Evaluation of Nanoemulsion to Improve the Fracturing Fluid Flowback

Baoshan Guan[1,2,a,*], Wei Jiang[1,2,b], Ping Liu[1,2,c],

Li Liang[1,2,d], Jiang Yang[1,2,e]

[1] Research Institute of Petroleum Exploration and Development CNPC, Langfang 065007, Hebei, China ;

[2] Key Laboratory of Reservoir Stimulation , CNPC, Langfang 065007, Hebei, China ;

[a]gbs_cq@petrochina.com.cn, [b]jiangwei69@petrochina.com.cn, [c]liup69@petrochina.com.cn, [d]ll69@petrochina.com.cn, [e]jyang98@yahoo.com

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Abstract Nanoemulsion (NE) has been widely added into fracturing fluid as flowback additive to enhance fracturing fluid recovery. An environmental friendly nanoemulsion has been formulated. The particle size distribution of the nanoemulsion has been determined. The surface tension and contact angle of the nanoemulsion and commercial flowback additives have also been studied. The new nanoemulsion has lower surface tension and higher contact angle than commercial flowback additives. Two flowback recovery test apparatuses have been constructed, and fluid flowback recovery and gas-fluid flowback recovery experiments have been conducted. The new nanoemulsion gives higher fluid and gas-fluid recovery than that of conventional flowback additives.

Introduction

Nanoemulsion (NE) is a thermodynamically stable combination of surfactant, co-surfactant, oil and water, which on the microscopic level consist of individual domains of oil and water separated by a monolayer of amphiphile [1-6]. NE appears as a single, optically clear phase. NE's particle size varies from 10 nanometers to 200 nanometers. NE has been widely used in oil field as cleanup additives which is added into fracturing fluid to improve the fracturing fluid flowback after fracturing work and has reaped huge success. NE is capable of reducing capillary pressure from reducing surface tension and increasing contact angle [7-14], in the meantime, NE can penetrate deeper into the formation to eliminate the "phase trapping". Thus, fracturing fluid can flowback "easier" and more efficient, in this way, the regained permeability to gas is increased [15-21].

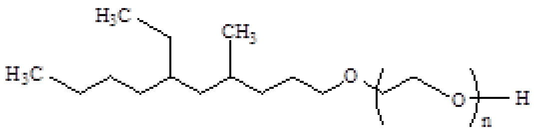
We hereby study nanoemulsion and their physical chemical properties. Two flowback recovery test apparatuses have been constructed, sand packed column with saturated test fluid driven by fluid gravity and sand packed column with saturated test fluid driven with nitrogen gas. The first test apparatus is used to evaluate the fluid flowback recovery and the second test apparatus is used to evaluate the gas-fluid flowback recovery.

Experiments

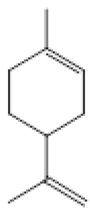
Material

D-limonene as the oil phase was purchased from Jiangsu Rich Native Animal Products CO., LTD; Nonionic surfactants, isotridecanol ethoxylate (i-C13EOn, n=3, 6, 10) was supplied by Huntsman Corporation-Hatc Labs. The structure of surfactant and oil is shown in scheme 1. Isopropyl alcohol (IPA) which as co-surfactant was bought from Beijing Shiying chemical plant, and the water was tap water. All the reagents were in analytical reagent grade and were used without future purification. Commercial flowback additives, DL-12 and F108 were obtained from Changqing oilfield Co.

i-C13EOn



D-limonene



Scheme 1 structure of surfactant and oil

Methods

The nanoemulsion was formulated by low energy emulsification methods through bicontimuous structure at room temperature. The NE particle size distribution was measured on nanosizer and zeta potential analyzer at temperature. Surface tensions were determined on the K12 at room temperature by Wilhelmy plate method. Contact angles were tested on the KRUSS DSA100 Drop Shape Analysis System.

Flowback recovery was divided into two phases to simulate the practical flowback process. At the beginning of the gas well flowback process, it is single fluid flowback. A period time after the gas well flowback process, it is gas-fluid two-phase flowback.

