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Research Article

Characterization of Gas Flow Ability and Contribution of Diffusion to Total Mass Flux in the Shale

[1]Rui Wang, [1, 2]Ningsheng Zhang, [2]Xiaojuan Liu, [2]Xinmin Wu and [2]Jian Yan
[1]College of Petroleum Engineering, China University of Petroleum-Beijing, Beijing 102249, China
[2]College of Petroleum Engineering, Xi'an University of Petroleum, Xi'an 710065, China

Abstract: The aim of this study is to search a parameter which characterize the flow ability and analyze the contribution of diffusion to total mass flux of gas flow in pore of shale whose size is as low as nanoscale. The diffusion coefficient of the flow region which was determined by Kundsen number was taken as the diffusion coefficient of system, then it was substituted into the equation which describes gas diffusive and flow in nano-porous media, the apparent permeability and mass flux were calculated and the impacts of the pore radius and gas type were analyzed finally. The result showed that the diffusion of gas in shale was mainly in the transition diffusion or Fick diffusion region; The ratio of the apparent permeability of considering the diffusion and slippage effect to Darcy permeability and the ratio of diffusion mass flux to total mass flux increased with the decreasing of the pore radius; The diffusion ability of the methane was stronger than ethane's. The present study implied that the calculated results of the diffusion coefficient which considers three kind of diffusion was less than that one considering Knudsen diffusion only; Considering diffusion and slippage effect, the apparent permeability of nanoscale pore of shale was 10^{-6} μm^2 level, not 10^{-9} μm^2 level in general temperature and pressure of shale reservoir.

Keywords: Apparent permeability, diffusion coefficient, diffusion flux, diffusion type, shale gas

INTRODUCTION

The minimum diameter of pores in shale reservoir is nanoscale, which is close to the diameter of the methane molecule (Javadpour *et al*., 2007; Javadpour, 2009). It was found that the gas flow in shale reservoirs is in slippage and transition flow region by calculating Kundsen number, so considering the slippage and diffusion effects were needed (Sondergeld *et al*., 2010b). Roy *et al*. (2003) established a mathematical model which describes gas diffuse in nanopores, it was based on gas mass transfer experiment that Ar, N_2 and O_2 flow in alumina filtration membrane whose aperture is 200 nm. Javadpour (2009) and Roy *et al*. (2003) model to describe gas diffuse and flow in shale (Javadpour *et al*., 2007). Sigal and Qin (2008) analyzed the importance of self-diffusion in process of gas mass transfer in shale by introducing an effective transfer coefficient. Javadpour (2009) established an equation which considers Kundsen diffusion and slipping and introduced a concept of apparent permeability (Javadpour, 2009). Sigal and Qin (2008) built a finite difference model about that.

These models didn't consider the type of diffusion. Javadpour (2009); Javadpour *et al*. (2007) and Shabro *et al*. (2009) used Knudsen diffusion model; Javadpour (2009) and Sigal and Qin (2008) used Fick diffusion model only. We determined the flow region by Kundsen number and took the diffusion coefficient of the flow region as the diffusion coefficient of system firstly, then calculated the apparent permeability and mass flux, after that calculated the ratio of the apparent permeability of considering the diffusion and slippage effect to Darcy permeability and the ratio of the diffusion mass flux to total mass flux, finally analyzed the impact of the pore radius and gas type.

METHODOLOGY

Motion equations of the mass transfer process of gas in nanopores: Motion equations of the mass transfer process of gas in nanopores (Javadpour, 2009):

$$J = J_D + J_a \quad (1)$$

where,
J = The total mass flux in kg/s/m^2
J_D = Mass flux of gas diffusion in kg/s/m^2
J_a = Mass flux of gas flow in kg/s/m^2

Roy *et al*. (2003) ignored viscous effect and introduced a constant diffusion coefficient to establish a mathematical model which describe gas diffuse in

