Study on the Mechanism of Nanoemulsion Removal of Water Locking Damage and Compatibility of Working Fluids in Tight Sandstone Reservoirs

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ABSTRACT: The invasion of external fluids, because of hydraulic fracturing for tight sandstone gas reservoirs, will cause the decrease of fracture conductivity and rock matrix permeability and decrease the flow of oil and gas. The nanoemulsion has a smaller molecular size and is used in combination with the fracturing fluid. After entering the formation, it can reduce the surface tension of gas/water, change the wettability of the rock surface, and improve the flowback rate of the fracturing fluid. In this study, a set of systematic evaluation methods was established in the laboratory to evaluate the mechanism and effect of removal of water locking additive in tight sandstone gas reservoirs. The adsorption experimental results of the nanoemulsion on the rock surface show that the adsorption of the nanoemulsion on the solid-phase particle surface is from strong to weak in the order of smectite, kaolinite, DB105X well rock powder, quartz sand, illite, chlorite, and ceramsite proppant. The experiment on the influence of the nanoemulsion on the spontaneous imbibition of reservoir rocks shows that when the gas permeability of reservoir rocks is $K_g < 5.0 \text{ mD}$, adding a nano-emulsion in the working fluid to change the wettability of reservoir rocks can effectively reduce the imbibition and retention of external fluids in reservoir rocks, thus reducing the “water locking damage”. When the gas permeability of reservoir rocks is $5.0 \text{ mD} < K_g \leq 1.0 \text{ D}$, the effect of changing the reservoir wettability to prevent the “water locking damage” is reduced. At the same time, the nanoemulsion has good compatibility with different types of fracturing fluid and is beneficial for improving the flowback rate.

1. INTRODUCTION

As the global demand for oil and gas increases, developers strive to maximize the production through more advanced technologies, such as horizontal well and high-temperature well drilling, whereas more and more technologies are being applied to the exploitation of unconventional oil and gas resources. Unconventional natural gas resources have played an increasingly important role in the current energy supply. At present, unconventional natural gas production accounts for more than 43% of the current energy supply in the United States, whereas tight sandstone natural gas accounts for approximately 70% of unconventional production, and most of the reserves are not developed.1,2 In the process of the hydraulic fracturing of tight oil and gas reservoirs, a large amount of water is pumped into the formation, and only 5−50% of the water can flow back.3−6 Most of the water will remain in the fractures and tight reservoirs formed after fracturing, and the water remaining in the fracture network will reduce the fracture conductivity, whereas the invasion of water in the reservoir matrix will cause “water locking damage” and decrease the flow of hydrocarbons.8,9 In order to improve the flowback rate in the process of fracturing, new chemical agents need to be added to the fracturing fluid to reduce “water locking damage”. From fracturing to the completion of the flowback, the formation of “water locking damage” in the whole process can be divided into the following two stages.

(1) It is a common phenomenon that the initial water saturation $S_{wi}$ is lower than the irreducible water saturation $S_{water}$ in the tight sandstone reservoir. At this time, the reservoir is in the state of ultralow water cut, and there is excess capillary pressure in the reservoir. The external fluid is easily sucked into the pores when in contact with the reservoir. The injected fluid in the process of fracturing will penetrate into the formation and reduce the relative permeability of the invading gas, and the gas permeability near the fracture is reduced to 0.

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mD. It can be known from the capillary force, Formula 1, that when the surface tension $\sigma$ of the inflow fluid and the gas phase is reduced and the triphase contact angle $\theta$ of the rock/inflow fluid/gas is close to 90°, the initial excess capillary force can be reduced, thus reducing the initial self-priming water volume and the "water locking damage".17,12

$$P_{cap} = \frac{2\sigma \cos \theta}{r}$$

(1)

In the formula, $P_{cap}$—capillary force, $\sigma$—surface tension of inflow fluid and gas phase, $\theta$—trihphase contact angle of rock/inflow fluid/gas, $r$—capillary radius. (2) After the completion of fracturing, the untimely flowback of the fracturing fluid and other external fluids and the capillary resistance of the tight sandstone pore throat will cause a large amount of fracturing fluid to remain in the reservoirs and form "water locking damage". Formula 2 is the time required for discharging a liquid column of length $L$ from a capillary of radius $r$.

$$t = \frac{4\mu L^2}{Pr^2 - 2\sigma \cos \theta}$$

(2)

