range, the E^* value increases with temperature because CH_4 -shale interactions weaken at higher temperatures. Consequently, higher energy is required to attach gas molecules when adsorbing the same quantity of methane. Conversely, under high adsorption conditions, the E^* value reduces as the temperature increases, due to adsorption nearing saturation at high temperatures, while a specified number of absorbable sites remain available on the surface of low-temperature samples. Consequently, the adsorption site energy is comparatively elevated under low-temperature conditions.

Figs. 31 and 32 illustrate the SED of CH_4 on shale. The SED curves for all samples exhibit a unimodal characteristic, which can be divided into two intervals: Within the low site range, the $F(E^*)$ value climbs sharply with rising E^* , until it reaches a peak. This phenomenon indicates that under higher pressure conditions, gas molecules adsorbing at lower-energy sites are relatively fewer in number (Duan et al., 2024b). When E^* exceeds E_m^* , the $F(E^*)$ value first decreases rapidly, then subsequently flattens as E^* further rises and ultimately approaches zero. This phenomenon suggests that the proportion of extremely higher-energy sites (i.e., $>25,000$ J/mol) is negligible compared to the total number of sites. In low-pressure conditions, gas molecules have a marked tendency to occupy higher energy sites. Specifically, when the site energy is below 10,000 J/mol, the $F(E^*)$ value descends with elevated temperature. This is ascribed to the reduction in the occurrence of

high-energy sites, consequently diminishing the number of effective sites available for gas attachment (Duan et al., 2025). However, within the high-energy site range, there is a marginal increase in the $F(E^*)$ value as temperature elevates.

As the site energy distribution is reflective of the frequency of occurrence for sites, the standard deviation, σ_e^* , deduced from the SED, has been demonstrated as an effective means of characterizing the energy heterogeneity of these adsorption sites (Hu et al., 2025).

$$\sigma_e^* = \sqrt{\mu(E^{*2}) - \mu(E^*)^2} \quad (18)$$

$$\mu(E^*) = \frac{\int_{E_1^*}^{E_2^*} E^* \times F(E^*) dE^*}{\int_{E_1^*}^{E_2^*} F(E^*) dE^*} \quad (19)$$

$$\mu(E^{*2}) = \frac{\int_{E_1^*}^{E_2^*} E^{*2} \times F(E^*) dE^*}{\int_{E_1^*}^{E_2^*} F(E^*) dE^*} \quad (20)$$

where $\mu(E^*)$ represents average site energy, E_1^* and E_2^* serve as the lower and upper bound of the site energy, respectively (He et al., 2019).

Tables 8 and 9 present the values for E_m^* , $F(E_m^*)$, $\mu(E^*)$, and σ_e^* , which have been calculated based on Eqs. (18–20). The E_m^* values

