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Surface Diffusion in Nanopores and Its Effects on Total Mass Transport in Shale Gas Reservoirs

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Abstract: In the 21st century, shale gas reservoirs have emerged as a significant and valuable source of natural gas. However, their distinct characteristics, particularly the nanoscale pore throat and pore-size distribution, set them apart from conventional reservoirs. These unique features have a profound impact on the storage and flow behavior of hydrocarbons within the shale, making them challenging to exploit using conventional methods. One of the primary challenges associated with shale gas reservoirs is the confined space phase behavior, which alters the fluid properties compared to what is typically observed in a standard PVT (Pressure-Volume-Temperature) cell. In particular, the increased surface adsorption of gas molecules in the shale leads to deviations in fluid properties. This means that the properties of gas within the shale differ from those predicted by conventional models, making it crucial to understand and account for these differences to efficiently extract gas from these reservoirs. Surface diffusion is a critical parameter in assessing the transport ability of adsorbed gas in shale organic matter. Surface diffusion refers to the movement of gas molecules along the surfaces of organic matter in the shale. It is a complex process influenced by various factors. Recent research has provided some insights, indicating that the shale-methane surface diffusion coefficient has a value of around 10^{-16} cm^2/g. However, accurately measuring this coefficient remains a challenge, and there is a need for a definitive and reliable method to do so. Despite the importance of surface diffusion, it has been found that its contribution to total mass transport in shale gas reservoirs is not as significant as previously anticipated. Other mechanisms, such as desorption and matrix diffusion, also play essential roles in the overall transport of gas within shale. To improve our understanding of shale gas reservoirs and optimize gas extraction, this paper proposes an interdisciplinary approach. It suggests combining insights and advances from different industries and fields of research to gain a comprehensive understanding of these complex reservoirs. By bringing together knowledge from geology, engineering, chemistry, and other relevant disciplines, researchers can develop more accurate models and strategies to unlock the full potential of shale gas reservoirs. In summary, shale gas reservoirs have revolutionized the natural gas industry in the 21st century, but their unique characteristics require a specialized approach. Surface diffusion is an important factor affecting gas transport in shale, but its contribution is not as significant as initially thought. Through interdisciplinary research, we can enhance our understanding of these reservoirs and develop more efficient methods for gas extraction.

Keywords: Surface Diffusion, Nanopores, Shale Gas Reservoirs, Adsorption, Diffusion Coefficient

1. Introduction

Natural gas from shale reservoirs has increasingly become a significant source of energy since the beginning of the 21st century. Shale reservoirs have unique properties that differ from conventional reservoirs, which are attributed to their nanoscale pore throat and pore-size distribution. This has made shale reservoirs an attractive area for exploration and exploitation.

The objective of this article is to conduct a comprehensive literature review on adsorption and surface diffusion in shale gas reservoirs. The article aims to investigate fluid, rock, and reservoir parameters that surface diffusivity is sensitive to and compare surface diffusion coefficient values from different industries. Shale reservoirs consist of silt and other clay-size fragments with varying mineralogy. Because of the small size of the clay particles, smaller than a few micrometers, these reservoirs experience different hydrocarbon storage and flow characteristics than conventional reservoirs. These characteristics are uniquely tied to nanoscale pore throat and pore-size distribution. Shale gas reservoirs store hydrocarbon in three types of pore space: the macropores in the in-organic rock matric, the space in the natural fractures, and finally, the nanopores in the organic matter, which are usually smaller than 10 nanometers.

The contribution of surface diffusion to total mass transport in the nanopores of shale gas reservoirs is still not very clear. Confined space phase behavior causes surface adsorption to become significant, leading to an increase in capillary, Van Der Waals, structural, electrostatic, and adsorption forces. These forces cause the physical and dynamic properties of fluids to deviate from those measured in a PVT (Pressure, Volume, Temperature) cell. Surface diffusion contributes to mass flux, but the extent is still unclear. Certain fluid, formation, and reservoir parameters impact surface diffusivity, with consensus that surface diffusion is sensitive to pore size, molecule size, pressure, and temperature changes. To evaluate the transport ability of adsorbed gas in shale organic matter, surface diffusion coefficient is a crucial and central parameter. This article aims to provide a comprehensive review of the current research on surface diffusion in shale gas reservoirs. The findings of the article will highlight the significance of surface diffusion in nanopores and its contribution to total mass transport, while also identifying the fluid, rock, and reservoir parameters that affect surface diffusivity. Furthermore, the article will compare surface diffusion coefficient values from different industries and explore the need for a specific method for measuring the surface diffusion coefficient in shale.