Corresponding Author: Rui Wang, College of Petroleum Engineering, China University of Petroleum-Beijing, Beijing 102249, China

nanopores by experiments that Ar, N_2 and O_2 mass transferred in what-man alumina filtration membrane (Anodisc13, pore diameter is 200 nm, length is 60μm) (Javadpour *et al*., 2007; Roy *et al*., 2003):

$$\frac{q\rho}{\phi AM} = D\frac{\Delta p}{RTL} \quad (2)$$

where,

q = Gas volume flow in m^3/s
ρ = Gas density in kg/m^3
$\emptyset$ = Porosity in %
A = The exposed area of alumina filtration membrane in m^2
M = Molar mass of gas in kg/mol
D = Diffusion coefficient (Javadpour, 2009) used Knudsen diffusion coefficient, we assumed to be the general case) in m^2/s
R = The universal gas constant (8.314) in J/mol/K
T = Temperature in K
Δp = The pressure drop across the filtration membrane in Pa
L = The thickness of filtration membrane in m

So, mass flux of gas diffusion is:

$$J_D = -\frac{MD}{RT}\frac{\Delta p}{L} \quad (3)$$

The mass flux of gas flow can be derived from Hagen-Poiseuille's equation:

$$J_a = -\frac{r^2}{8\mu}\rho\frac{\Delta p}{L} \quad (4)$$

The calculation of diffusion coefficient: The diffusion of gas or liquid diffusive in porous solid medium can be divided into the Knudsen diffusion (*Kn*>10), Fick diffusion (*Kn*<0.01), transition diffusion (0.01<*Kn*<10) and surface diffusion according to the Knudsen number in the chemical field.

Knudsen number is defined as:

$$Kn = \frac{\lambda}{\Lambda}, \lambda = \frac{k_b T}{\sqrt{2}\pi\delta^2 p} \quad (5)$$

where,

λ = Gas mean-free-path (calculated using the Eq. (5) usually, or Loeb method (Civan *et al*., 2011) in m;

Λ = Diameter of pore in m
k_b = The Boltzmann constant (1.3805×10^{-23}) in J/K, δ is the collision diameter of the gas molecule in m

Table 1: Classification of the flow regime by Kn Number

Kn number	Flow regime
Kn>10	Knudsen diffusion
0.1<Kn<10	transition diffusion
0.01<Kn<0.1	Fick diffusion
0.001<Kn<0.01	slippage flow
Kn<0.001	Darcy flow

T = Temperature in K
P = Pressure in Pa

In fact, the analysis of Knudsen flow was initially for the purpose of research to flow of gas at low pressure, Martin Knudsen explained theoretically and demonstrated experimentally the flow of gas at low pressure by the term of molecular flow for the first time in 1909 (Steckelmacher, 1999). There was a classification standard of gas flow region according to the Knudsen number (Chen and Pfender, 1983). Civan *et al*. (2011) used this classification standard and showed the corresponding relationship among the shale pore type, flow type, dominant particle motion and flow regime. The standard that we used is described in Table 1:

Getting diffusion coefficient of fluid diffusive in porous solid medium required determining the flow region by *Kn* number firstly, then took the diffusion coefficient of the flow region as the diffusion coefficient of system. Additionally, there was a method of taking diffusion coefficient and permeability as a function of *Kn* number (Civan *et al*., 2011).

The equation of Knudsen diffusion coefficient expressed as:

$$D_{knusden} = \frac{2}{3}ur = \frac{2r}{3}\left(\frac{8RT}{\pi M}\right)^{0.5} \quad (6)$$

where,

$D_{knudsen}$ = Knudsen diffusion coefficient in m^2/s
r = Radius of pore in m
u = Average velocity of gas molecules in m
R = The universal gas constant (8.314) in J/mol/K
T = Temperature in K

Fick diffusion coefficient is calculated by Stokes-Einstein equation. Stokes-Einstein equation was used to calculate the diffusion coefficient of molecule in liquids, describe the spherical particles or molecules diffusive in a dilute solution especially. Fluid Fick diffusive in solid pore medium is mainly a collision among fluid molecules rather than collision between fluid molecules and wall surface of pore, as same as that gas diffusive in liquids. So we should use the viscosity of fluid which saturated in porous medium rather than the diffusive gas (Sigal and Qin, 2008) while we calculated the Fick diffusion coefficient:

$$D_{\text{fick}} = \frac{k_b T}{6\pi\mu_B r_A} \tag{7}$$

where,
D_{fick} = Fick diffusion coefficient in m^2/s
r_A = Radius of gas molecular in m
μ_B = Viscosity of fluid in the pore of shale in Pa/s
k_b = Boltzmann constant 1.38×10^{-23} in J/K
T = Absolute temperature in K

In our research, we assumed the fluid saturated in shale is N_2.