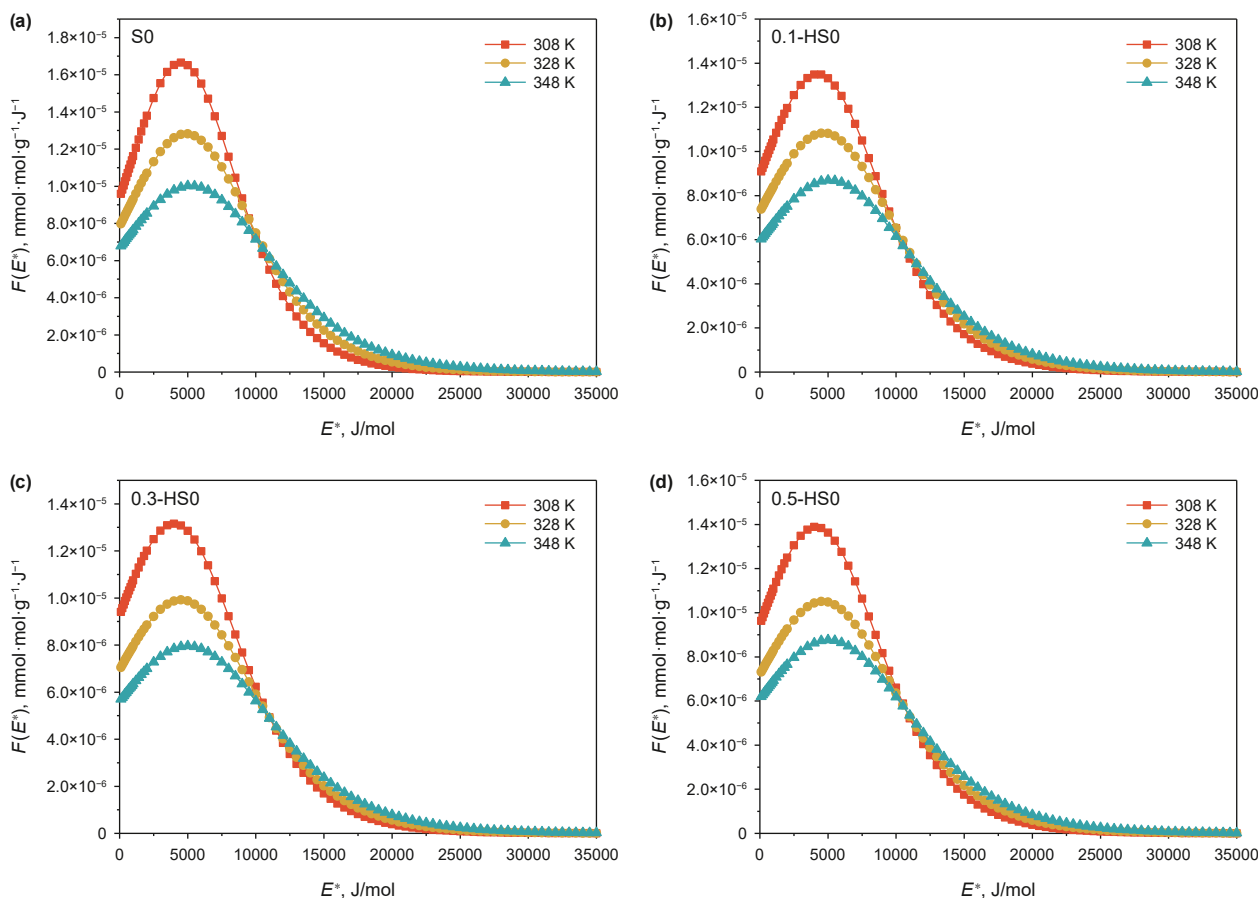


Fig. 31. The site energy distribution for shale: (a) S0, (b) 0.1-HS0, (c) 0.3-HS0, (d) 0.5-HS0.

increase with rising temperature, implying that the energy of the most frequently appearing sites also increases. This phenomena is due to that adsorbing CH_4 molecules onto high-energy adsorption sites requires more energy at higher temperatures (Duan et al., 2020). $F(E_m^*)$ represents the maximum occurrence frequency of adsorption site energies (Duan et al., 2026). The $F(E_m^*)$ value demonstrates a negative correlation with temperature, which is attributable to the reduced frequency of high-energy adsorption sites at elevated temperatures, consequently decreasing the number of effective binding sites for CH_4 adsorption. The average site energy $\mu(E^*)$ reflects the strength of interactions between CH_4 molecules and shale. At lower temperatures, more of the shale surface is occupied by CH_4 molecules, thereby weakening the contact between CH_4 and shale. Consequently, the $\mu(E^*)$ value rises with rising temperature. The surface energy heterogeneity intensifies as the temperature rises, as evidenced by the increase in the σ_e^* value with temperature. At lower temperatures, higher molecular coverage results in a greater uniformity of site distribution across the shale surface.

3.5.2. Effect of slickwater on sites energy distribution of methane adsorption

For the same shale sample, the trend in site energy changes at different temperatures exhibits a similar pattern. Taking adsorption at 308 K as an example, Fig. 33 illustrates the site energy variation characteristics of treated shale with different concentrations of slickwater. The site energy changes of treatment, as a function of adsorption amounts at other temperatures, are

described in Figs. S7 and S8. At the same adsorption amount, the E^* value after treatment decreased. This observation is ascribed to the higher CH_4 adsorption amount of raw shale, which consists of more sites with higher energy. Hence, the same number of CH_4 molecules occupies sites with higher energy in raw shale. Additionally, as the slickwater concentration increases, the site energy initially decreases and subsequently increases. This phenomenon is concomitant with alterations in CH_4 adsorption capacity. As the magnitude of adsorption grows, the disparities in CH_4 site energies on disparate shales gain greater clarity.

