

Measurement of the organic saturation and organic porosity in shale

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ABSTRACT

Shale formations are fine-grained, clastic sedimentary rocks composed of a mix of clay mineral flakes and tiny fragments of quartz and calcite, with both inorganic and organic content and porosities. The inorganic content, such as clay minerals, is hydrophilic, while the organic pores are largely hydrophobic and therefore form the main ad- and absorbed sites for hydrocarbons. The complex wettability of shale formation has a significant impact on fluid storage and flow behavior of shale oil reservoirs. Oil content in a given shale oil formation includes free oil which is primarily contained in inorganic pores and ad- and absorbed oil in kerogen. Assessment and quantitative evaluation of oil content in shale is challenging. Oil saturation in a given shale oil formation consists of two components: inorganic saturation (free oil-dominated) and organic saturation (ad- and absorbed oil-dominated). Shale porosity includes inorganic and organic porosity. There is no reported research that identifies the two porosities and saturations. We therefore recently performed, for the first time, two types of vacuum-imbibition tests - water imbibition and oil imbibition - on 20 shale oil core samples to distinguish these two saturations. The final imbibed oil volume represents the total oil saturation, the final imbibed water volume is the inorganic saturation, and the difference between the two represents the organic oil saturation. Helium saturation tests were conducted to determine the total pore volume in shale. The amount of ad- and absorbed oil can be obtained from the difference between the total imbibed oil volume and pore volume. The difference between organic saturation and absorbed oil represents the organic pore volume, thereby obtaining the organic and inorganic porosity. Our results indicate that, for the shale core samples tested, the oil saturation in organic matter ranges from 6% to 55% of the total oil saturation in shale, and 50% to 90% of the organic saturated oil is ad- and absorbed in kerogen. The organic porosity ranges from 2% to 50% of the total porosity. Both the organic oil saturation and the effective organic porosity exhibit positive correlation with total organic carbon.

Keywords: vacuum-imbibition; organic saturation; inorganic saturation; organic porosity; inorganic porosity, total organic carbon

1. Introduction

Shale oil formation is a complex and heterogeneous system, with both organic and inorganic content [1-2]. Because of the coexistence of minerals and organic matter, shale reservoir rock properties such as wettability are more complex than in conventional oil reservoirs. The complex wettability of shale formations and the wide range of pore volumes and pore size distributions have a significant impact on hydrocarbon saturation and production performance of shale oil reservoirs. The determination of hydrocarbon saturation and porosity in shale is difficult, because no single fluid-probe-based porosimetric technique can satisfactorily measure the wide range of pore volumes. The oil content in a given shale oil formation includes free oil and ad/absorbed oil. The latter can represent a significant portion of total oil content, yet production of shale oil by current technologies targets only the free oil rather than the ad- and absorbed oil in kerogen [3]. The assessment and quantitative evaluation of oil content in shale is critical, which is the fundamental parameter for understanding the potential recovery of shale oil resource and modeling hydrocarbon multiphase transport. Oil content and porosity in shale has not been well characterized due to the complexity of shale formation structure and properties.

In this paper, for the first time, two types of vacuum-imbibition tests - water imbibition and oil imbibition - were carried out to evaluate inorganic saturation and organic saturation. Twenty shale oil core samples and one sandstone sample were tested to distinguish between these two saturations. Helium saturation tests were also conducted in combination with vacuum-imbibition tests to determine effective organic porosity and inorganic porosity. The TOC of shale samples were characterized to analyze the controlling factors for organic saturation and organic porosity.

2. Samples and Experiments

The shale rock Samples #1-#8 were collected from Well FY-1, Well LY-1, and Well NY-1 in the Dongying Depression, which is located in Dongying, Shandong Province in eastern China. The shale rock Samples #9-#20 were collected from Well L-67 in the Zhanhua Sag. The tight sandstone sample (#21) was collected from Well XYS-9 in the Zhanhua Sag. The mass, porosity, total organic carbon mass fractions, and vitrinite reflectance are shown in Table 1. The lithology of the shale core samples is kerogen-rich lime mudstone, argillaceous limestone, and sandstone. The total organic carbon content of the shale samples in this study ranged from 1.44 to 5.97 wt.%. The vitrinite reflectance ranged from 0.68 to 1.05 %.

