

Microscopic surface wettability electrochemical characterization of tight sandstone with infrared spectra testing

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Abstract. The distribution of charge density on the surface of microscopic tight oil is studied by using Stern double electric layer theory, and the mathematical flow model of polar fluid with micro powers in tight oil reservoir is established. The Fourier transform infrared (FTIR) were used to investigate the interaction of rock surface functional groups with fluids. The results show that: (1) When the external fluid of the polar group passes through the dense micro-nano pore, it will form an electric double layer on the surface of the rock, there will be a certain thickness of the liquid membrane, the fluid migration has a certain Of the electrical viscosity effect, will have a certain flow resistance. (2) The Fourier transform infrared spectroscopy of the Chang 7 tight reservoir rock samples exists and distributes different kinds of peaks. The left peak trend determines the presence of hydroxyl groups. The four fronts and types of the right side can be used to obtain that calcium carbonate CO_3^{2-} exists. (3) There are CO_3^{2-} and hydroxyl functional minerals in the Chang 7 tight sandstone samples. It is consistent with the basic mineral analysis measured by X-ray diffraction. When the external fluid affects the rock surface, the surface will occur in the physical van der Waals force and chemical bond interaction, so it will affect the flow of water on the surface.

1. Introduction

Tight oil is an important component of unconventional oil. Because of the prospect of mining and the prospect of large reserves, it has become a hot spot in the world at home and abroad. Many scholars have carried a lot of research on the pore structure, oil and water occurrence status and permeability of tight sandstone reservoir [1]. Compared with conventional oil and gas, tight oil reservoirs have low oil saturation [2], low porosity and low permeability [3]. And the pore and throat size of the tight sandstone reservoir is smaller, the pore network model is more complicated, the fluid is more complicated in the micro-nano pore throat, and the wettability of the rock surface has great influence on the seepage of the fluid.

Wettability is a major factor influencing the occurrence and flow of fluid in the pores of tight reservoirs [4], while directly restricting the relative permeability of oil and water [5], capillary force [6] as well as oil recovery [7]. In the micro-nano pores of the dense oil reservoir, the complex fluid containing the polar functional groups will have a certain effect on the surface of the rock, which affects the flow effect and the wettability is the macroscopic nature under the influence of many



microscopic factors. This paper reveals the effect from the microscopic scale through mathematical models and physical experiments.

2. Materials

All the experimental samples were taken from Chang 6 to Chang 8 of Yanchang oil layer in the Ordos Basin. The basic parameters of the samples are shown in table 1. The porosity of these samples are between 6.98~13.16%, an average of 10.38%; Water based permeability is between $0.05\sim0.23\times10^{-3}\mu\text{m}^2$, an average of $0.14\times10^{-3}\mu\text{m}^2$, which is a typical low porosity and permeability in tight reservoirs. The X-ray diffraction results show that the mineral composition of the samples is mostly quartz, feldspar and clay. The content of quartz is 30.20~54.1%, an average of 42.31%, the content of Feldspar is 16.10~42.10%, an average of 29.54% [8] which is consistent with the parameters of the rock basin. The content of Clay mineral is high, an average of 18.21%, and chlorite is the main component of clay minerals, an average of 9.48%; the content of Mixed-layer illite and illite are the second most. In addition, there is also a small amount of kaolinite.

Table 1. Physical property of tight oil samples and mineral composition.

Sample serial number	Porosity	Permeability	quartz	Feldspar	Calcite	Dolomite	Illite montmorillonite mixed layer	Illite	Chlorite
	/%	$/10^{-3}\mu\text{m}^2$	/%	/%	/%	/%	/%	/%	/%
YC-7	13.16	0.23	33.40	42.10	0.70	4.40	4.46	1.75	13.19

Quartz, feldspar and other minerals can support a rigid overburden pressure, which helps the preservation of the original grain holes; meanwhile, feldspar, calcite and other minerals can easily generate corrosion hole, thereby improving the quality of the reservoir [8]. Chlorite usually grows along the surface of the mineral skeleton. On the one hand the formation of chlorite envelope can prevent the growth of secondary quartz, which is an effective protection for the reservoirs; On the other hand, with the growth of a large number of chlorite, a network structure forms, and it will destroy the original pore structure. Illite mainly distributes in the pores as silky or silk thread-like bridging formula, which greatly reduces the porosity of percolation. Kaolinite and feldspar solution openings are generally associated, and Kaolinite is a book-like or lamellar shape, it has a great effect on remodeling corrosion holes transformative [9, 10].