In conclusion, this article provides an in-depth review of the literature on surface diffusion in shale gas reservoirs. It highlights the significance of surface diffusion in nanopores and its contribution to total mass transport, the fluid, rock, and reservoir parameters that affect surface diffusivity, the need for a specific method for measuring the surface diffusion coefficient in shale, and the unclear extent of surface diffusion's contribution to mass flux. Previous research has produced a wide range of values for the surface diffusion coefficient, highlighting the importance of identifying the fluid, formation, and reservoir parameters that impact surface diffusivity.

2. Methodology

This section describes the methodology used for conducting the literature review on surface diffusion in nanopores. The review aimed to gather knowledge on the subject, trace the intellectual progression of research (including major debates), evaluate and provide comments on the research (methods, theories used, etc.), and identify where gaps exist, if any, to recommend ways forward. To achieve this, published journal papers on topics relating to surface diffusion in nanopores were reviewed.

The methodology for the literature review involved a systematic search of electronic databases such as Google Scholar, Science Direct, and Elsevier. The search terms used included "surface diffusion," "nanopores," and "shale gas reservoirs." The search was conducted on papers published between 1986 and 2023. A total of 16 papers were identified as relevant to the topic of surface diffusion in nanopores [1-9]. These papers were then reviewed to identify key findings and to evaluate the methods and theories used.

The review process involved reading each paper thoroughly and taking notes on the key findings, methods, and theories used. The papers were also evaluated for their relevance to the topic, the quality of the research, and the validity of the conclusions. The notes taken were then used to develop a comprehensive and critical review of the literature on surface diffusion in nanopores.

The literature review revealed that surface diffusion cannot be ignored in nanopores where the pore size and the specific surface area available per molecule increase its significance. Consensus amongst the available research was reached that surface diffusion is sensitive to pore size, molecule size, pressure, and temperature. Furthermore, a lot of work has been conducted on the subject of surface diffusing in the oil and gas industry and in other industries as well, like physical chemistry.

The methodology used for the literature review on surface diffusion in nanopores involved a systematic search of electronic databases, a thorough review of relevant papers, and the evaluation of key findings, methods, and theories used. The review revealed that surface diffusion is a significant factor in nanopores, with its contribution being sensitive to certain parameters. The review also highlighted the need for a specific method to measure the surface diffusion coefficient in shale and the importance of interdisciplinary research to integrate advances in research from different industries.

3. Result

Gas from shale reservoirs has become an increasingly important source of natural gas since the start of this century. Shale reservoirs exhibit different hydrocarbon storage and flow characteristics than conventional reservoirs due to their unique nanoscale pore throat and pore-size distribution. Confined space phase behavior causes surface adsorption to become significant, leading to an increase in capillary, Van Der Waals, structural, electrostatic, and adsorption forces. These forces cause the physical and dynamic properties of fluids to deviate from those measured in a PVT cell. Surface diffusion contributes to mass flux, but the extent is still unclear. Certain fluid, formation, and reservoir parameters impact surface diffusivity, with consensus that surface diffusion is sensitive to pore size, molecule size, pressure, and temperature changes.

In this article, we conduct a comprehensive literature review on adsorption and surface diffusion in shale gas reservoirs. We aim to investigate fluid, rock, and reservoir parameters that surface diffusivity is sensitive to and compare surface diffusion coefficient values from different industries. Shale reservoirs consist of silt and other clay-size fragments with varying mineralogy. Because of the small size of the clay particles, smaller than a few micrometers, these reservoirs experience different hydrocarbon storage and flow characteristics than conventional reservoirs. These characteristics are uniquely tied to nanoscale pore throat and pore-size distribution.

Surface diffusion is a crucial factor that influences the total mass transport in the nanopores of shale gas reservoirs. However, the contribution of surface diffusion to total mass transport in these nanopores is still unclear. Despite the considerable work and progress achieved in measuring gas diffusion coefficients in rocks and porous media, there is a wide range in values. The big range in values is due to different materials and rocks being used for the experiments. Recent research suggests that the methane/shale surface diffusion coefficient value is around 10^{-16} cm^2/g.

The literature review revealed that surface diffusion cannot be ignored in nanopores where the pore size and the specific surface area available per molecule increase its significance. Consensus amongst the available research was reached that surface diffusion is sensitive to pore size, molecule size, pressure, and temperature. Furthermore, a lot of work has been conducted on the subject of surface diffusing in the oil and gas industry and in other industries as well, like physical chemistry.