Table 1. Geochemical characteristics, mass and porosity of shale samples and a tight sandstone sample

Number	Samples	Mass (g)	Porosity ^a (%)	TOC (wt.%)	Kerogen type	S ₁ (mg/g)	S ₂ (mg/g)	S ₃ (mg/g)	T _{max} (°C)	HI	OI	Ro (%)
#1	FY-3255	47.92	11.69	1.44	II	2.90	4.43	0.26	424	308	18	-
#2	FY-3129	48.52	8.80	4.98	II	1.16	22.51	0.07	445	452	1	0.81
#3	FY-3200	46.76	9.59	3.90	II	0.43	17.19	0.04	446	441	1	0.84

#4	FY-3178	63.47	8.21	1.86	II	1.39	6.74	0.18	443	362	10	0.76
#5	FY-3415	59.99	7.84	1.96	II	0.61	5.16	0.09	442	263	5	0.84
#6	LY-3745	58.05	11.79	5.97	II	0.26	20.96	0.21	447	351	4	1.05
#7	LY-3624	55.03	13.30	2.39	III	0.09	4.36	0.27	447	182	11	1.02
#8	NY-3493	60.79	12.99	1.56	III	0.60	2.81	0.26	437	180	17	-
#9	LUO-3275	45.21	10.26	2.84	II	3.29	9.79	0.48	439	341	17	0.75
#10	LUO-3245	49.34	6.95	1.70	II	3.41	7.78	0.28	441	405	15	0.68
#11	LUO-3382	62.58	8.13	1.38	I	6.59	11.50	0.24	439	401	8	0.85
#12	LUO-3340	66.14	10.22	1.40	II	2.80	5.28	0.42	419	293	14	0.80
#13	LUO-3312	71.06	8.02	1.58	II	1.73	3.22	0.33	433	307	31	0.81
#14	LUO-3347	62.62	8.68	1.91	II	3.30	5.45	0.42	419	306	24	0.83
#15	LUO-3307	67.64	7.05	2.84	II	2.29	8.53	0.21	442	374	9	0.79
#16	LUO-3299	65.42	7.70	4.09	III	1.69	10.51	0.26	445	414	10	0.81
#17	LUO-3276	63.02	7.87	2.84	II	3.29	9.79	0.48	439	341	17	0.75
#18	LUO-3250	67.20	8.14	3.41	II	5.30	13.93	0.27	443	409	8	0.70
#19	LUO-3315	63.36	10.42	1.50	II	0.13	6.03	0.25	437	370	15	-
#20	LUO-3239	56.60	10.53	2.44	II	1.20	14.84	0.32	440	608	13	-
#21	XYS-4047	68.32	10.89	-	-	-	-	-	-	-	-	-

^aCalculated from pressure pulse decay method.

An apparatus for vacuum-imbibition tests is designed and set up. The schematic diagram of the apparatus is shown in Figure 1. The experimental setup consisted of two sealed test cells, two high precision burettes (minimum scale: 0.01 ml), and a temperature controlling air bath. The burette was connected to the test cell to measure the imbibed water or oil volume. The top opening of the burette was sealed with plastic wrap and aluminum foil to avoid vaporization of the liquid. Since the liquid imbibition rate in shale is very slow and the amount imbibed into shale is small, a high precision burette and large volume of core sample were used.