Fig. 34 shows the SED curves for treated shale with various slickwater concentrations at 308 K. SED curves at other temperatures are presented in Figs. S9 and S10. Following treatment with the slickwater, the E_m^* values at 348 K changed. The E_m^* value of the treated shale enlarges compared to raw shale S0, implying that after slickwater treatment, CH_4 molecule adsorption requires higher site energy. The E_m^* values of the low-concentration treated shale exceeded those of raw shale S1, while the opposite trend occurs at high-concentrations. The $F(E_m^*)$ of the treated shale was also lower compared to raw shale. Additionally, both E_m^* and $F(E_m^*)$ decreased with increasing slickwater concentration, indicating that higher concentrations reduced the frequency of high-energy sites, thereby impairing CH_4 adsorption on the shale.

The relationship between σ_e^* value and shale clay content is shown in Fig. S11. The σ_e^* values increase as clay content decreases, indicating that slickwater treatment enhances shale surface heterogeneity (Duan et al., 2026). The heterogeneity of the shale surface gradually enhances with rising slickwater concentration.

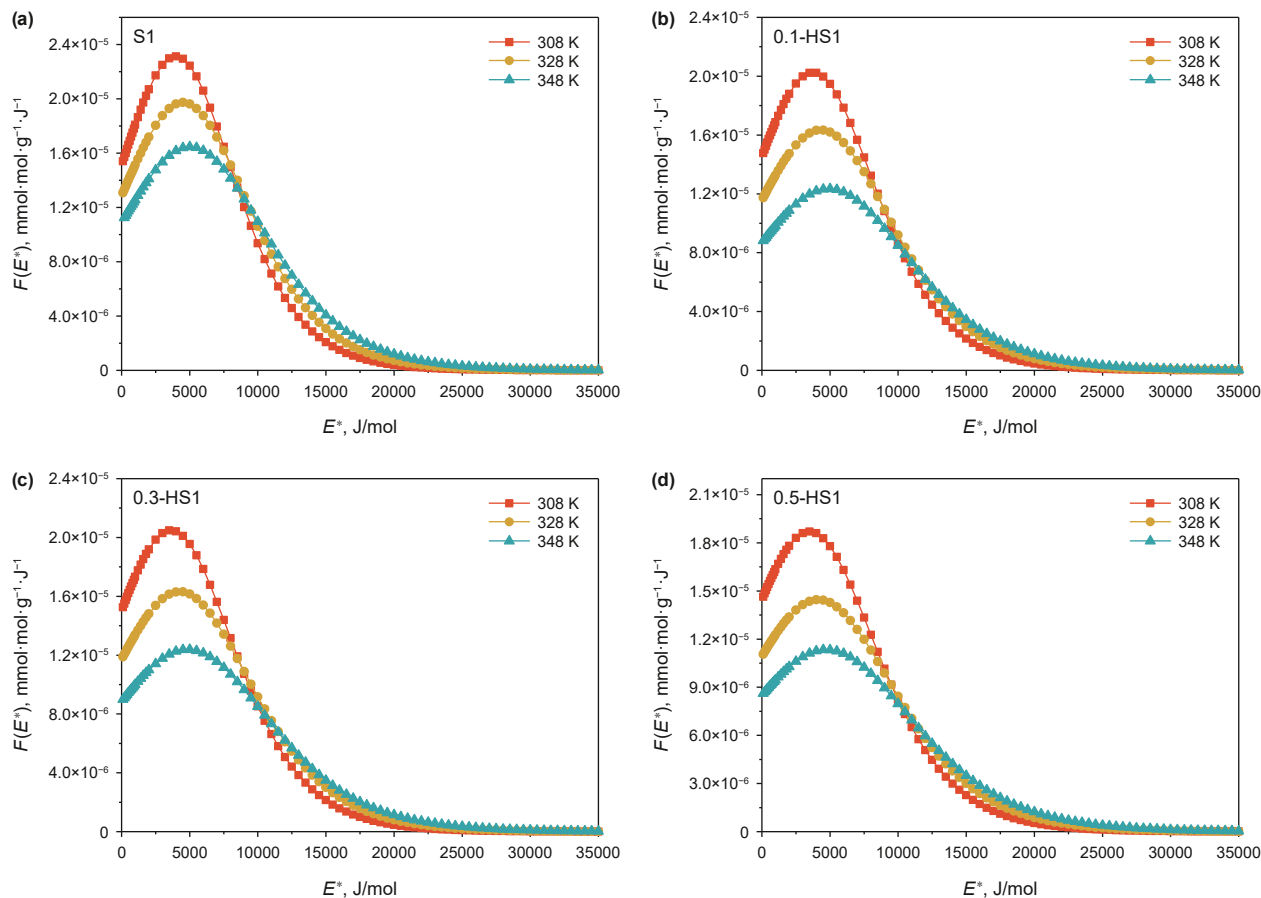


Fig. 32. The site energy distribution for shale: (a) S1, (b) 0.1-HS1, (c) 0.3-HS1, (d) 0.5-HS1.

Table 8
Site energy distributions parameters for CH₄ adsorption on shale S0.

Adsorbent	Temperature, K	E_m^* , J·mol ⁻¹	$F(E_m^*)$, $\times 10^{-5}$ mmol·mol ⁻¹ ·J ⁻¹	$\mu(E^*)$, J·mol ⁻¹	σ_e^* , J·mol ⁻¹
S0	308	4492.50	1.6649	6076.98	3949.06
	328	4882.99	1.2860	6906.83	4594.80
	348	5233.79	1.0076	7869.39	5365.82
0.1-HS0	308	4235.78	1.3505	6336.32	4314.17
	328	4683.29	1.0869	7081.50	4842.71
	348	5116.25	0.8749	7853.46	5394.82
0.3-HS0	308	3988.67	1.3159	6299.14	4372.19
	328	4502.46	0.9955	7074.49	4903.03
	348	5001.09	0.8016	7909.26	5486.24
0.5-HS0	308	4109.19	1.3890	6301.93	4330.45
	328	4620.88	1.0547	7113.11	4895.56
	348	5037.42	0.8818	7874.59	5442.30

Table 9
Site energy distributions parameters for CH₄ adsorption on shale S1.