Fluid flowback recovery was evaluated with 25 cm long and 2.5 cm diameter column packed with 20/40 mesh sand, the sand packed column was shaken same times each time to make sue the permeability at the same level. The column was loaded with test fluid, and left undisturbed for 24 hours making the sand was saturated with test fluid thoroughly; then turn on the valve at the bottom of the sand packed column, the fluid was collected at the bottom of column by gravity as shown in Fig. 1. The fluid recovered vs. time was recorded with computer.

In the gas-fluid flowback recovery test, 25 cm long and 2.5 cm diameter column packed with 20/40 mesh sand was saturated with test fluid for 24 hours. Then turn on the valve at the bottom of the sand packed column, the fluid was collected at the top of column by nitrogen gas as shown in Fig. 2. The fluid recovered and the driving pressure vs. time was recorded with computer.

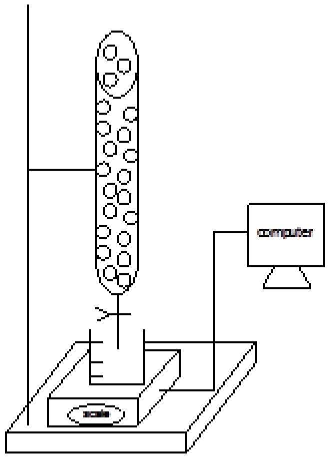


Fig. 1 Test apparatus for fluid flowback recovery

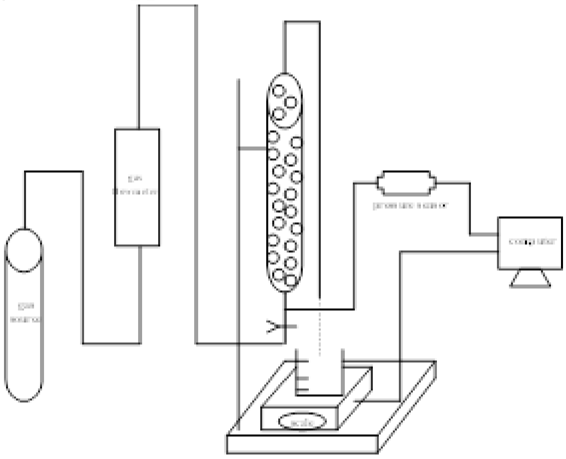


Fig. 2 Test apparatus for gas-fluid flowback recovery

Results and Discussion

Formation and Characterization of Nanoemulsion

The E1306 and isopropanol were mixed at 4/1 ratio and combined as one component. The nonionic surfactant (E1306), isopropanol, and d-limonene are miscible with each other and form one single phase. D-limonene belongs to cyclic terpene with six member ring structure. D-limonene is immiscible with water. Isopropanol was used as co-surfactant. Then the mixture was stirred on the swirl shaker for several minutes until the oil and water dispersed into each other and became one single phase. Than the sample were left undisturbed at least three days for equilibrium.

The tested NE fluid in surface tension, contact angle and flowback recovery were formulated by diluting the concentrated fluid with tap water to 0.2% active concentration.

The particle size of prepared NE varies from 10 nanometers to 100 nanometers as shown in Fig. 3, the peak size is 42.76 nanometers.

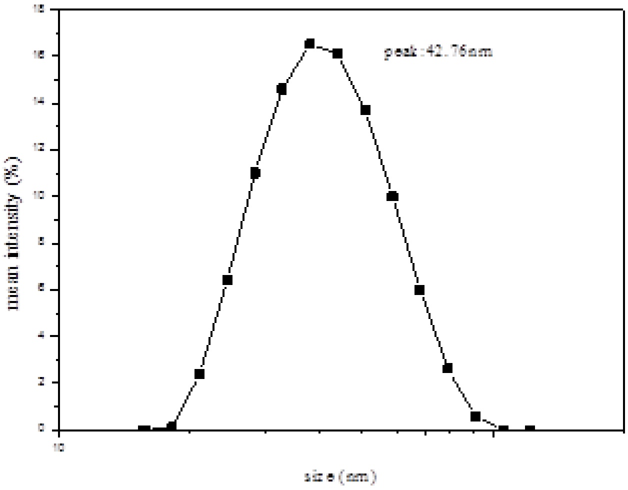


Fig. 3 Size distribution of Nanoemulsion

Physical Chemical Properties of Nanoemulsion

The surface tension and contact angle are related to capillary pressure of fluid trapped in reservoir. Capillary pressure is defined as Eq. 1 below:

