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RESEARCH PAPER

A high-density organoclay-free oil base drilling fluid based on supramolecular chemistry

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Abstract: Based on supramolecular chemistry, a rheology modifier CFZTQ-1 for oil base drilling fluids was developed, and an innovative high-density organoclay-free oil base drilling fluid system centering on CFZTQ-1 was designed, evaluated and applied in the field. CFZTQ-1 can strongly increase the elasticity of invert emulsion due to the supramolecular structure assembled in water phase; CFZTQ-1 has stronger effect in elevating the yield point and suspension ability than several foreign rheology modifiers; the synergistic effect with organoclay also makes CFZTQ-1 available in traditional clay-contained invert emulsion drilling fluids. Through the category and dosage optimization of related additives, the formula of the high-density organoclay-free oil base drilling fluid was established and its performance was evaluated. The organoclay-free drilling fluid owns favorable rheology with density of 2.40–2.60 g/cm^3, yield point of 13–17 Pa, moderate apparent viscosity and relative low plastic viscosity; after hot rolling at 240 °C, the drilling fluid still keeps a stable performance as its viscosity only increases slightly, its high temperature and high pressure (HTHP) filtration loss is about 10 mL and its electrical stability is greater than 400 V. This innovative drilling fluid system achieves excellent field application as well.

Key words: oil base drilling fluid; supramolecular chemistry; rheology modifier; viscoelasticity; drilling fluid performance

Introduction

Orangoclay-free oil base drilling fluid (OBF), an innovative oil base drilling fluid system, has the unique rheologic property of “fragile gel”, higher rate of penetration, stronger water-resistance, thinner filter cake and much higher permeability recovery than traditional invert emulsion drilling fluid[1–3]. Substituting rheology modifiers for organoclay, Halliburton Baroid Corporation firstly developed high-performance organoclay-free oil based mud (OBM) systems such as INNOVERT and INTEGRADE™. However, due to the limitation of the rheology modifiers in elevating suspension capability, the current organoclay-free OBF has limited weighing capacity, which makes them unsuitable for high-pressure formations. Apparently, improving gelation capacity of rheology modifiers has become the key to the development of high-density orangoclay-free OBF.

Rheology modifiers commonly used in OBFs, mostly oil-soluble polymers[4–5], have poor gelation capacity since they have limited polar group quantity, and the continuous oil phase of OBFs is an apolar environment which inhibits the gelation of these rheology modifiers. A number of researches have proven that the bulk rheology of invert emulsions can be strongly influenced by the property change of dispersed water phase, the polar space in the invert emulsion system[6]. Based on the supramolecular theory, the self-assembly of low molecular weight gelators driven by non-covalent bonds forms supramolecular structure in water, which makes the water solution turn into weak hydrogel[7–10], so the water phase can be used to modify the rheology of invert emulsion. The objective of this research is to develop a high-density organoclay-free oil base drilling fluid based on the high-performance water-soluble low molecular weight rheology modifier CFZTQ-1 and the self-assembly principle of supermolecule.

1. Mechanism of CFZTQ-1

1.1. Self-assembly of CFZTQ-1

CFZTQ-1 is a mixture of water-soluble low molecular weight compounds. The molecular structure of CFZTQ-1 is shown in Fig. 1, where R represents alkyl groups and X represents hydrophilic groups. As CFZTQ-1 has an amphiphilic structure like surfactants, it will assemble spontaneously,

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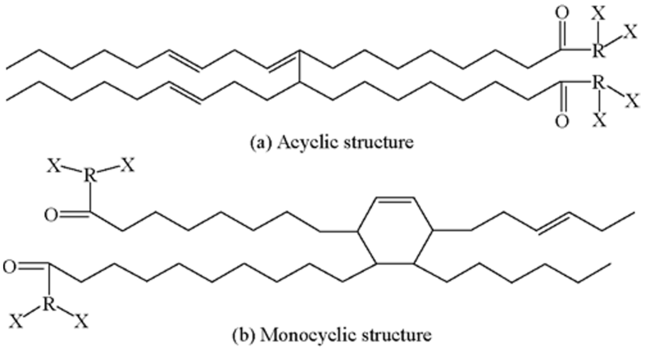

Fig. 1. Molecular structure of CFZTQ-1.