3. Two-layer model of rock interface

The main mineralization minerals in the tight sandstone reservoir include quartz, potassium feldspar, plagioclase, calcite, dolomite and clay mineral content. In the water, the mineral surface is susceptible to water and inorganic ions, and charged particles (ions, peeling ions, etc.) in the solid-liquid interface range of power transfer, resulting in mineral and water interface and potential difference, so that the surface of mineral particles Charging, electric double layer formed in the interphase interface(As shown in figure 1). There are two main ways to change the number of mineral particles on the surface of the belt: (1) Adsorption or cleavage of H^+ [11]; (2) Ion exchange [12].

In the vicinity of the mineral surface will attract the opposite sign ions in the liquid medium, and the two-phase interface state distributes the diffusion of the opposite sign ions of the double layer. The surface charge of the surface of the electric double layer is mainly concentrated in the surface layer thickness of 1 ~ 2 atoms, forming the inner layer of the electric double layer. In the area near 1 to 2 water molecules, the number of liquid medium ions is strongly attracted by the solid surface (electrostatic interaction and van der Waals attraction) to form a strong adsorption layer, called fixed adsorption layer or Stern layer. The Stern layer is the diffusion layer of the counter ion. In the diffusion

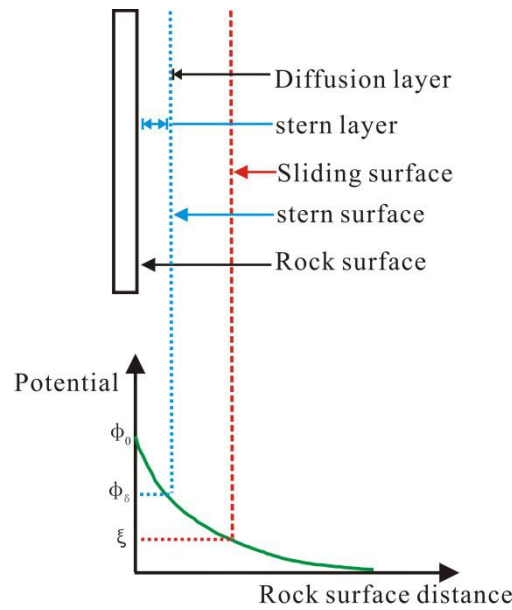


Figure 1. Double-layer model of tight reservoir surface.

layer, the counter ion concentration gradually decreases from the Stern layer to the inside of the liquid. ϕ_0 represents the potential difference between the solid surface and the solution, also known as the surface potential. Φ_δ denotes the potential difference between the electric center plane and the solution of the counter ion in the Stern layer, also called the Stern potential. ζ represents the potential difference between the solid surface and the solution when moving relative to the sliding surface, also known as the potential or zeta potential. In general, since the distance between the Stern surface and the sliding surface is small, the difference between the Zeta potential and the Stern potential can be ignored. For the silicate minerals with H^+ or OH^- , the pH of the solution is called zero point (PZC) at the surface potential $\phi_0 = 0$, and the pH of the solution at zeta potential $\zeta = 0$ is called the isoelectric point (IEP). When there is no special adsorption, the chemical potential of any ion in the salt solution is [13]

$$\mu = ze\phi_x + kT \ln n_x \quad (1)$$

Where ϕ_x is the potential at the distance from the solid surface x ; n_x is the ion number density (number of ions/L) at the solid surface x ; z is the valence of the ion; e is the unit charge; k is the Boltzmann constant; T is the reaction temperature.