The transition diffusion coefficient calculated by Knudsen diffusion coefficient and Fick diffusion coefficient, is Bosanquit equation:

$$D_{\text{transition}} = (D_{\text{fick}}^{-1} + D_{\text{knudsen}}^{-1})^{-1} \tag{8}$$

It was found that by the formula (8), the transition diffusion coefficient is smaller than not only Knudsen diffusion coefficient but also Fick diffusion coefficient.

The calculation of apparent permeability of considering the diffusion and slippage effect: The flow velocity was equal to mass flux divided by density of fluid and then the permeability can be obtained by contrasting with Darcy equation.

The Darcy permeability which didn't consider the slippage effect was obtained by Hagen-Poiseuille equation:

$$J_a = -\frac{r^2}{8}\rho_{\text{avg}}\frac{\Delta p}{\mu L} \tag{9}$$

$$k_{\text{darcy}} = \frac{r^2}{8} \tag{10}$$

There is slippage effect in gas flow in nanopores that can express by introducing a theoretical dimensionless coefficient to correct the Hagen-Poiseuille equation (Javadpour, 2009):

$$\begin{aligned} J_a &= -k_S\frac{r^2}{8\mu}\rho_{\text{avg}}\frac{\Delta p}{L} \\ &= -\left[1+\left(\frac{8\pi RT}{M}\right)^{0.5}\frac{\mu}{p_{\text{avg}}}\left(\frac{2}{\alpha}-1\right)\right]\frac{r^2}{8\mu}\rho_{\text{avg}}\frac{\Delta p}{L} \end{aligned} \tag{11}$$

where,
k_s = Correct coefficient of slippage effect in dimension
p_{avg} = Average pressure in Mpa
α = Tangential momentum accommodation coefficient depending on pressure, temperature, gas type and smoothness of wall surface, the value of it is 0~1 in dimension, we took 0.5
r = Radius of pore in m

The calculation model of diffusion coefficient what was selected by the value of Kn:

$$D = \begin{cases} D_{\text{fick}}, kn < 0.1 \\ D_{\text{transition}}, 0.1 < kn < 10 \\ D_{\text{knusden}}, kn > 10 \end{cases} \tag{12}$$

So, the mass flux of gas diffusion and the mass flux of gas flow of considering slippage effect were:

$$J = J_D + J_a = -\left\{\frac{MD\mu}{RT} + \left[1+\left(\frac{8\pi RT}{M}\right)^{0.5}\frac{\mu}{p_{\text{avg}}r}\left(\frac{2}{\alpha}-1\right)\right]\frac{r^2\rho_{\text{avg}}}{8}\right\}\frac{1}{\mu}\frac{\Delta p}{L} \tag{13}$$

Using the concept which was proposed by Javadpour (2009), the apparent permeability is:

$$k_{\text{app}} = \frac{MD\mu}{RT\rho_{\text{avg}}} + \left[1+\left(\frac{8\pi RT}{M}\right)^{0.5}\frac{\mu}{p_{\text{avg}}r}\left(\frac{2}{\alpha}-1\right)\right]\frac{r^2}{8} \tag{14}$$

where, k_{app} is apparent permeability of considering diffusion in m^2. The apparent permeability can characterize the flow ability of gas flow in pore of shale which as low as nanoscale.

The ratio of apparent permeability to Darcy permeability is:

$$\frac{k_{\text{app}}}{k_{\text{dacy}}} = \frac{MD\mu}{RT\rho_{\text{avg}}}\frac{8}{r^2} + \left[1+\left(\frac{8\pi RT}{M}\right)^{0.5}\frac{\mu}{p_{\text{avg}}r}\left(\frac{2}{\alpha}-1\right)\right] \tag{15}$$

RESULTS AND DISCUSSION

The parameters which involved in the calculations and their range of value: The system of productive shale gas included four porous Medias, inorganic matter, organic matter, natural fractures and artificial fractures. According the size of pore, there were two types of pore in shale matrix, micropore and nanopore. Javadpour (2009) presented the images of nanopores obtained by AFM firstly. Sondergeld *et al*. (2010a) discovered the size of pores in shale were 300-800 nm in diameter by SEM image. Zou *et al*. (2011) discovered nano-pores in the research of unconventional tight sandstone and shale gas reservoir in China based on the SEM and the nano CT reconfiguration technique and their diameter was 5~300 nanometers and mainly was 80~200 nanometers. For the size of the pore throat, Sondergeld *et al*. (2010a) obtained incremental curves of Barnett gas shale samples and showed that maximum injection pressure was 60,000 psi which equated to a pore throat size of 1.8 nm. About natural fractures, Gale and Holder (2008) discovered natural fractures were commonly narrow (<0.05 mm) in the Mississippian Barnett shale. The size of natural fractures can be considered to microsize scale. The size of artificial fractures was considered to millisize scale.