In the formula, $r$—capillary radius, $L$—liquid column length, $P$—drive pressure, $\mu$—viscosity of the external fluid, $\sigma$—surface tension of the inflow fluid and gas phase, and $\theta$—trihphase contact angle of rock/inflow fluid/gas. It can be seen that the smaller the capillary radius $r$ is, the longer the drainage time will be. With the flowback processing, the liquid is gradually discharged from the large to small capillary, and the discharge speed decreases afterward. The tight gas reservoir has a small throat radius, obvious pore tortuosity, tremendous specific surface area, outstanding liquid adsorption capacity, and extremely difficult drainage, and it is difficult to effectively remove the water phase trap damage, which is serious.13–16

Therefore, according to the capillary force formula, the lower the gas—liquid surface tension is, the smaller the resistance of the liquid into the reservoir will be, which is conducive to the liquid flowing into the deep part of the gas reservoirs and releasing the nanoemulsion in the solution to achieve the deep improvement effect. Therefore, it is particularly important whether the nanoemulsion can reduce the surface tension of the injected liquid. As shown in Figure 1.

Because of the high price and environmental protection problems of fluorocarbon surfactants, they have not been widely promoted and applied, and they are still in the stage of indoor experiments. Therefore, it is particularly necessary to develop and apply nonfluorocarbon nanosurfactants for tight sandstone gas reservoirs. In this study, a set of systematic evaluation methods was established in the laboratory to evaluate the mechanism and effect of removal of water locking additive in tight sandstone gas reservoirs. The environmentally friendly removal of water locking damage nanoemulsion CNDAD1# was synthesized by the nanodispersion emulsion method, and then the basic physical and chemical properties of the nanoemulsion were evaluated, including surface tension reduction, wettability improvement, static, dynamic, and microscopic adsorption properties, and so forth. In order to clarify "water locking damage" reduced by a nanoemulsion in reservoir rocks, the influence of different permeability core wettabilities on a self-priming amount was studied through the core spontaneous imbibition experiment. Finally, the nanoemulsion is mixed with the slick water and the guar fracturing fluid to determine the compounding performance of the additive and the ability to reduce the "water locking damage".

2. RESULTS AND DISCUSSIONS

2.1. Surface Tension Test. In the process of hydraulic fracturing of tight sandstone gas reservoirs, when the external liquid is in the initial contact with the reservoir rocks, the nanoemulsion in the solution is not completely adsorbed on the rock surface. Therefore, according to the capillary force formula, the lower the gas—liquid surface tension is, the smaller the resistance of the liquid into the reservoir will be, which is conducive to the fluid flowing into the deep part of the gas reservoirs and releasing the nanoemulsion in the solution to achieve the deep improvement effect. Therefore, it is particularly important whether the nanoemulsion can reduce the surface tension of the injected liquid. As shown in Figure 1.

![Figure 1](https://dx.doi.org/10.1021/acsomega.9b03744)

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when no chemical agent was added to the distilled water, the surface tension of "air—water" measured in the laboratory is 72.71 mN/m. When the concentration of the nanoemulsion in the solution increases from 0.05 to 0.5 wt %, the surface tension of "air—water" decreases from 31.08 to 28.14 mN/m, which is not a significant decrease. But compared with water, when the concentration is 0.05 wt %, the surface tension of the solution decreases by 43.67 mN/m, which significantly reduces the "air—water" surface tension.

2.2. Static Contact Angle Measurements. From the above experimental results, the liquid containing the nanoemulsion will preferentially enter the reservoir, but the efficient
flowback of the external fluid after the completion of the fracturing is also one of the factors to evaluate the low damage of the external fluid to the reservoir. In the process of the flowback of the fracturing fluid, the gas in the gas reservoirs displaced the liquid in the reservoir into the fracture and the wellbore, and changed the water phase wettability on the rock surface into a nonwetting phase, which is not only conducive to stripping the water phase off the rock surface, but also changed the capillary force during the gas driving water phase into power. In order to clarify the influence of the amount of nanoemulsion on the wettability of the reservoir rocks, the wettability reversal effect and the optimal amount of the chemical agent on the solid surface were determined. After the same soaking time of 24 H, the “air−water” contact angle of the rock surface after soaking in different concentrations of nanoemulsion was measured. As shown in Figure 2, the “air−water” contact angle of the solid phase surface without the nanoemulsion is 38.5°, whereas with the increase of the nanoemulsion, the “air−water” contact angle of the rock surface increased to 112.9°, indicating that the water phase completely changed from the wetting phase to the nonwetting phase in the solid phase. Therefore, the nanoemulsion of 0.5 wt % concentration is the optimal amount.