So the charge density ρ from the solid surface x can be expressed as

$$\rho_x = -\frac{e^2 \phi_x}{kT} \sum_i n_{i\infty} z_i^2 \quad (2)$$

The Poisson equation [14] is the excess charge density from the solid surface x

$$\rho_x = -\epsilon_0 \epsilon \left(\frac{d^2 \phi_x}{dx^2} \right) \quad (3)$$

Where: ϵ_r is the relative permittivity of the solution (relative to water, 78 at room temperature); ϵ_0 is the vacuum dielectric constant; combined with equations (2) and (3) is [15-19]:

$$\frac{d^2 \phi_x}{dx^2} = \phi_x \frac{\sum_i n_{i\infty} e^2 z_i^2}{\epsilon_0 \epsilon kT} = \phi_x \lambda^2 \quad (4)$$

Where λ is the reciprocal of the thickness of the electric double layer [38]:

$$h = \lambda^{-1} = \sqrt{\frac{\epsilon_0 \epsilon kT}{\sum_i n_{i\infty} e^2 z_i^2}} \quad (5)$$

The boundary condition of equation (4):

$$\varphi_{\infty} = 0, \varphi_{x=0} \rightarrow \varphi_0 \quad (6)$$

The relationship between the potential and the surface potential at a distance x from the surface can be described by Boltzmann's law:

$$\varphi_x = \varphi_0 e^{-\lambda x} \quad (7)$$

According to the above-mentioned double-layer theory, the potential difference between the solid surface and the solution interface due to the uneven distribution of charge. Therefore, in the electrolyte solution, the solid surface charges density and the surface potential of the corresponding relationship. For example, in the solution of NaCl and CaCl₂ electrolyte, a simplified model of diffusion double electric layer proposed by Gouy-Chapman can be used to calculate the surface charge density of solid as follows:

$$\rho = \sqrt{8\epsilon_0 \epsilon kT} \sinh\left(\frac{e\varphi_0}{2kT}\right) \left\{ [Na^+]_{\infty} + [Ca^{2+}]_{\infty} \left(2 + e^{-e\varphi_0/kT}\right) \right\}^{1/2} \quad (8)$$

4. Fourier transforms infrared spectroscopy

4.1. Infrared spectroscopy features

The analysis of FTIR has the following characteristics: speed, easy operation, good repeatability, high sensitivity, and high signal to noise ratio advantages. It could rapidly and accurately qualitative analysis of solids, liquids, samples containing more than 30% of the gas content. The Vertex70 Fourier transform infrared spectrum is a third generation infrared spectrum with a spectral range of 15000 ~ 370 cm⁻¹. It has the characteristics of high accuracy, high resolution and higher accuracy than 0.01 cm⁻¹ (usually In the analysis of minerals 4 cm⁻¹), high flux, low noise, fast measurement, easy operation, good repeatability, high sensitivity, low sample consumption, simple instrument structure, etc., which can effectively detect different crystals structure [20-28].

The infrared spectrum of the mineral in the 3800-3400cm⁻¹ high frequency range within the original absorption curve changes, generally caused by the material with a large molecular structure of vibration, such as the molecular structure of water, organic molecules C-O, C-H key and so on. For example, the absorption peak of chlorite is 3580 cm⁻¹- 3440 cm⁻¹, the absorption peak of montmorillonite is 3620 cm⁻¹, and the absorption peak of illite is 3650 cm⁻¹.

4.2. FTIR of tight sandstone in Yanchang formation

The core of the Chang7 Formation of the extension of the Ordos Basin was tested by using the Vertex70 Fourier Transform Infrared Spectrometer, Hyperion Microscope, manufactured by Brooke Company, Germany.