In conclusion, surface diffusion is an essential factor that cannot be ignored when calculating total mass transport in shale gas reservoirs. The sensitivity of surface diffusivity to certain parameters such as pore size, molecule size, pressure, and temperature highlights the importance of understanding these parameters. Future research should focus on measuring the surface diffusion coefficient in shale accurately using a specific method. This research will help in integrating advances in research from different industries to better understand surface diffusion in shale gas reservoirs. Finally, interdisciplinary research is recommended to integrate advances in research from different industries.

4. Discussion

4.1. Confined-Space Phase Behavior

In confined spaces, surface adsorption becomes significant due to an increase in capillary, Van Der Waals, structural, electrostatic, and adsorption forces. These forces cause the physical and dynamic properties of a fluid to deviate from those measured in a PVT cell [16]. In simpler terms, this means that when fluids are in small spaces, such as the pores in rocks or other materials, they behave differently than they would in a larger space. In porous media, by holding molecule size and weight constant, a decrease in pore size leads to an increase in surface area available per molecule on the inner walls of a pore. This means that there is more area available for the fluid to interact with, which can cause changes in its behavior. The increase in these forces is directly related to the increase in specific surface area available per molecule. Specifically, the more surface area there is, the more these forces will come into play. Fluid viscosity, wall/ fluid interfacial tension, freezing/ melting points, critical temperature, and critical pressure are some of the fluid properties that change with an increase in the previously mentioned forces. Essentially, the behavior of the fluid changes in small spaces due to the increase in these forces, which can have an impact on its properties and behavior.

4.2. Parameters Effecting Surface Diffusion

Surface diffusion is a crucial factor that influences the total mass transport in nanopores of shale gas reservoirs. Surface diffusion occurs due to the impact of various fluid, rock, and reservoir parameters, such as pore size, molecule size, pressure, and temperature changes. Although surface diffusion has been studied for many years, its impact on total mass transport in shale gas reservoirs is still not entirely clear.

One significant parameter that affects surface diffusivity is pore size. Studies have shown that the smaller the pore radius, the higher the contribution of surface diffusion to the total mass flux. A negative correlation was established between pore radius and surface diffusion, as evident from the findings of the 2016 study by Ning et al. [14] The study also presented the effects of molecule size on surface diffusion, which affects the specific surface area available per molecule. The research found that specific surface area showed a positive correlation with surface diffusion. Figure 1 shows the surface diffusion effects for different pore radii in both case of different specific surface areas and different temperature. As can be clearly seen in Figure 1, the increase in surface area caused a drastic decrease in the effect of surface diffusion on the mass flux on the other hand in Figure 2, contribution of surface diffusion increased when temperatures increase.

Pressure and temperature are other important parameters that affect surface diffusivity. The effect of pressure on surface diffusion was found to decrease as pressure increased. Temperature, on the other hand, resulted in an increase in surface diffusion with an increase in temperature. This effect is due to the change in kinetic energy of the molecules. Thus, it is crucial to understand the impact of these parameters on surface diffusivity to accurately measure the surface diffusion coefficient in shale.

The surface diffusion coefficient is a crucial parameter that determines the transport ability of adsorbed gas in shale organic matter. Different materials and testing methods have resulted in a wide range of values for the surface diffusion coefficient. A specific method should be used to measure the surface diffusion coefficient in shale to avoid discrepancies in the results. Recent research suggests that the methane/ shale surface diffusion coefficient value is around 10^{-16} cm^2/g.

In conclusion, surface diffusion is an essential factor that cannot be ignored when calculating total mass transport in shale gas reservoirs. The sensitivity of surface diffusivity to certain parameters such as pore size, molecule size, pressure, and temperature highlights the importance of understanding these parameters. Future research should focus on measuring the surface diffusion coefficient in shale accurately using a specific method. This research will help in integrating advances in research from different industries to better understand surface diffusion in shale gas reservoirs.