Figure 3 shows the air−water static contact angle measured after soaking of the rock slice in the 0.5 wt % nanoemulsion for different time periods. The measurement time was 0, 6, 12, 24, 48 H, respectively, corresponding to the average contact angle of 38.5, 95.3, 104.4, 112.9, and 126.0°. According to the experimental results, with the increase of the soaking time, the contact angle of air−water on the sandstone surface increases gradually. When the immersion time is 6 H, the average contact angle changes the most, from 38.5° at the initial time to 95.3° with the increase of 56.8°, the water phase changes to the nonwetting phase; with the increase of soaking time, the contact angular variation gradually decreases, indicating that the adsorption amount of the chemical agent on the sandstone surface gradually reaches the dynamic equilibrium.

2.3. Macrosopic Adsorption Experiments. Based on the above studies, it can be known that the nanoemulsion solution and the gas phase have lower surface tension and can preferentially enter the deep part of the reservoir, and change the rock water phase wettability into a nonwetting phase. However, the adsorption capacity of the nanoemulsion on the rock surface is the key to determine whether nanoemulsion can enter the deep part of the reservoir and play a role. The following two studies were conducted to study the static and dynamic adsorption capacity of the nanoemulsion on the surface of the reservoir rock and different clay minerals.

2.3.1. Static Adsorption Experiment. Wang et al. studied the static adsorption performance of the DB105X well rock powder with different meshes on the 0.5 wt % CNDAD1# nanosolution, and found that the larger the mesh of the rock powder is, the stronger the adsorption performance of chemical agents will be.25 Also, the signal of the chemical agent decreased the most in the initial 20 min, and basically tends to a balance at 60 min. In addition to quartz sand, the tight sandstone reservoir rocks also contain other kinds of clay minerals, which are the main adsorbing substances of chemical agents. Therefore, it is necessary to further study the adsorption strength of different kinds of clay minerals on chemical agents.

Figure 4 shows the results of static adsorption experiments of different types of clay minerals and solid phase particles with a 100/120 mesh on nanoemulsions. According to the experimental results, most of the clay minerals and solid phase particles have the highest adsorption capacity when the nanoemulsion is statically adsorbed at 20 min, and reach the adsorption equilibrium at 60 min. The adsorption capacity of different substances to nanoemulsions is from strong to weak in the order montmorillonite, kaolinite, DB105X well rock powder, quartz sand, illite, chlorite, and ceramsite proppant. It was measured by a spectrophotometer that the signal strength of the solution after immersion in the ceramsite proppant did not change with the increase of soaking time. The results showed that the adsorption amount of ceramsite proppant to the nanoemulsion is small, which was conducive to the imbibition of more effective components of the nanosolution.

Figure 2. Static contact angle measurement of a core soaked in different concentrations of nanoluid (“air−water” contact angle, soaked for 24 H).

Figure 3. Relation curve between soaking time of the rock in a chemical agent and the contact angle.

Figure 4. Signal strength curve of the nanosolution with time after immersion in different clay minerals.
into the formation after fracturing and the interaction with reservoir rocks. The adsorption capacity of nanoemulsions on different mineral surfaces is different, which is related to mineral composition and surface morphology, including monolayer adsorption and multilayer adsorption.

According to the results, if the content of montmorillonite and kaolinite in the rocks is high, the adsorption amount of the nanoemulsion is large, and the effect of the deep part of the nanosolution is weakened. The content of quartz sand in DB105X rock powder is 68.8%, and the adsorption amount of the nanoemulsion is relatively small, which is conducive to the nanosolution to have more effective content into the deep part of the formation. The combined effect of different mineral compositions in the reservoir rocks ensures the nanoemulsion absorbed on their surface and has a deep effect.

2.3.2. Dynamic Adsorption Experiment. Different from the static adsorption experiment of the nanoemulsion, the dynamic adsorption experiment is mainly to evaluate the dynamic adsorption capacity of the nanoemulsion during deep migration. When the nanoemulsion is injected into the formation together with the fracturing fluid for reservoir stimulation, the nanoemulsion will adsorb on the rock surface, and the concentration of the nanoemulsion will decrease, corresponding to the surface tension change of the outlet production fluid. The initial concentration of the solution was 0.5 wt % CNDAD1# nanosolution, the corresponding surface tension was 28.14 mN/m, and the surface tension of 2 wt % KCl brine solution was 69.82 mN/m. Figure 5 shows the relationship between the surface tension of different types of solid phase particles and the injected PV number. It can be seen from the diagram that when injected into 6 PV, the surface tension of the outlet liquid of montmorillonite and kaolinite still has a decreasing trend, whereas that of other solid phase particles tends to be stable when injected into 3 PV. Therefore, the more components of montmorillonite and kaolinite there are in the reservoirs, the less effective the content of the injected liquid will be deep in the reservoir.