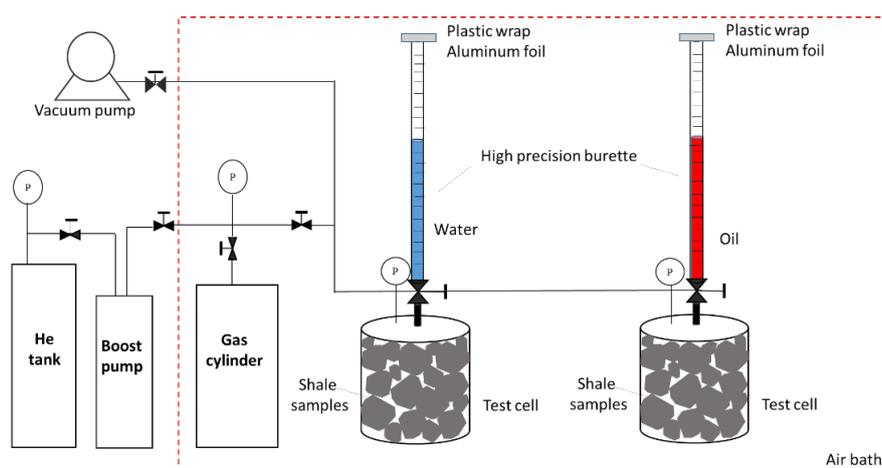


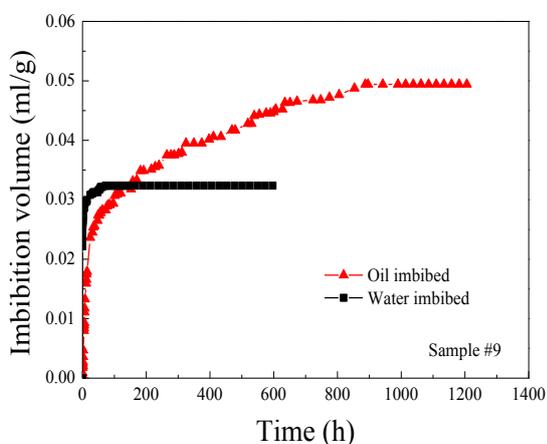
Figure 1. Schematic of the vacuum-imbibition test

The shale core samples and the tight sandstone sample were broken into blocks of about 1-2 cm in diameter and extracted with mixtures of toluene and ethanol for about 10 days and then extracted with dichloromethane for about 10 days, and dried at 100 °C for several days until the weight of the sample was constant. The cleaned block samples were accurately weighed and sealed into the test cell at test temperature. Then the test cell was evacuated with a molecular vacuum pump after the leak test was completed. For helium tests, helium gas was injected into a test cell and tested at different pressure points, steadily increasing from a lower pressure to the highest desired pressure. Every pressure point typically reached equilibrium in no less than 5 hours, after which the pressure was raised gradually to the next pressure point until the highest desired pressure was attained.

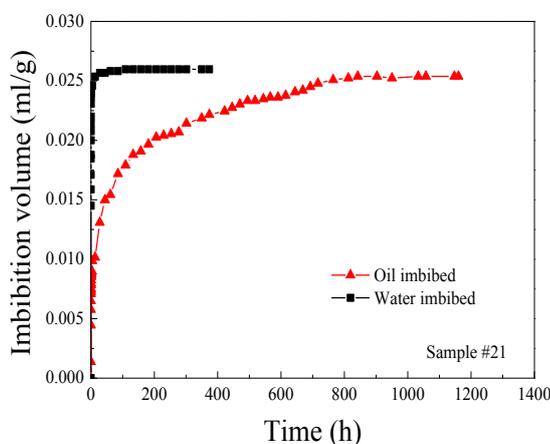
After helium saturation tests, the block samples were divided into two parts and sealed separately into two test cells, one for water imbibition, another for oil imbibition. Before each imbibition test, the sample was maintained under vacuum for at least 12 hrs, until the pressure reached 0.000001% of atmospheric pressure (10^{-3} Pa). Then, the valve between the test cell and the burette was opened to allow oil or brine to imbibe into the corresponding test cell. The volume change of the liquid in burette was recorded with time until there was no change. In the oil imbibition tests, n-dodecane was used, and the water is high concentration KCl brine.

3. Results and Discussion

Two types of vacuum-imbibition tests and helium saturation tests were performed on 20 shale samples to evaluate the different saturations and porosities. In order to verify the rationality of the above mechanisms of the water/oil imbibition process in shale, the water and oil imbibition test for a tight sandstone sample was also tested for comparison, with and without organic matter. This tight sandstone was collected from the same sag with shale samples #9-#20. The lithology of tight sandstone samples is fine sandstone, contains no organic matter, and the clay mineral content is about 9%. The porosity and permeability of the tight sandstone are close to that of shale. The parameters of the tight sandstone sample were also listed in Table 1.