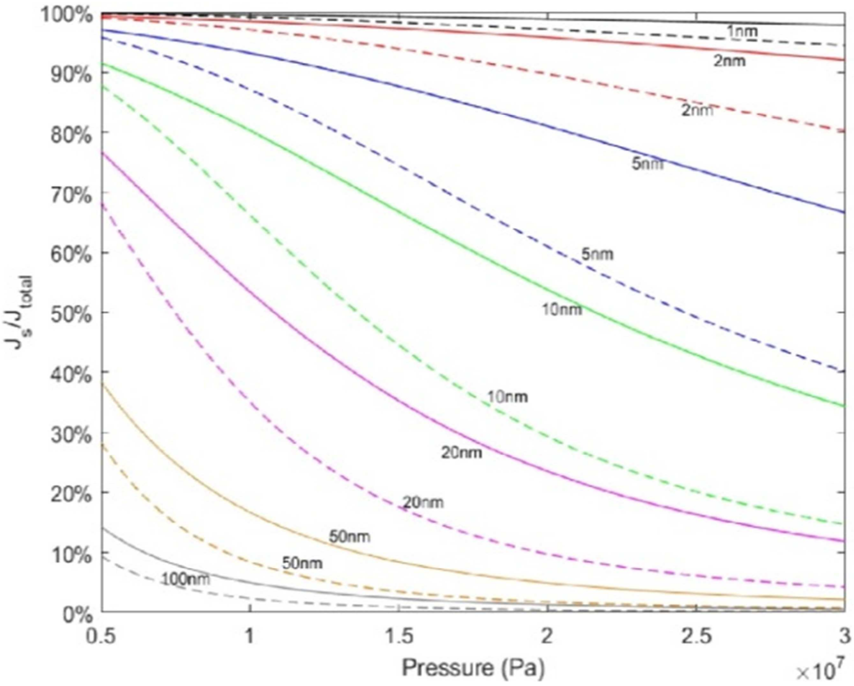

Figure 1. *Surface diffusion effects for different average pore radii and temperature [14].*

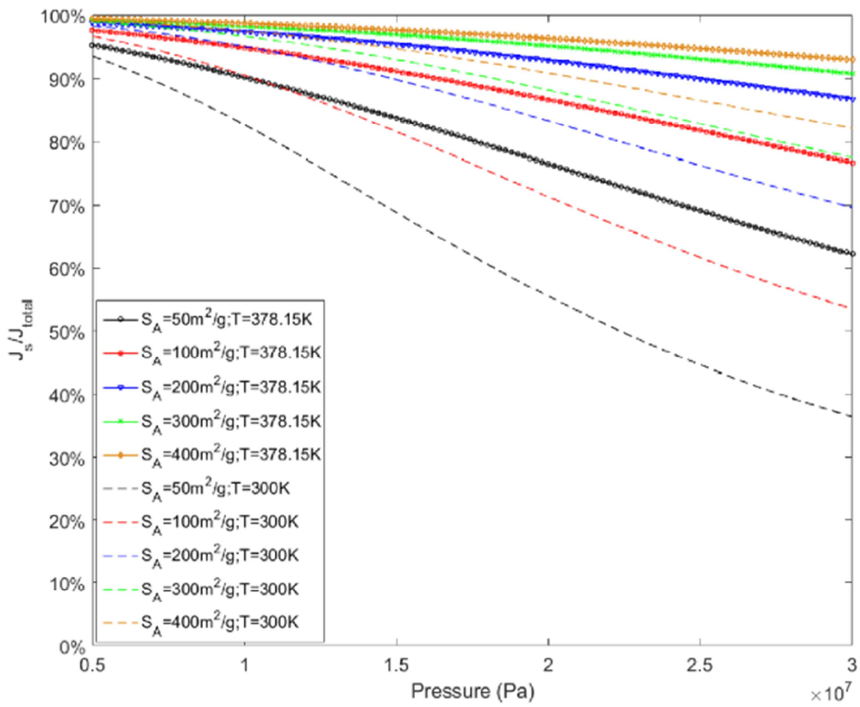

Figure 2. *Effect of specific surface areas on surface diffusion [14].*

4.3. Surface Diffusion Coefficient

The exploration and exploitation of shale reservoirs have become an attractive area due to their unique properties that differ from conventional reservoirs, which are attributed to their nanoscale pore throat and pore-size distribution. These properties have made shale reservoirs a crucial area for research, particularly in evaluating the transport ability of adsorbed gas in shale organic matter. One crucial parameter in this evaluation is the surface diffusion coefficient.

Despite the considerable work and progress achieved in measuring gas diffusion coefficients in rocks and porous media, there is a wide range in values, ranging from 10^{-4} to 10^{-16} cm^2/g. The big range in values is due to different materials and rocks being used for the experiments. Table 1 lists the surface diffusion coefficient for different rock and materials. However, there is some disagreement between surface diffusion coefficient values for the same rock type, which could be attributed to testing methods and determination of diffusion types.