Adsorbent	Temperature, K	E_m^* , J·mol ⁻¹	$F(E_m^*)$, $\times 10^{-5}$ mmol·mol ⁻¹ ·J ⁻¹	$\mu(E^*)$, J·mol ⁻¹	σ_e^* , J·mol ⁻¹
S1	308	3977.65	2.3129	5896.24	3997.82
	328	4500.75	1.9717	6657.39	4514.06
	348	5018.06	1.6240	7501.59	5106.75
0.1-HS1	308	3738.24	2.0257	6022.45	4205.54
	328	4323.47	1.6516	6863.36	4772.91
	348	4912.62	1.2597	7749.79	5373.33
0.3-HS1	308	3624.79	2.0486	5976.11	4202.06
	328	4264.82	1.6388	6866.62	4796.42
	348	4842.11	1.2493	7762.50	5409.05
0.5-HS1	308	3488.99	1.8706	6140.52	4394.82
	328	4139.45	1.4523	7067.45	5018.92
	348	4729.18	1.1440	7987.71	5644.92

This phenomenon is attributed to the decline in clay content, as clay constitutes the primary material responsible for adsorption sites. Consequently, fewer sites are available for CH₄ adsorption, leading to increased adsorption heterogeneity. This finding aligns with the correlation between clay content and saturated adsorption capacity. Other parameters also exhibit significant changes with variations in fracturing fluid concentration, but the relationship is non-linear. This observation indicates that changes in the composition and microstructure of shales after slickwater treatment introduce a certain degree of complexity into the parameter values representing site energy distribution.

The area beneath the $F(E^*)$ - E^* curve is considered to represent the number of available adsorption sites within a specified energy range (Bai et al., 2021). Therefore, the curve at 308 K was integrated, yielding the results shown in Fig. 35 and Table 10. It has been observed that the total number of sites, low-energy sites, and high-energy sites declined after slickwater treatment. As the concentration of slickwater increases, the number of low- and high-energy site shows only minor decreases, consistent with previous studies. The percentage of high-energy site slightly increases with higher slickwater concentration, ranging between 61% and 68%. Although the SED model is widely used in adsorption