Table 2: The basic parameters of the gases

Gas	Molecular formula	Relative molecular mass	Molecular diameter (nm)
methane	CH_4	16 .034	0.434
ethane	C_2H_6	30.070	0.496
Nitrogen	N_2	28.013	0.421

Table 3: Calculation methods, units and range of values of the parameters

Parameter	Calculation methods and range of values
M (kg/mol)	Molar mass of gas
	Temperature,300~450
r_B (m)	Radius of pore,10^{-10}~10^{-3}
μ_A,μ_B (Pa/s)	Viscosity of N_2 and CH_4(C_2H_6) ,calculated by lee-Gonzalez-eakin method (Lee *et al*., 1966)
ρ_{avg} (kg/m^3)	Density of CH_4(C_2H_6),Calculated by Dranchuk-Purvis-Robinson method
p_{avg} (MPa)	Average pressure,0.1~100
Δp (Pa)	Pressure difference,10

So, in order to analyze the impact of pore size to diffusion and flow, the pore diameter that we assumed is 0.1~10^6 nm, including fracture.

The Barnett shale has gas pressure of several thousand psi, temperature around 350 K (Sigal and Qin, 2008).We assumed pore pressure in shale gas reservoir is 0.1~100 MPa, temperature is 300~400 K and normal pressure is 5 MPa, temperature is 350 K.

There are a little experimental data of composition of gas in shale. Zhan Jinchuan found that methane content of shale gas was 42.43% and ethane content was 0.42% by chromatographic analysis of gas samples which came from well Yuye 1, Penshui county of Chongqing in China (Zhang *et al*., 2010). We assumed methane or ethane content is 100%.

The parameters involved in calculation were as Table 2 and 3:

Calculations and analysis's of *Kn* and diffusion coefficient: That the *Kn* numbers of methane flowed in shale with different diameter of pore (0.1~10^6 nm) and pressure (0.1~100 MPa) at 350 K were calculated by formula (5).

Figure 1 shows *Kn* decreased with the increasing of pressure and increased with decreasing of pore diameter. The value of *Kn* ranged from 6 to 0.03 while the pressure ranged from 0.1 to 100 MPa and the diameter of pore was 10 nm. So the flow was in Fick diffusion or transition diffusion region.

The values of diffusion coefficient of methane diffuse in shale with different radius (0.1~10^6 nm) at 300 K and 5 MPa were calculated by formula (6), (7), (8), (12).

Figure 2 shows Fick diffusion coefficient was independent of the change of pore radius, Knudsen diffusion coefficient increased with the increasing of pore radius. The Fick diffusion coefficient was equal to the Knudsen diffusion coefficient if pore radius is 0.2 nm. The transition diffusion coefficient was smaller than Knudsen diffusion coefficient if pore radius <10 nm and the Fick diffusion coefficient was less than Knudsen diffusion coefficient too if pore radius >10 nm. So the diffusion coefficient of system considering

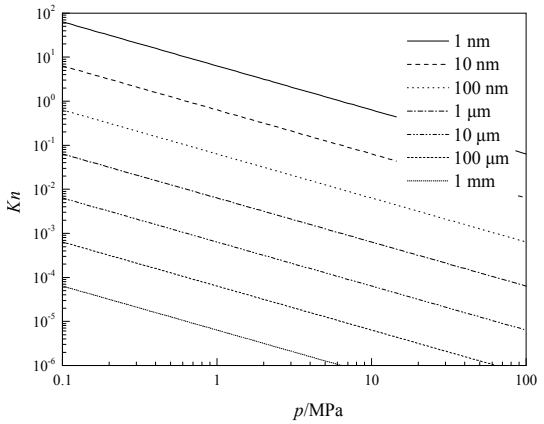

Fig. 1: The trends of *Kn* number with the different pore diameter and pressure (350 K)