2.4. Microscopic Adsorption Experiment. The microscopic effects of nanoemulsions on the surface of different types of solid phase particles are studied below to further explain the wettability improvement mechanism of nanoemulsions. The change of surface morphology can be observed by SEM imaging technology. Figure 6a–d is the SEM scans of the surface of the main clay minerals and rock powder in the reservoir rocks before the nanoemulsion treatment. Compared with the change of surface morphology before and after the treatment shown in Figure 7a–d, it can be known that after the nano-emulsion treatment, the surface roughness of different types of solid phase particles increased, and the surface roughness of montmorillonite and DX105X rock powder changed the most. Gahrooei and Ghazanfari believe that the gas-wetting reversal agent achieves a hydrophobic effect mainly by adsorbing on the surface of the solid phase, increasing its roughness and reducing the free energy of the solid surface.

Therefore, after adsorbing on the surface of different types of solid phase particles, the nanoemulsion can change the roughness of the solid phase surface and reduce the free energy of the solid phase surface material to achieve the effect of wettability change.

2.5. Influence of Nanoemulsion on the Spontaneous Imbibition of Reservoir Rocks. From Section 2.1–2.4, it is known that the nanoemulsion preferentially enters the reservoir by reducing the gas/liquid surface tension, and adsorbs on the rock surface to change the rock wettability of rock surface to a non-water-wetting phase. The following rock spontaneous imbibition experiment is used to study the influence of the change of rock surface wettability on water absorption volume. In this experiment, the DB105X well core was selected with permeability distributed in three ranges (gas permeability $K_g \leq 0.1 \text{ mD}$, $0.1 \text{ mD} < K_g \leq 5.0 \text{ mD}$, $5.0 \text{ mD} < K_g \leq 1.0 \text{ D}$). The core was 2.5 cm in diameter and 1.5–2.0 cm in length. The core surface was treated with different concentrations of nanosolutions to obtain different wettability cores distributed in different permeability ranges. Figures 8–10 shows the corresponding spontaneous imbibition amount relation curves when the core wettability of different gas permeabilities changes.

As shown in Figure 8a, b, when the core gas permeability is $K_g \leq 0.1 \text{ mD}$, the correlation coefficients $R^2$ obtained by the fitting curve are 0.4021 and 0.5421, respectively. It indicates that when $K_g < 0.1 \text{ mD}$, the core self-priming amount is affected by both the gas permeability and the wetting angle. However, the wettability correlation coefficient is higher than the permeability, so in this range, the influence of wettability...
on the imbibition quantity is greater than permeability. According to the results, the larger the “air–water” wetting angle is, the smaller the imbibition quantity will be; the lower the permeability is, the larger the imbibition quantity will be.

As shown in Figure 9a,b, when the core gas permeability is \( 0.1 \text{ mD} < K_g < 5.0 \text{ mD} \), the correlation coefficients \( R^2 \) obtained by the fitting curve are 0.5619 and 0.5832, respectively. It indicates that when \( 0.1 \text{ mD} < K_g < 5.0 \text{ mD} \), the core self-priming amount is affected by both the gas permeability and the wetting angle and the difference between them is small. According to the results, the larger the “air–water” wetting angle is, the smaller the imbibition quantity will be; the lower the permeability is, the larger the imbibition quantity will be.

As shown in Figure 10a,b, when the core gas permeability is \( 5.0 \text{ mD} < K_g < 1.0 \text{ D} \), the correlation coefficients \( R^2 \) obtained by the fitting formula are 0.8549 and 0.1086, respectively. As the correlation coefficient between core imbibition quantity and permeability is much higher than that of wettability, it indicates that the core imbibition quantity is mainly affected by gas permeability when \( 0.1 \text{ mD} < K_g < 5.0 \text{ mD} \), whereas the wetting angle has relatively less influence on imbibition quantity. Similarly, the larger the “air–water” wetting angle is, the smaller the imbibition quantity will be; the lower the permeability is, the larger the imbibition quantity will be.