As the 3600 ~ 3000 cm⁻¹ band is mainly the vibration absorption band of hydroxyl, 3000 ~ 2800 cm⁻¹ band is mainly methyl and methylene symmetrical and asymmetric vibrating absorption band in alkane. According to the analysis on the left side of figure 2, and there is a peak at 3650 ~ 3200 cm⁻¹. There is a strong peak at 800 cm⁻¹, which indicates that the core contains almost free hydroxyl groups and can be related to the H⁺ in the external fluid, OH⁻ and other hydrogen bond force and chemical bond.

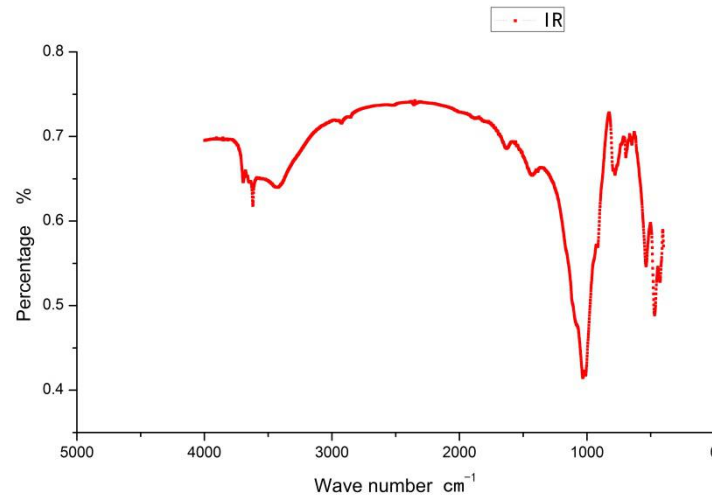


Figure 2. Chang 7 tight sandstone infrared spectra.

As can be seen from the right side of figure 2, it is observed that there are generally 4 to 5 absorption bands in the range of 1000 to 300 cm^{-1} in the infrared spectrum, including:

- including calcium carbonate CO_3^{2-} anti-symmetrical stretching vibration (ν_3) $800 \text{ cm}^{-1}\pm$;
 - Outside bending vibration (ν_2) $657 \text{ cm}^{-1}\pm$,
 - In-plane bending vibration (ν_4) $524 \text{ cm}^{-1}\pm$,
 - Symmetrical stretching vibration (ν_1) $1050 \text{ cm}^{-1}\pm$ infrared absorption peak is very weak.
- Among them, the anti-symmetrical stretching vibration (ν_3) absorption peak is strongest, and the peak width is larger;

From the above analysis, it can be seen that there are more CO_3^{2-} and hydroxyl functional minerals in the long 7-tight sandstone, which are consistent with the basic mineral analysis measured by X-ray diffraction. In the case where the external fluid affects the surface of the rock, Van der Waals force and chemical bond interaction, thus affecting the seepage.

5. Flow model with ion potential micro-nano pore

5.1. Wall potential distribution equation

As a result of the above analysis, we can see that there are electrostatic ions on the surface of the micro-rock of the dense reservoir. When the external fluid containing the dot ions passes through, the mechanism of the electric double layer will affect the distribution of charge on the surface of the rock and produce the surface potential. Since the surface charge of the rock attracts the opposite charge closer to the wall, the distribution of the charge in the fluid follows the Boltzmann distribution. The pore channel of the model is assumed to be a tube, as shown in figure 3, and because of the symmetry, Area to establish a mathematical model. The charge density of the microscopic rock surface potential ϕ and the solution volume per unit volume ρ is described by the following two-dimensional Poission-Boltzmann equation

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} = -\frac{\rho}{\epsilon_r \epsilon_0} \quad (9)$$

The net charge density is

$$\rho = (n^+ - n^-) z_0 e = -2 n_0 z_0 e \sinh\left(\frac{z_0 e \phi}{k_B T}\right) \quad (10)$$