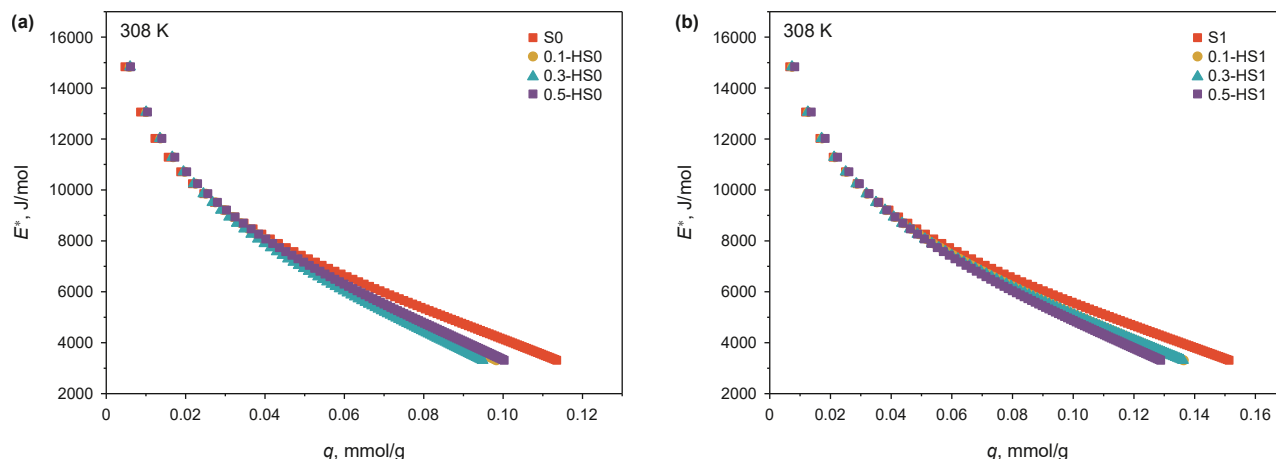


Fig. 33. Adsorption site energy (E^*) with adsorption capacity for shale at 308 K: (a) S0, (b) S1.

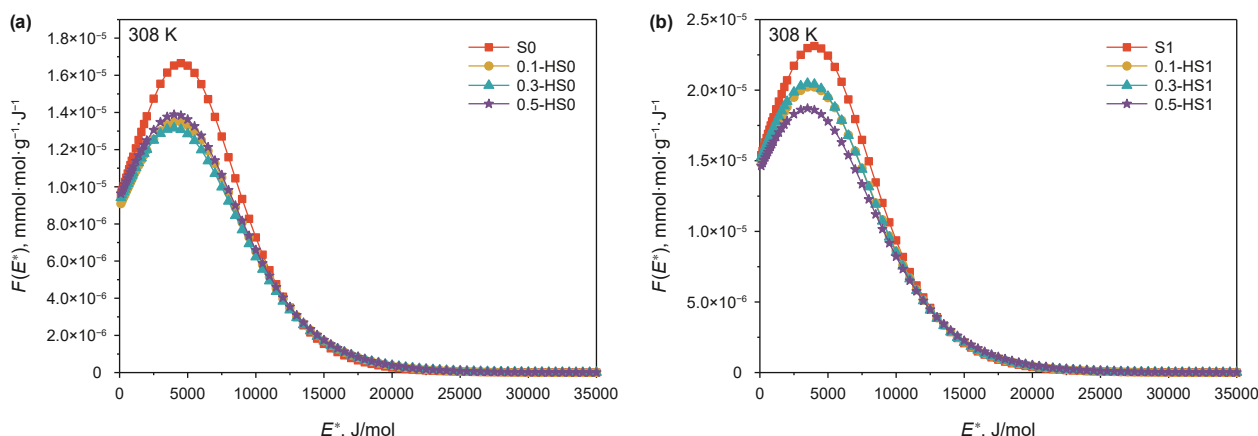


Fig. 34. Site energy distribution for shale samples at 308 K: (a) S0, (b) S1.