(a) Shale sample



(b) Tight sandstone sample

Figure 2. Vacuum-imbibition curves of water and oil in (a) shale oil core sample, and (b) sandstone core sample

Figure 2 shows the representative vacuum-imbibition curves of water and oil in shale sample and sandstone sample. The vacuum-imbibition curves of water and oil in shale oil core samples exhibit a similar pattern. In all tests, at the early stage, the amount of water/oil imbibed increases rapidly. The water imbibition rate is higher than the oil imbibition rate. At the later stage, the amount of water/oil imbibed increases slowly until it no longer changes. The water imbibition curves quickly reach equilibrium, but the oil imbibition curves take a long time to reach equilibrium. The amount of oil imbibition gradually approached and exceeded the amount of water imbibition. The final imbibed oil volume is higher than the imbibed water volume. The water and oil imbibition curves of the sandstone sample also exhibit two stages, but the amount of oil imbibition gradually approached the amount of water imbibition at late stage. Therefore, the total oil imbibition time is much longer than the water imbibition time, but the final imbibed oil volume is much closer to the imbibed water volume.

The results show that oil and water can enter the same pore space due to the homogeneous wettability in tight sandstone samples (without organic matter). Therefore, the final oil imbibed volume is much closer to the final water imbibed volume. Considering the kerogen contained in shale samples, oil can enter more space in kerogen, and the difference between the amounts of oil and water imbibition should represent the organic saturation (oil stored in kerogen). Therefore, the final oil imbibed volume is higher than the final water imbibed volume.

This heterogeneous wettability of shale samples is expected to impact the location and the stored volume of different fluids, such as water and oil. Figure 3 shows the schematic of water and oil imbibition processes into different wettability capillary tubes. The tubes were vacuumed before imbibition tests. Water and oil will evaporate to gas phase upon entering the tubes; therefore, there is some dilute gas in pores during the imbibition process, and the oil-gas and water-gas capillary pressure still exists. The pressure gradient of fluid in the tubes is the sum of capillary pressure and atmospheric pressure.

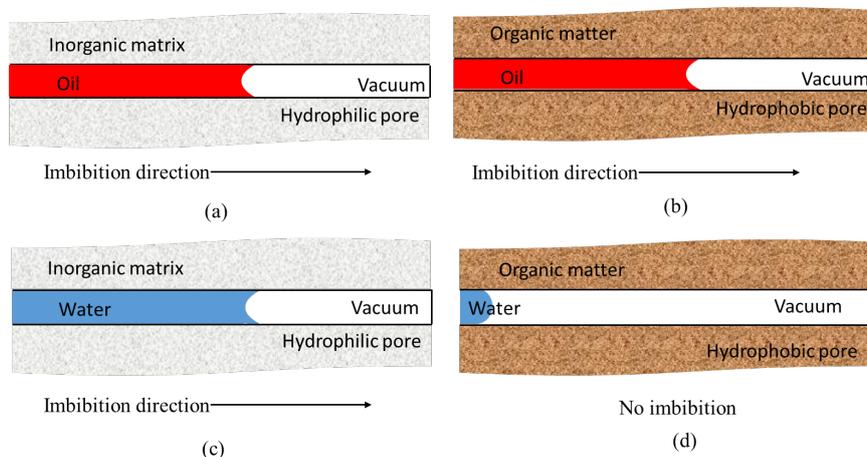


Figure 3. Schematic of water and oil imbibes into pores with different wettabilities: (a) oil imbibes into hydrophilic pore; (b) oil imbibes into hydrophobic pore; (c) water imbibes into hydrophilic pore; (d) water stops at the entrance of hydrophobic pore

When water or oil imbibes into the hydrophilic tube, the capillary pressure is in the same direction as the fluid flow; both water and oil can imbibe into hydrophilic tubes under the power of capillary pressure (Figure 3 (a) and (c)), and the higher the capillary pressure, the greater the driving power for imbibition. When oil imbibes into hydrophobic tubes, the capillary pressure is still a driving force (Figure 3 (b)). However when water contacts hydrophobic tubes, the capillary pressure becomes a resistance; the higher the capillary pressure, the more resistance. As an example, the capillary pressure of water is 576 kPa when the pore width is 500 nanometers. The capillary pressure will increase to 28.8 MPa when the pore diameter decreases to 10 nm. With pore size decrease, the capillary pressure of water increases dramatically. According to the analysis of the pore structure, the pore size of organic pores within kerogen ranged from 1 nm to 500 nm, which means the resistance to water flow into those organic pores is 500 kPa to 288 MPa minus 101 kPa for the vacuum condition. Therefore, water cannot imbibe into the organic pores even under vacuum condition (Figure 3 (d)).