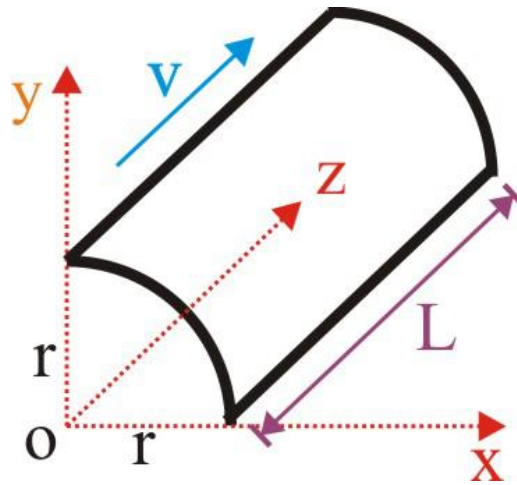


Figure 3. Model coordinate system.

where: n_0 is a Boltzmann constant; z_0 is the valence; n^+ , n^- are positive and negative ions; e is the basic charge ($1.602 \times 10^{-19} \text{C}$); k_B is Boltzmann constant ($1.38 \times 10^{-23} \text{J} \cdot \text{K}^{-1}$);

5.2. Electrostatic force distribution equation

The downstream current caused by the downstream current produces a conduction current in the opposite direction, which is defined as

$$I_s = \int_A w(x,y) \rho(x,y) dA \quad (11)$$

A is the cross-sectional area of the pore channel. Can be introduced by the above formula, the resulting electrostatic field E according to the charge balance, the conductivity σ and seepage morphology as follows

$$E = -\frac{1}{\sigma A} \int_0^r \int_0^r w(x,y) \rho(x,y) dx dy \quad (12)$$

In the absence of an applied electric field, the electrostatic force F is distributed by the potential distribution near the dense reservoir surface ϕ and the electrostatic charge density ρ is as follows

$$F = E_z \rho(x,y) \quad (13)$$

5.3. Momentum equation

According to the above analysis, we can see that for the incompressible NS equation, in addition to the water supply and so on to provide energy, there are dense reservoir rock surface double electric layer area by the net charge generated by the electrostatic force F, for steady flow, The control equation for v is

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = \frac{1}{\mu} \frac{dp}{dz} - \frac{1}{\mu} F \quad (14)$$

Substituting equation (13) into the above equation

$$\frac{\partial^2 v}{\partial x^2} + \frac{\partial^2 v}{\partial y^2} = \frac{1}{\mu} \frac{dp}{dz} - \frac{1}{\mu} E_z \rho(x,y) \quad (15)$$

5.4. The boundary condition of the control equation

For the potential equation (1), the boundary condition is as follows

$$x = 0, \varphi(0, y) = \varphi_s; x = r, \frac{d\varphi}{dx} = 0 \quad (16)$$

$$y = 0, \varphi(x, 0) = \varphi_s; y = r, \frac{d\varphi}{dy} = 0 \quad (17)$$

φ_s is the potential of the inner wall of the pore channel.

For the momentum equation (7), the boundary condition is

$$x = 0, v = 0; y = r, \frac{\partial v}{\partial x} = 0 \quad (18)$$

$$y = 0, v = 0; y = r, \frac{\partial v}{\partial y} = 0 \quad (19)$$

6. Conclusion

When there are polar ions of the external fluid through the dense reservoir micro-nano-pore, the rock surface will form an electric double layer, there will be a certain thickness of the liquid membrane, the fluid migration to produce a certain electrical viscosity effect.

The long 7 tight reservoir rocks measured Fourier infrared spectroscopy and the distribution of different types of peak, the left peak trend is willing to determine the hydroxyl, the right side of the four fronts and types can be obtained calcium carbonate CO_3^{2-} widely exist.

The long 7 sandstone contains more CO_3^{2-} and hydroxyl-containing minerals, and the above X-ray diffraction measured by the basic mineral analysis of the results consistent with the external fluid to the surface of the rock, the surface will occur in the physical van der Waals force And the interaction of chemical bonds, thus affecting the seepage.

The flow model of the electromechanical model is established.

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