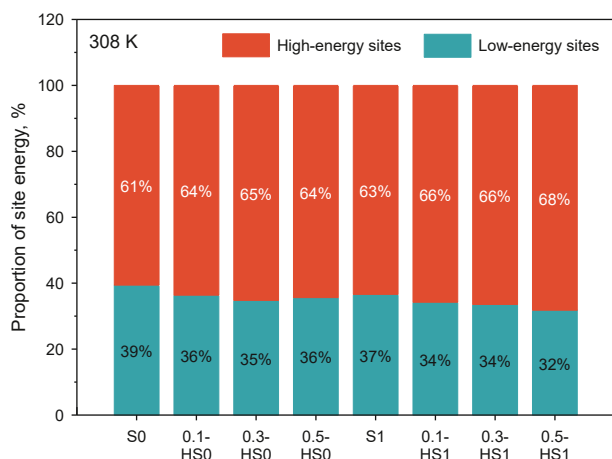


Fig. 35. Proportion of site energy for shale samples before and after slickwater treatment at 308 K.

studies, it still has some limitations. First, its physical assumptions are overly simplified, making it difficult to accurately capture surface heterogeneity. Second, under conditions of high coverage or non-ideal conditions, its predictions may exhibit significant deviations. Furthermore, the model is sensitive to experimental

noise and is easily influenced by curve-fitting assumptions, thereby limiting the reliability of the results.

3.6. Influence mechanism of slickwater on CH_4 adsorption and implication for shale gas exploitation

Investigating the effect mechanism of slickwater on shale gas adsorption behavior offers a theoretical basis for optimizing fracturing fluid formulations and enhancing shale gas development processes. The objective is to enhance the efficiency of fracturing operations in boosting shale gas production (Qin et al., 2021). This study systematically elucidates how slickwater influences CH_4 adsorption behavior in shale from both physical interaction and chemical action perspectives (see Fig. 36). This is based on prior characterization of shale pore structure and experimental determination of adsorption isotherms. The results of the XRF and XRD characterization indicate a significant decrease in Si content within fractured shale samples, accompanied by varying degrees of reduction in Al, Fe, Mg, S, and clay mineral content. This observation suggests that specific components in slickwater may modify shale mineral composition through clay mineral dissolution or chemical reactions. However, infrared spectroscopy analysis revealed that while slickwater treatment did not alter the fundamental types of surface functional groups on the shale, it significantly affected their relative abundances. This phenomenon suggests that chemical reactions may have occurred on the surface

Table 10
Site energy area for CH₄ adsorption on shale at 308 K.

	S0	0.1-HS0	0.3-HS0	0.5-HS0	S1	0.1-HS1	0.3-HS1	0.5-HS1
Total site area	0.15535	0.13501	0.13179	0.13865	0.21454	0.19424	0.19529	0.18394
Low-energy site area	0.06123	0.04910	0.04585	0.04941	0.07856	0.06646	0.06554	0.05847
High-energy site area	0.09412	0.08591	0.08594	0.08924	0.13598	0.12778	0.12975	0.12547

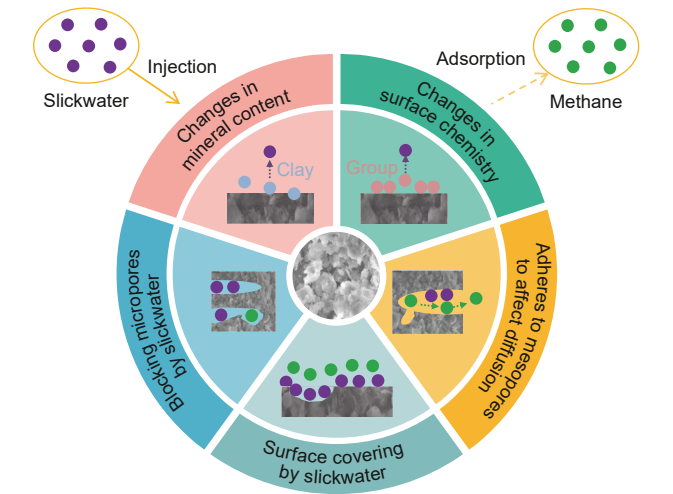


Fig. 36. Effect mechanism of slickwater on CH₄ adsorption from the viewpoint of shale characterization.

of the “shale-slickwater residue” composite system (Duan et al., 2026). It is important to note that although the drag reducer polyacrylamide employed in slickwater exhibits weak acidity, its addition rate is extremely low (mass fraction of only 0.1 to 0.5 wt%). Consequently, the chemical modification has a relatively limited effect on the shale surface. This finding suggests that physical mechanisms also play a significant role alongside chemical mechanisms.