Analysis of the above three cases shows that when the gas permeability of reservoir rock is \( K_g \leq 0.1 \text{ mD} \) and \( 0.1 \text{ mD} < K_g < 5.0 \text{ mD} \), adding nanofluid to the working fluid to change the
wettability of the reservoir rock can effectively reduce the imbibition and retention of external fluid in the reservoir rock, thus reducing "water locking damage". When the gas permeability of the reservoir rock is 5.0 mD < \( K \leq 1.0 \) D, the effect of reducing the "water locking damage" by changing the reservoir wettability will be reduced.

2.6. Study on Compatibility of the Nanoemulsion with Different Working Fluids. The interaction mechanism between the nanoemulsion, gas, and reservoir rock as well as the effect of reducing the imbibition quantity of the reservoir rock were studied above. However, in the practical application of the nanoemulsion, it is often used in combination with slick water, guar gum fracturing fluid, and other working fluids. Therefore, it is necessary to study the compatibility between nanoemulsions and different working fluids. The compatibility of the nanoemulsion with slick water, guar gum fracturing fluid, and other working fluids was studied.

2.6.1. Study on Compatibility of Nanoemulsion and Slickwater Fracturing Fluid. The main performance indexes of the slick water fracturing fluid include solution surface tension, kinematic viscosity, drag reduction rate, and residual liquid flowback rate after fracturing. The surface tension of the slick water solution was prepared by using 0.05 wt % DR800 drag reducing agent to be 53.43 mN/m, the surface tension of the solution was reduced to 32.88 mN/m after adding a 0.5 wt % nanofluid into the mix with the slick water solution, indicating that the nanofluid has the effect of reducing the surface tension of the slick water, and the lower capillary force is conducive for the flowback of the slick water after the completion of fracturing. Before and after the addition of the nanofluid, the kinematic viscosity of the slick water fracturing fluid was 1.383 and 1.331 mm²/s, respectively, and the difference between the two was not significant, and the kinematic viscosity of the slick water was not affected.

The drag reduction rate of different concentrations of nanoemulsions was measured by the loop method. The result is shown in Figure 11. According to the test results, when the}

![Figure 11. Experimental results of drag reduction rate after the compatibility of slick water and different concentrations of the nano-emulsion.](image)

nanoelemulsion is added to the slick water solution at a relatively high flow rate, the difference is small. When the linear flow rate is lower than 3 m/s, the nanoelemulsion is conducive to improving the drag reduction rate of the slip water solution, reducing the frictional energy consumption in the process of fracturing, and improving the fracturing effect. Figure 12 shows the experimental results of the flowback rate of the sand filling pipe after the compatibility of slick water and different concentrations of the nanoelemulsion. The sand filling pipe is uniformly filled with 100/120 mesh quartz sand with a length of 50 cm, and the permeability of the four groups of sand filling pipe is about 1 D, which is used to simulate the flowback rate of slick water in the fracture with high conductivity formed after fracturing. According to the results, with the increase of the concentration of the nanoelemulsion in the slick water, the flowback rate of the slick water in the sand filling tube gradually increases. When the concentration of the nanoelemulsion is 0.5 wt %, the flowback rate of the slick water can be increased by more than 15%. Therefore, the mixing of the nanoelemulsion with the slick water fracturing fluid can not only improve the performance parameters of the slick water, but also improve the flowback after fracturing and reduce the "water locking damage" of the reservoir.

2.6.2. Study on Compatibility of the Nanoemulsion and the Guar Fracturing Fluid. The main performance indexes of the guar fracturing fluid include shear resistance, gel breaking performance, residue content, surface tension, viscosity, and flowback rate of the gel breaking fluid. In this study, a high-temperature-resistant guar fracturing fluid formula was adopted: 0.5 wt % guar gum +0.3% wt YC-150 stabilizer +0.4 wt % YP-150 cross-linker +0.1 wt % gel breaker. Different concentrations of the nanoelemulsion were added to the fracturing fluid, and the relevant properties of the guar gum fracturing fluid before and after the addition were tested.

Different concentrations of the nanoelemulsion were mixed with the guar fracturing fluid and put into a beaker, and then the beaker was placed in an 80 °C water bath. After 4 H, all the guar fracturing fluids with different concentrations of the nanoelemulsion were broken. The concentration of CNDAD1# was 0.0, 0.10, 0.25, and 0.50 wt %, respectively; the corresponding residue content of the guar fracturing fluid was 0.01407, 0.01199, 0.01105, and 0.01155 wt %; the kinematic viscosity was 1.053, 1.008, 0.988, 0.937 mm²/s; surface tension was 31.97, 31.83, 31.42, 30.93 mN/m. Under the action of the nanoelemulsion, the guar fracturing fluid is more thoroughly broken, which has the effect of reducing the residue content of the guar fracturing fluid. At the same time, the nanoelemulsion also has the effect of reducing the kinematic viscosity and surface tension of the gel breaking fluid.