According to the analysis of the water/oil imbibition process, the final imbibed oil volume represents the total oil saturation, the final imbibed water volume is the inorganic saturation, and the difference between the two represents the organic oil saturation. The helium saturation volume represents the total effective pore volume of both inorganic and organic media. The amount of total ad- and absorbed oil can be obtained from the difference between the total imbibed oil volume and pore volume which was measured by the helium saturation test. The total ad/absorbed oil includes adsorbed oil on the minerals and the ad/absorbed oil within the kerogen. The total ad/absorbed oil represents the ad/absorbed oil within kerogen in this paper, and the difference between organic saturation and ad/absorbed oil within kerogen represents the organic pore volume, thereby obtaining organic porosity. Inorganic porosity can be calculated by the difference between the whole pore volume and the organic pore volume.

In this work, the kerogen type of the test samples was mainly type II, and the vitrinite reflectance R_o of the shale samples was relatively close to 0.8%. Fig. 4 shows the relationship between organic saturation (a), organic porosity (b), ad/absorbed oil (c) with TOC of the shale samples. The results showed that there were nearly positive correlations between organic saturation, organic porosity, ad/absorbed oil in kerogen and TOC.

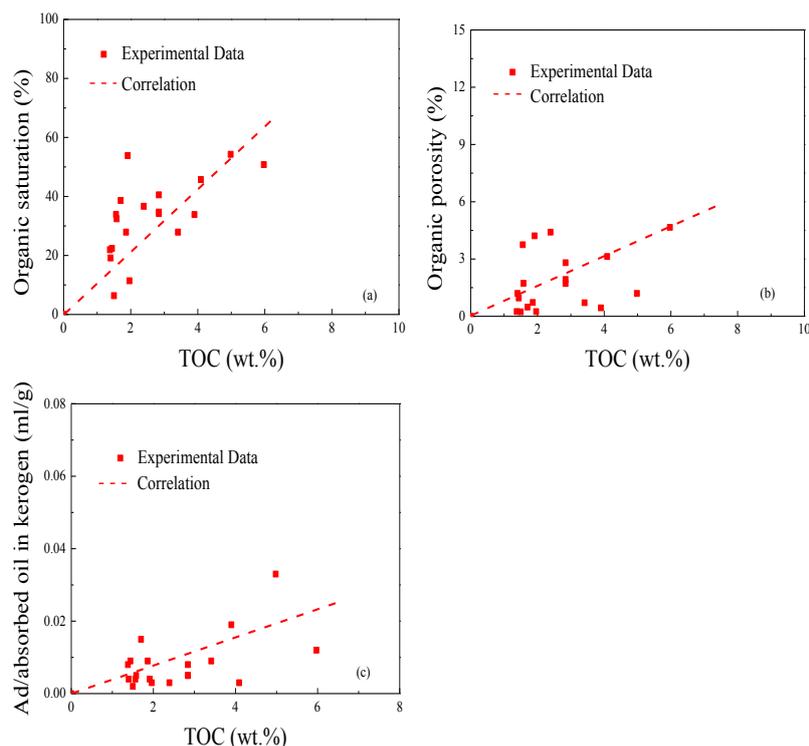


Figure 4. Relationship between (a) organic saturation and TOC; (b) organic porosity and TOC; (c) ad/absorbed oil in kerogen and TOC

4. Conclusions

In this study, a method has been proposed to measure the effective saturations and porosities based on the interconnected pores which are accessible to fluids. Two types of vacuum-imbibition tests - water imbibition and oil imbibition - have been conducted to measure organic and inorganic saturation. The effective organic porosity and inorganic porosity were also measured in combination with helium saturation tests.

In the water/oil imbibition process, the final imbibed oil volume represents the total oil saturation, the final imbibed water volume is the inorganic saturation, and the difference between the two represents the organic oil saturation. In helium saturation tests, the volume of helium saturation represents the total pore volume in shale. The amount of ad- and absorbed oil can be obtained from the difference between the total imbibed oil volume and pore volume. The difference between organic saturation and absorbed oil represents the organic pore volume, thereby obtaining organic porosity and inorganic porosity. TOC is an important factor influencing organic saturation and organic porosity. There were positive correlations between organic saturation, organic porosity, and TOC.

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