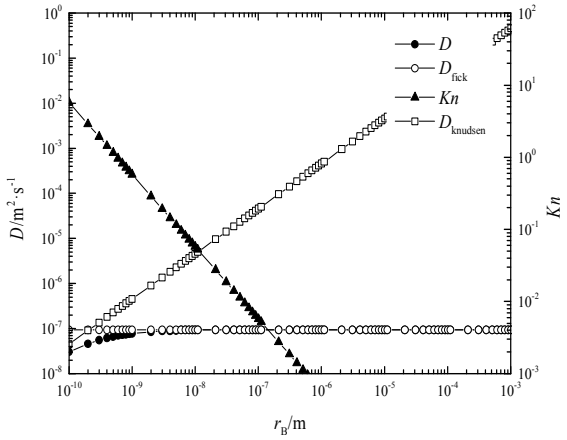

Fig. 2: The methane diffusion coefficient in different pore radius (300K, 5MPa)

Knudsen diffusion was bigger than the one which considered three kinds diffusion.

The effect of pore radius to the ratios of the apparent permeability of considering the diffusion and slippage effect to Darcy permeability and the diffusion mass flux to total mass flux: The permeability of methane flowed in shale with different

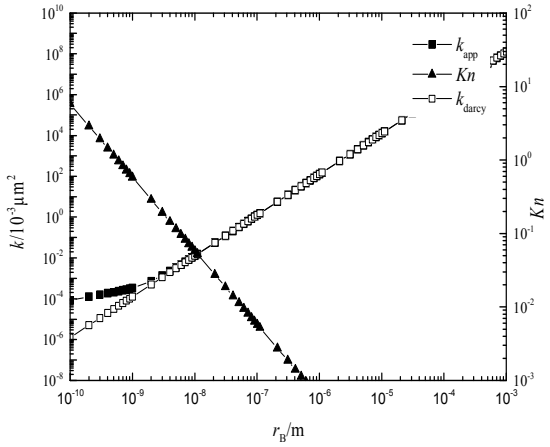

Fig. 3: The methane apparent permeability with the different pore diameter (350 K, 5MPa)

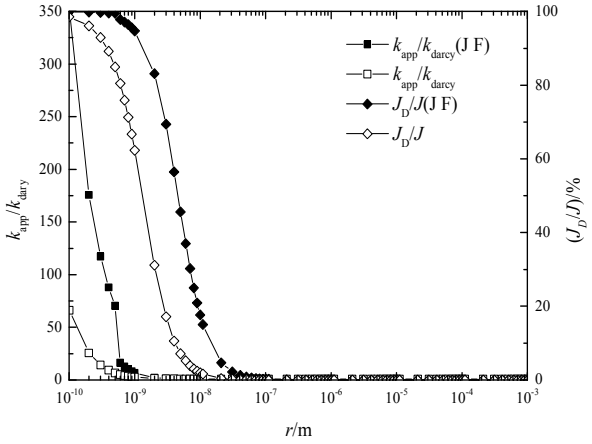

Fig. 4: The ratio of the methane apparent permeability to Darcy permeability and diffusion flux to total mass flux with the different pore radius (350 K, 5MPa)

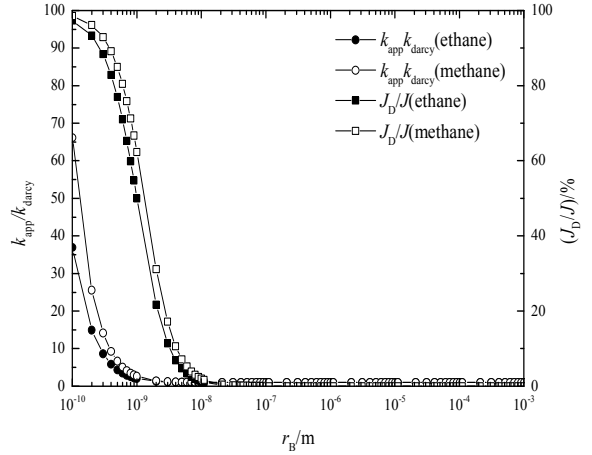

Fig. 5: The ratios of the methane and ethane apparent permeability to the Darcy permeability and diffusion flux to total mass flux with the different pore radius (350 K, 5 MPa)

radius ($0.1\sim10^6$ nm) at 300 K and 5 MPa were calculated by formula (10) (14).