Figure 13 shows the shear resistance of the guar fracturing fluid under different concentrations of the nanoelemulsion. According to the results, when the concentration of the nanoelemulsion in the guar gum fracturing fluid is different, shearing at 170 S⁻¹, 150 °C for 60 min, the viscosity of the fracturing fluid remains above 100 mPa.s, and the nanoelemulsion does not affect the shear resistance of the guar fracturing fluid. Figure 14 shows the results of the flowback rate of the sand
filling pipe after the compatibility of the guar fracturing fluid and the different concentrations of the nanoemulsion. With the increase of the concentration of the nano-emulsion in the gel-breaking fracturing fluid, the flowback rate of the gel-breaking fluid in the sand filling pipe gradually increased, and when the concentration of the nanoemulsion is 0.5 wt %, the flowback rate of the gel breaking fluid can reach more than 16%.

According to the experimental study on the compatibility of the nanoemulsion and different working fluids, it can be known that the original properties of the solution will not be changed when the nano-emulsion is mixed with the slick water and the guar fracturing fluid. The experiment of the sand filling tube shows that the nanoemulsion can effectively reduce the surface tension of the solution. At the same time, combining with the results of the wetting reversal experiment, it can be known that the nanoemulsion in the flowback liquid adsorbed on the surface of the sandstone and improved the flowback efficiency of the working fluid by changing the wettability of the solid phase medium and reducing the capillary resistance of the gas phase displacement liquid, and so forth.

3. CONCLUSIONS

During hydraulic fracture of tight sandstone reservoirs, a large amount of water is filtered to the formation, and nanoemulsion CNDAD1# can be added as an additive into the fracturing fluid to alleviate the “water locking damage” caused by the invasion of external water. The nanofluid synthesized by the microemulsion method has a particle size as low as 160 nm, which solves the injectivity problem of chemical agents in tight sandstone reservoirs. The main conclusions are as follows:

(1) The nanoemulsion has an effect of reducing the surface tension of the solution and changing the surface wettability of the solid phase particles. The surface tension of the gas—liquid of 0.5 wt % nanosolution is as low as 28.14 mN/m, and the contact angle of the water surface of the rock surface can be changed to 126.0°.

(2) Static and dynamic adsorption experiments show that the adsorption of nanoemulsion on the surface of solid phase particles is from strong to weak in order to be montmorillonite, kaolinite, DB105X well rock powder, quartz sand, illite, chlorite, and ceramic propellant. The static adsorption has the fastest adsorption speed in the initial 20 min and tends to balance in about 60 min; montmorillonite and kaolinite still did not reach the dynamic adsorption equilibrium when injected at 6 PV, whereas other solid phase particles reached dynamic adsorption equilibrium when injected at 3 PV.

(3) Experiments on the influence of wettability and permeability on the spontaneous imbibition of rock show that when the gas permeability of the reservoir rock is $K_g < 5.0 \text{ mD}$, adding nanoemulsion into the working fluid to change the wettability of the reservoir rock can effectively reduce the imbibition and retention of external fluid in reservoir rock, thus reducing “water locking damage”. While the gas permeability of reservoir rock is $5.0 \text{ mD} < K_g \leq 1.0 \text{ D}$, the effect of preventing “water locking damage” will be reduced by changing the wettability of the reservoirs.

(4) According to the experimental study on the compatibility between nanoemulsion and different working fluids, it can be known that the original properties of the solution will not be changed when the nanoemulsion is mixed with the slick water and the guar fracturing fluid. The experiment of the sand filling tube shows that the nanoemulsion can improve the flowback rate of the slick water and the working fluid after fracturing. Therefore, in the actual fracturing operation, the nanoemulsion can be added into the fracturing fluid to improve the flowback rate of the low-permeability reservoir fracturing fluid, so as to reduce the invasion damage of the external fluid to the reservoir.