Following slickwater treatment, there was a substantial decrease in the surface area. For example, the S_{BET} of sample S0 reduced from 12.8756 to 9.1739 m²/g. Subsequent to the elimination of interference from slickwater residue itself on CH₄ adsorption, the deposition of residue on shale surfaces physically covers the shale, thereby reducing its effective surface area and occupying active sites, thereby inhibiting CH₄ adsorption by the shale. Hydraulic fracturing field practice demonstrates that slickwater residue retained in formations after fracturing operations coats shale surfaces, thereby weakening the adsorption of mobile methane. This observation indicates that surface coverage

significantly promotes methane desorption and migration processes (Lu et al., 2019). Pore structure analysis indicates that slickwater treatment leads to a reduction in shale micropore volume, varying in degree. For example, the pore volume of sample S0 reduced from 0.0041 to 0.0006 cm³/g. This indicates that particular constituents within the slickwater may penetrate the shale pore system, locally blocking pores. This reduces methane adsorption capacity and decreases desorption rates. In hydraulic fracturing operations, methane naturally present in the shale matrix interacts with the slickwater, which acts as an invasive phase post-fracturing. The resultant pore blockage impedes the effective desorption and diffusion of methane molecules, thereby affecting methane recovery efficiency (Sun et al., 2018a). Notably, slickwater residue exhibits a distinctive mechanism for pore blockage: When incomplete blockage occurs, although the effective cross-sectional area of pores decreases and diffusion coefficients decline, methane molecules can still circulate within the pore network and undergo adsorption reactions on their surfaces. While this partial blockage does not significantly reduce methane adsorption capacity, it does have a negative effect on methane recovery by reducing diffusion rates.

As indicated by preceding research, following the interaction between slickwater and shale, there is a substantial decline in clay mineral content within the shale, a substantial reduction in the specific surface area, and a reconstruction of the micro-pore structure (resulting in a shift in pore size distribution towards larger pores). This phenomenon results in a reduction in the CH₄ adsorption amount. This mechanism is of considerable significance for the development of shale gas (Huang et al., 2024; Guo et al., 2018). However, in actual shale gas extraction, methane migration involves not only desorption behavior but also transport mechanisms such as diffusion and seepage. Consequently, a thorough evaluation of the multiscale ramifications of slickwater injection on shale gas development is imperative from a systems engineering standpoint. Statistical physics analysis indicates that under slickwater influence, methane’s n -value decreases across the board, reflecting a reduction of molecular attachment per adsorption site (see Fig. 37). Changes in receptor site density (N_m) reveal spatial variations in methane molecules available for attachment per unit receptor. Subsequent to treatment, a significant decrease in the ΔE values is observed, indicating a weakening

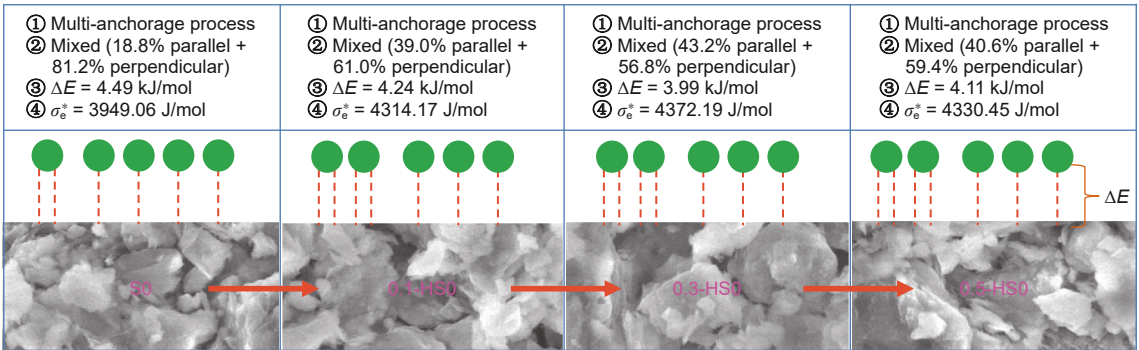


Fig. 37. Effect mechanism of slickwater on CH₄ adsorption on shale S0 from the perspective of statistical physics.