Table 1. *Surface Diffusion Coefficients.*

Material - Fluid	Diffusion Coefficient (cm^2/s)	Source
Mudstone – CH_4	10^{-7} – 10^{-6}	[13]
Kerogen – CH_4	10^{-16}	[12]
Carbon nanotubes – CH_4	10^{-7}	[10]
Activated Carbon – CH_4	10^{-4}	[15]
Activated Carbon – CO_2	10^{-5}	
Zeolites – C_2H_6	10^{-13} – 10^{-14}	[11]
Zeolites – CH_4	10^{-12} – 10^{-13}	
Zeolites – Propylene	10^{-15} – 10^{-16}	
Zeolites – Ethylene	10^{-13}	

Surface diffusion is a crucial factor that influences the total mass transport in nanopores of shale gas reservoirs. However, variation within the oil and gas industry exists due to different testing methods and uncertainty in determining the diffusion types. Different testing methods can significantly affect the surface diffusion coefficient values obtained. For example, some experiments do not account for the effect of stress, which cannot be ignored. Not accounting for the effects of stress would overvalue the surface diffusion coefficient since the coefficient decreases with an increase in stress. Recent work has simulated in-situ gas flow more effectively by replacing particle samples with shale core plugs under stressful conditions. Furthermore, some studies calculated an overall coefficient that may include the Fick diffusion, Knudsen diffusion, and surface diffusion under particular conditions, where the Knudsen number determines the diffusion type. Fick diffusion and Knudsen diffusion are part of the bulk phase transport and not the adsorption phase transport. Failure to remove the bulk phase transport contribution to account for this split may exaggerate the surface diffusion values. Therefore, a specific method needs to be developed to measure the surface diffusion coefficient in shale accurately. Future research should focus on measuring the surface diffusion coefficient in shale accurately using a specific method. This research will help in integrating advances in research from different industries to better understand surface diffusion in shale gas reservoirs.

In conclusion, the surface diffusion coefficient is a crucial parameter that determines the transport ability of adsorbed gas in shale organic matter. However, the range in values obtained from different materials and rocks and the potential exaggeration of surface diffusion values due to certain testing methods highlight the need for a specific method for measuring the surface diffusion coefficient in shale. The development of a specific method will enable the accurate determination of surface diffusion coefficients and provide a more comprehensive understanding of the role of surface diffusion in nanopores of shale gas reservoirs. It will allow for more accurate predictions of fluid, rock, and reservoir parameters that affect surface diffusivity, which can lead to more efficient and effective exploration and exploitation of shale reservoirs.

5. Conclusion

This article provides a comprehensive review of the literature on surface diffusion in shale gas reservoirs. The unique properties of shale reservoirs, such as their nanoscale pore throat and pore-size distribution, make them an attractive area for exploration and exploitation. Surface diffusion is a crucial factor that influences the total mass transport in nanopores of shale gas reservoirs. Confined space phase behavior causes surface adsorption to become significant, leading to an increase in capillary, Van Der Waals, structural, electrostatic, and adsorption forces. These forces cause the physical and dynamic properties of fluids to deviate from those measured in a PVT cell. Certain fluid, formation, and reservoir parameters impact surface diffusivity, with consensus that surface diffusion is sensitive to pore size, molecule size, pressure, and temperature changes.

The literature review revealed that surface diffusion cannot be ignored in nanopores where the pore size and the specific surface area available per molecule increase its significance. Despite the considerable work and progress achieved in measuring gas diffusion coefficients in rocks and porous media, there is a wide range in values for surface diffusion coefficients. The big range in values is due to different materials and rocks being used for the experiments. Recent research suggests that the methane/shale surface diffusion coefficient value is around 10-16 cm^2/g. A specific method should be used to measure the surface diffusion coefficient in shale to avoid discrepancies in the results. Furthermore, interdisciplinary research is recommended to integrate advances in research from different industries to gain a better understanding of shale gas reservoirs.

Future research should focus on measuring the surface diffusion coefficient in shale accurately using a specific method. This research will help in integrating advances in research from different industries to better understand surface diffusion in shale gas reservoirs. The development of a specific method will enable the accurate determination of surface diffusion coefficients and provide a more comprehensive understanding of the role of surface diffusion in nanopores of shale gas reservoirs. It will allow for more accurate predictions of fluid, rock, and reservoir parameters that affect surface diffusivity, which can lead to more efficient and effective exploration and exploitation of shale reservoirs.

In conclusion, surface diffusion is an essential factor that cannot be ignored when calculating total mass transport in shale gas reservoirs. The sensitivity of surface diffusivity to certain parameters such as pore size, molecule size, pressure, and temperature highlights the importance of understanding these parameters. The review also highlighted the need for a specific method for measuring the surface diffusion coefficient in shale and the importance of interdisciplinary research to integrate advances in research from different industries. This article recommends interdisciplinary research to integrate advances in research from different industries to gain a better understanding of shale gas reservoirs.

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