4. EXPERIMENT DISCUSSIONS

4.1. Experimental Material and Equipment. 4.1.1. Synthesis Method of Waterproof Lock nanoemulsion CNDAD1#. The nanoemulsion CNDAD1# was synthesized by the nanodispersion emulsion method in the laboratory, mainly composed of water phase, oil phase, and surfactant. The selected nanofluid (CNDAD1#) is formed by a dilute suspension of nanoscale oil droplets (i.e., nanomicelles) in brine. CNDAD1# consists of approximately 10 wt % alkane and/or olein as the oil core of the micelle, 30–50 wt % nonionic surfactant (e.g., alcohol ethoxylate) to stabilize the micelle, and 20–40 wt % alcohol as the cosolvent. To prepare the CNDAD1# auxiliary fracturing fluid, the stock solution was diluted to 0.00–0.50 wt % and mixed with 2 wt % KCl in distilled water. As CNDAD1# is a microemulsion, it has long-term stability at room temperature. This method is conducive to fluid preparation and transportation. The synthesis method is shown in Figure 15.

The Zetasizer Nanolaser nanoparticle size analyzer is used to measure its particle size and the results are shown in Figure 16. The two measured nanoparticle sizes were 160.8 and 160.9 nm, respectively. Because of the small pore throat size of the
tight sandstone reservoir, the gas wetting chemical agent has nanometer size and is one of the prerequisites for achieving its injectability.

4.1.2. Core & Clay Mineral Sample Preparation. The core of the experiment was taken from the natural core of the DB105X well in Tarim Oilfield at the depth of 4762.79 m. The mineral composition obtained through X-ray diffraction (XRD) mineral analysis is shown in Table 1, which belongs to the sandstone core. Then, the natural core was washed with a Soxhlet extractor and dried in an oven at 80°C for 48 H for the next experiment. Different types of clay minerals (montmorillonite, kaolinite, quartz sand, illite, chlorite) with a mesh number of 100/120 mesh were selected for the adsorption performance test.

Table 1. DB105X Well Core XRD Mineral Composition

| types of minerals | quartz | albite | titanomagnetite | illite | chlorite |
|-------------------|--------|--------|-----------------|--------|----------|
| mol %             | 68.80  | 10.10  | 3.20            | 8.60   | 9.30     |

to the sandstone core. Then, the natural core was washed with a Soxhlet extractor and dried in an oven at 80 °C for 48 H for the next experiment. Different types of clay minerals (montmorillonite, kaolinite, quartz sand, illite, chlorite) with a mesh number of 100/120 mesh were selected for the adsorption performance test.

The experiments mainly include the particle size measurement of the CNDAD1# nanosolution, the effect evaluation of the nanoagent on reducing the solution surface tension and wetting revise, the macro- and microadsorption performance evaluation of the nanoemulsion on the clay mineral surface, core spontaneous imbibition experiment, the compatibility test of the nanofluid and different working fluids, and so forth. The main experimental equipment includes a UK Zetasizer Nanolaser nanometer particle size analyzer, Japan XRD-6000 X-ray diffractometer, China JYW-200A automatic table interface tension meter, China JY-PHb contact angle tester, China LS UV–visible spectrophotometer, spontaneous imbibition experimental device, sand filling tube, and so forth. The experimental process is shown in Figure 17, drawn by the first author Jie Wang.

4.2. Mainly Experimental Section. 4.2.1. Surface Tension Test. First, distilled water and alcohol were used to calibrate interface tension meter; then, CNDAD1# nanosolutions of different concentrations were prepared, and the surface tension between the solution and air is tested by the lifting ring method five times for each concentration, and then the arithmetic mean value was taken.

4.2.2. Static Contact Angle Measurements. The dry rock pieces were placed on the stage of the contact angle tester, and 10 μL of 2 wt % KCL brine solution was dropped onto the surface with a micropipette. The droplet image was taken with a digital microscope, and the contact angle of “air–brine” was measured and calculated by the analysis software; then, the rock was dried in an 80 °C oven for 24 H, and the rock pieces were placed in different concentrations of the CNDAD1# nanosolution. After soaking at room temperature, the rock pieces were taken out in different time periods and dried in an 80 °C oven for 24 H. The same method was used to test the wetting angle of the dried rock pieces after the chemical treatment.