$$p_c = \frac{2\sigma \cos\theta}{r} \quad (1)$$

Where σ is the fluid/gas interfacial tension in mN/m, θ is the contact angle at the rock/fluid/gas interface; r is the effective pore throat radius. When flowback the injected fracturing fluid, the capillary pressure is resistance force, as the r is very small, capillary pressure could be very high. In order to expel the formation fluid, it should overcome the capillary pressure, so low surface tension and high contact angle result low capillary pressure which is benefit to loaded fluid recovery.

The surface tension and contact angle of water, two commercial flowback additives, DL-12 and f108, NE are compared. The results are shown in Table 1.

Table 1 Surface tension and contact angle of nanoemulsion and commercial flowback additives

Fluid	Surface tension [mN/m]	Contact angle [deg]
water	73.26	40.31
DL-12	23.54	31.28
F108	27.35	27.88
NE	29.18	54.34

As it can be seen from Table 1, commercial flowback additives have relatively low surface tension and low contact angle. In order to achieve low capillary pressure as defined by equation 1, high contact angle is preferred. The nanoemulsion has the highest contact angle while surface tension is at acceptable level. As surfactant concentration in nanoemulsion increases and reaches to CMC (critical micelle concentration), surfactant begins to form micelle and surface tension decreases while contact angle maintains at relative high value below CMC. The surfactant adsorbed on solid surface as mono layer, the hydrophobic tail is extended out. Hence, hydrophilic surface become hydrophobic surface, the contact angle will be high.

Fluid recovery

The flowback recovery of flowback additives was studied. Flowback recovery was divided into two phases to simulate the practical flowback process. At the beginning of the gas well flowback process, it is single fluid flowback. A period time after the gas well flowback process, it is gas-fluid two-phase flowback.

Fluid single phase flowback recovery

Fluid flowback recovery was collected at the bottom of column by gravity. The fluid recovered vs. time was recorded with computer as shown in Fig. 4 and Table 2.

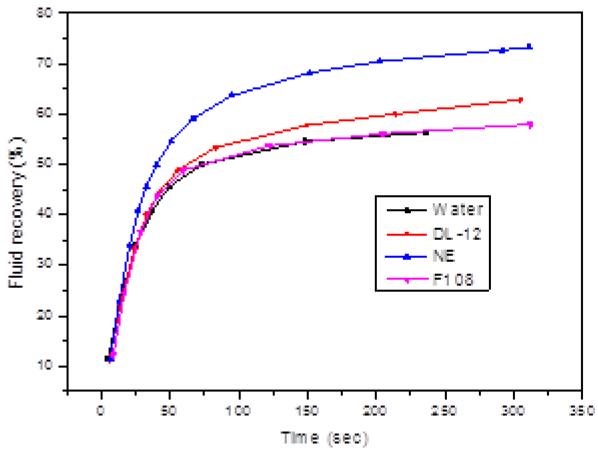


Fig. 4 Comparison of commercial and nanoemulsion flowback additives

Table 2 Comparison of commercial and nanoemulsion flowback additives

Fluid	Flowback recovery [%]
water	56.32
DL-12	62.84
F108	57.93
NE	73.25

It can be seen that NE has the highest fluid flowback recovery. DL-12 is in the middle. F108 and water have the similar low fluid recovery. NE gives the highest performance due to the higher contact and moderate surface tension. The ultralow surface tension of DL-12 and lower contact angle contributes its middle fluid flowback recovery.

Gas-fluid two-phase flowback recovery

In the gas-fluid flowback recovery test, the fluid was collected at the top of column by nitrogen gas. The fluid recovered and the driving pressure vs. time was recorded with computer as shown in Fig. 5 and Table 3.