of the interaction forces between methane and shale (Duan et al., 2025). Statistical thermodynamic analysis reveals that in the adsorption system of shale and methane after slickwater treatment, the values of E_{int} , G_a , and S_a decline. This finding suggests that the slickwater–shale interaction reduces the spontaneity of methane adsorption, resulting in a more disordered CH_4 adsorption of shale. This result provides confirmation, from an energy perspective, that slickwater injection has the capacity to promote methane desorption and enhance development efficiency (Duan et al., 2020). Furthermore, a detailed site energy analysis indicates that slickwater leads to alterations in the SED of methane on the shale surface. In comparison to the raw shale, there is a significant decrease in the number of low-energy and high-energy sites, a trend that continues as slickwater concentration increases. The site energy restructuring mechanism elucidates the principle by which slickwater promotes methane desorption from a surficial physicochemical perspective. It is essential to recognize that the heterogeneity of shale reservoirs, encompassing complex pore types, high-temperature and high-pressure conditions, and the presence of formation water, significantly impacts how slickwater alters shale mineral composition and pore structure. This, in turn, affects methane adsorption and desorption kinetics within the shale (Sun et al., 2018a). Consequently, future research should establish multi-field coupled models to systematically analyze the synergistic influence mechanisms of various geological and engineering factors on shale gas recovery rates following slickwater fracturing.

4. Conclusion

Slickwater treatment selectively dissolves clay minerals such as illite and montmorillonite in shale, resulting in a significant decrease in Si content and varying reductions in Al, Fe, Mg, and S content. This treatment markedly alters the relative abundance of surface functional groups. The treated shale exhibited a marked decrease in specific surface area and micropore volume. The proportion of mesopores increased while micropores decreased, and the average pore diameter enlarged. SEM observations confirmed that slickwater caused crystalline residues to form on the shale surface, thereby blocking some smaller-diameter pores.

The CH_4 adsorption amount of treated shale was remarkably reduced, exhibiting a decreasing trend with increasing slickwater concentration. The monolayer model with one energy (M1E) is the most suitable model for describing the adsorption data before and after slickwater treatment. The n -values, all less than 1 and greater than 0.5, indicate that CH_4 molecules attach to the shale surface via parallel or perpendicular multimolecular mixed adsorption. The reduction in n -values after slickwater treatment suggests a reduction in the number of molecules attached to a single adsorption site. The substantial decline in the ΔE values post-slickwater treatment suggests a weakening of the force interaction between methane and shale.

Statistical thermodynamic analysis indicates that methane adsorption exhibits spontaneous, exothermic behavior, with elevated temperatures increasing both the spontaneity of adsorption and the degree of disorder. After slickwater treatment, the E_{int} , G_a , and absolute S_a values of the shale–methane adsorption system all declined. This suggests that the slickwater–shale interaction reduces the spontaneity of CH_4 adsorption, thereby increasing the disorder of adsorption. As the slickwater concentration increases, the E_{int} , G_a , and S_a values all increase.

Site energy analysis indicates that CH_4 adsorption on shale surfaces exhibits a characteristic pattern where high-energy sites are preferentially occupied before low-energy sites. After slickwater treatment, the site energy decreased compared to the raw

shale. Increasing slickwater concentration led to reductions in both E_m^* and $F(E_m^*)$ values, indicating that the slickwater decreased the frequency of high-energy sites, thereby adversely affecting CH_4 adsorption on shale. The number of both low- and high-energy sites decreased significantly compared to the raw shale. This study elucidates the dual-scale mechanism (microscopic and macroscopic) by which slickwater reduces CH_4 adsorption on shale, as revealed by multiscale shale characterization and statistical physics modeling. Crucially, these findings not only provide new insights into how slickwater influences methane adsorption on shale but also bridge the gap between laboratory mechanisms and field production enhancement, filling a critical knowledge gap in the field of unconventional reservoir development.

CRedit authorship contribution statement

Shuo Duan: Supervision, Methodology, Investigation, Writing – original draft, Writing – review & editing. **Yong-jian Zhang:** Investigation, Software, Writing – original draft. **Xiang-Yang Ling:** Methodology, Investigation. **Peng-Fei Shen:** Investigation, Funding acquisition. **Ling-Zao Zeng:** Investigation. **Ze-Yu Li:** Project administration, Investigation.

Conflict of interest

The authors declare no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.petsci.2026.06.009>.

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