4.2.3. Macroscopic Adsorption Experiments. First, the optimal wavelength of the CNDAD1# nanosolution was determined by a spectrophotometer and it was set as the test wavelength of the static adsorption experiment. Wang et al. found that the optimal wavelength of the CNDAD1# nanosolution is 213.4 nm, corresponding to the signal strength of 3.771 A (as shown in Figure 18) and obtained the standard concentration measurement curve of the CNDAD1# nanosolution, as shown in Figure 19.²³

4.2.3.1. Static Adsorption Experiment. In addition to quartz sand, the tight sandstone reservoir rocks also contain montmorillonite, illite, kaolinite, chlorite and other ingredients. In order to study whether there are differences between different components on the adsorption properties of nanoemulsion, different types of clay minerals with the same mesh number (100/120) were selected, respectively, and the signal strength of the nanosolutions after the immersion of different clay minerals was tested to determine the adsorption capacity of different clay minerals on the nanoemulsion, whereas the...
fluid passed through the ceramsite proppant during fracturing. Therefore, the adsorption performance of the proppant surface also needs to be considered. The main experimental steps are as follows: weigh respectively six parts of 1 g of 100/120 mesh, different kinds of clay minerals, and solid particles (including DB105X well reservoir rock powder, pure quartz sand, ceramsite proppant, montmorillonite, illite, kaolinite, chlorite) into a beaker; weigh 20 g of 0.5 wt % CNDAD1# nanosolution and pour it into another beaker; soak them for different time periods at room temperature and make the centrifuge rotate for 30 min under 3000 rpm to separate the solid phase and the liquid; take the supernatant liquid to measure the spectrophotometric values of 20, 40, 60 min, 3, 6, and 24 h. The spectrophotometric curves of different numbers of rock powders at different times were drawn. The adsorption speed and strength of nano-emulsion on different components were determined by spectrophotometric values.

4.2.3.2. Dynamic Adsorption Experiment. For a 100/120 mesh, different kinds of clay minerals and proppant were uniformly mixed according to 3:7, and then filled in different sand filling glass tubes. As the nanosolution adsorbed on the mineral surface after flowing through the sand filling tube, the surface tension of the outflow liquid changed. By testing the surface tension value of the 0.5 wt % CNDAD1# nanosolution before and after flowing through the sand filling tube, the adsorption strength of different clay minerals on the nanosuspension was determined. At the same time, the surface tension values of 1 PV, 2 PV, 3 PV, 4 PV, 5 PV, and 6 PV outflow solutions were measured to determine the number of injected PV when the clay mineral reached the dynamic adsorption equilibrium.

4.2.4. Microscopic Adsorption Experiment. SEM imaging technique was used to characterize the surface characteristics of clay minerals before and after CNDAD1# treatment. Different types of clay minerals were first washed with 2 wt % KCl brine and dried at 80 °C for 24 h, then washed with ethanol and dried again. The cleaned rock powder was soaked in 0.5 wt % CNDAD1# nanosolution for aging for 2 days at room temperature, and the solid phase and liquid were separated by rotating under 3000 rpm for 30 min in a centrifuge, the supernatant was poured out, and the solid phase powder was put into an oven at 80 °C for 24 h for drying, and then the solid phase powder was coated on the sampler for SEM testing.

4.2.5. Spontaneous Imbibition Experiment. The imbibition quantity of core samples is affected by multiple factors such as core permeability, wettability, lithology, and temperature. However, for a fixed reservoir, the lithology and temperature are basically similar. Therefore, the changes of reservoir heterogeneity and surface wettability are the main factors leading to the great differences in core imbibition quantity. In order to study the influence of permeability and wettability on the spontaneous imbibition of the core, different permeability cores were selected and treated with nanomulsions of different concentrations to obtain cores with different wettabilities for experimental studies on spontaneous permeability of the core. The main test indexes include the imbibition quantity of brine into the saturated air in the dry core.

4.2.6. Compatibility of the Nanoemulsion with Different Working Fluids. In the process of hydraulic fracturing, the retention of the flowback fluid in the reservoirs after the completion of fracturing is one of the main reasons for the formation of external fluid “water locking damage”. Whether the mixture of nanoemulsion and fracturing fluid can reduce the “water locking damage” is one of the prerequisites for its commercial application. The 0.5 wt % nanoemulsion was mixed with slick water or guar fracturing fluid, and the influence of the nanoemulsion on the performance of the fracturing fluid and the improvement of flowback rate after fracturing were determined. The test indexes of mixing the nanoemulsion with slick water fracturing fluid include solution surface tension, kinematic viscosity, drag reduction rate, and residual liquid flowback rate after fracturing; the test indexes of mixing the nanoemulsion with guar fracturing fluid include shear resistance of guar fracturing fluid, gel breaking performance, residue content, surface tension of the breaker, viscosity, and flowback rate of the gel breaking fluid.

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Figure 18. Optimal wavelength measurement curve of nanosolution CNDAD1#.

Figure 19. Standard CNDAD1# concentration measurement curve.
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Notes
The authors declare no competing financial interest.

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