Figure 3 shows apparent permeability was bigger than Darcy permeability if pore radius <20 nm and apparent permeability was equal to Darcy permeability if pore radius >20 nm. The Darcy permeability was $10^{-9}\mu m^2$ if pore radius was 0.1 nm, however apparent permeability was $10^{-7}\mu m^2$ under same condition. This shows that Darcy permeability of shale was really as low as expressed in general idea what pore minimum size of shale was nanoscale and permeability of it was nanodarcy, but permeability was $10^{-7}\mu m^2$ level barely if considering diffusion effect. So, excepting slippage, the diffusion must be considered to research the flow mechanism of shale gas and excepting permeability, the diffusion coefficient must be considered to characterize the flow ability of shale exactly. Besides the measuring of diffusion coefficient was easier than measuring of permeability, since the permeability of shale is too low.

The ratios of the apparent permeability of considering the diffusion and slippage effect to Darcy permeability and the diffusion mass flux to total mass flux with different radius ($0.1\sim10^6$ nm) at 300 K and 5 MPa were calculated by formula (13) (15). The results were as Fig. 4, the cure marked "J F" were calculated by Javadpour (2009) F's model.

Figure 4 shows the ratio of apparent permeability to Darcy permeability calculated by formula (15) was less than the one calculated by Javadpour F's model. The reasons maybe were that Javadpour F used the square of the density and only considered one kind of diffusion. The general laws were the ratio of apparent permeability to Darcy permeability decreased with the increasing of pore radius, the decreasing was outstanding if pore radius <1 nm, from 66.13 at 0.1 nm to 1.02 at 10 nm, then closed to 1.0. The ratio of diffusion flux to total mass flux decreased with the increasing of pore radius too, the decreasing was outstanding if pore radius <10 nm, from 98.48% at 0.1 nm to 1.06% at 10 nm. And the ratio diffusion flux to total mass flux was 50% if pore radius was 1~2 nm, means that the contribution of diffusion and flow to total mass flux is same as half.

The effect of gas type to the ratios of the apparent permeability of considering the diffusion and slippage effect to Darcy permeability and the diffusion mass flux to total mass flux: Javadpour (2009) analyzed the effect of gas molar mass to diffusion. But the gas characteristic parameters of effecting diffusion were not only molecular diameter, density, viscosity, expect for molar mass, but also there were interactions among them. So in order to analyze comprehensively, the type of gas instead of molar mass should be analyzed. The methane and ethane were analyzed as follow.

The ratio of the methane and ethane apparent permeability to Darcy permeability and diffusion flux

to total mass flux at 300 K and 5 MPa with different pore radius were calculated.

Figure 5 shows the ratio of the methane apparent permeability to Darcy permeability and diffusion flux to total mass flux is greater than ethane's under same condition. It means the diffusion ability of methane is stronger than ethane's. So the effect of using methane was more obvious than using ethane in experiment. But the diffusion and adsorption of methane is too difficult to distinguish, so whether there are non-hydrocarbon gas should be seek.

ANALYSIS AND DISCUSSION

The mathematical model of gas diffusion in nanopores was established by experiments that Ar, N_2 and O_2 mass transferred in what-man alumina filtration membrane and the diffusion was in Knudsen diffusion region. Whether this model can be used under the condition considering three kind diffusions is unknown. Besides, the difference of fluid saturated in shale when calculated Fick diffusion coefficient and the corrections of porosity and tortuous of diffusion path to diffusion coefficient were not considered, besides the influents of pressure and temperature to total process weren't analyzed too.

CONCLUSION

Getting diffusion coefficient of fluid diffusion in the shale required determining the flow region by *Kn* number firstly, then took the diffusion coefficient of the flow region as the diffusion coefficient of system. Gas flow in shale was in Fick diffusion or transition diffusion region. The diffusion coefficient of shale which considered three kinds of diffusion was less than the one considered Knudsen diffusion only.

The apparent permeability of gas flow in shale was $10^{-7}\mu m^2$ instead of $10^{-9}\mu m^2$ level if considering diffusion and slipping effect under the condition of general pressure temperature of shale reservoir. The ratio of apparent permeability to Darcy permeability and the diffusion flux to total mass flux increased with the decreasing of pore radius, the increasing was outstanding if pore radius <10 nm.

In order to analyze comprehensively, the type of gas instead of molar mass should be analyzed. The diffusion ability of methane is stronger than ethane's.

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