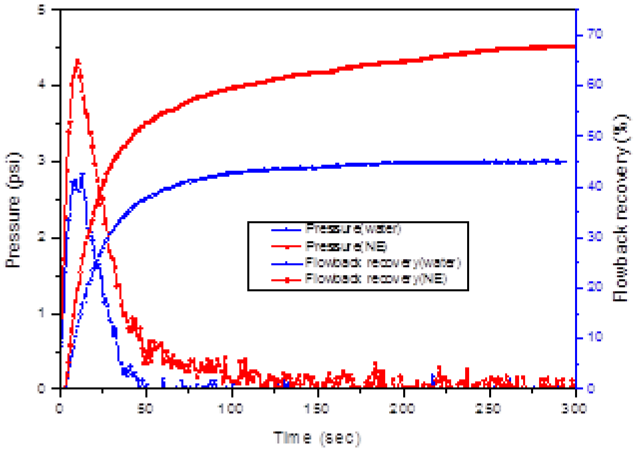


Fig. 5-1 Gas-fluid flowback recovery comparisons of Water and NE

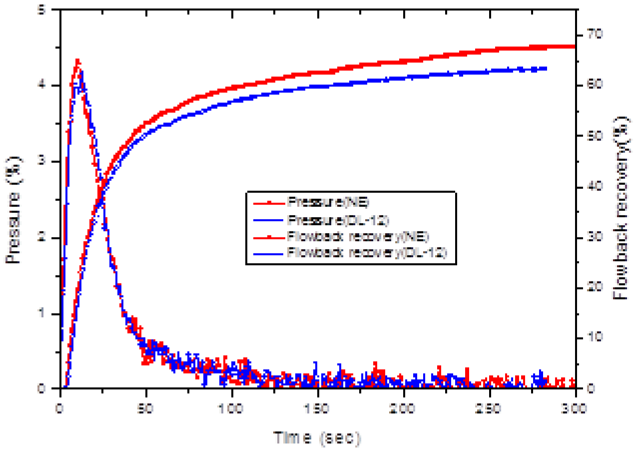


Fig. 5-2 Gas-fluid flowback recovery comparisons of Dl-12 and NE

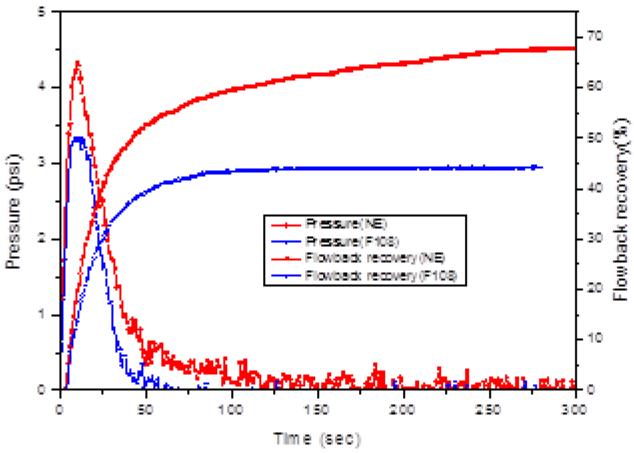


Fig. 5-3 Gas-fluid flowback recovery comparisons of F108 and NE

Fig. 5 Gas-fluid flowback recovery comparisons commercial and nanoemulsion flowback additives

Table 3 Comparison of commercial and nanoemulsion flowback additives

Fluid	Pressure [psi]	Flowback recovery [%]
water	2.84	45.00
DL-12	4.17	63.43
F108	3.34	44.23
NE	4.34	67.80

It can be seen that NE has the highest gas-fluid flowback recovery. DL-12 is in the middle. F108 and water have the similar low fluid recovery. This is consistent with the fluid recovery. In the meanwhile, NE has the highest gas-fluid driving pressure. DL-12 is in the middle. F108 and water have the similar low gas-fluid driving pressure. NE gives the highest performance due to the higher contact and moderate surface tension. The ultralow surface tension of DL-12 and lower contact angle contributes its middle gas-fluid flowback recovery. The higher the driving pressure, the higher the gas-fluid flowback recoveries are.

Conclusions

The environmental friendly d-limonene nanoemulsion was prepared from optimum formulation. The nanoemulsion has high contact angle with mono layer surfactant coverage. The formulated nanoemulsion as flowback additive gives higher fluid recovery and gas-fluid recovery than that of conventional flowback additives.

Acknowledgement

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