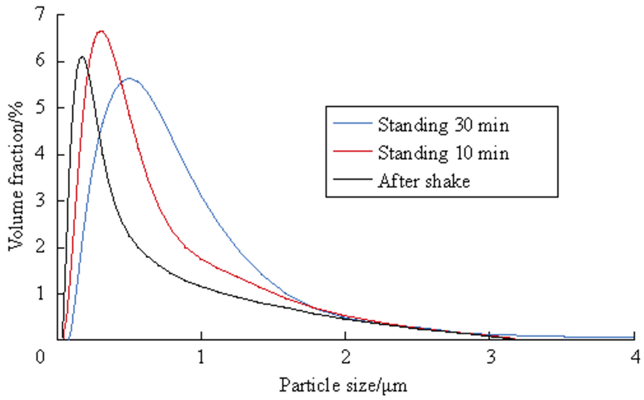

Fig. 2. Particle size distribution of CFZTQ-1 solution (1%wt).

forming micelles with a hydrophobic centre and hydrophilic heads. Particle size distribution (Fig. 2) was used to analyze the self-assembly behavior of CFZTQ-1, it can be seen from Fig. 2 that the mean particle size of CFZTQ-1 solution (1%wt) measured immediately after shaken is about 0.1 μm, at this point, the CFZTQ-1 exists in the form of primary micelle; as standing time increases, multi-grade micelle structure such as α-gel, lamellar gel or coagel, is created driven by hydrogen bonds of CFZTQ-1 hydrophilic groups and water, and the mean particle size increases as well, after standing for 30 min, the mean particle size of CFZTQ-1 solution has approached 1 μm[11].

1.2. Influence of CFZTQ-1 on stability of invert emulsion

Though amphiphilic, CFZTQ-1 does not have emulsifying ability mainly due to its obvious steric hindrance and strong hydrophilicity, rather it will disperse in the water phase of invert emulsion. CFZTQ-1 aggregates tend to adsorb near the oil-water interface because of the existence of non-covalent bonds between the hydrophilic heads of CFZTQ-1 and W/O emulsifiers. The aggregation of CFZTQ-1 at the interface of invert emulsion increases the interfacial tension and strength of interfacial film, and consequently the stability of invert emulsion.

The influence of CFZTQ-1 on the stability of invert emulsions at different water cuts has been tested. All the emulsion samples in the test were made of mineral oil, 30%wt calcium chloride solution and 4%wt sorbitane monooleate, namely Span 80. The test results are shown in Fig. 3, from which we

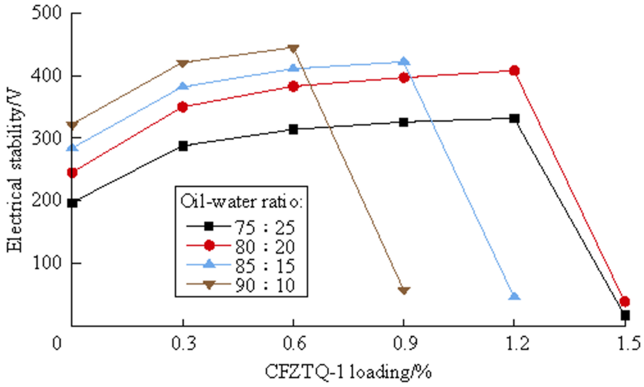

Fig. 3. Influence of CFZTQ-1 on stability of invert emulsions at different oil-water ratio.

can see low dosage of CFZTQ-1 increases the electrical stability of invert emulsions, while high dosage of CFZTQ-1 leads to demulsification. Moreover, the amount of CFZTQ-1 needed to accomplish such transition above increases as the oil-water ratio of invert emulsion decreases. Since the stability of emulsion depends on interfacial tension and strength of interfacial film, though low dosage of CFZTQ-1 increases interfacial tension slightly, the strengthening effect of CFZTQ-1 on interface will improve the stability of invert emulsions, as the interfacial tension in such case is still low enough to form stable emulsion. However, when the interfacial tension of invert emulsion increases too much due to high dosage of CFZTQ-1, demulsification happens inevitably.

1.3. Influence of CFZTQ-1 on viscoelasticity of invert emulsion

Different from suspension of solid globules, the phase interface of emulsion is flexible, floating and elastic. The elastic modulus of phase interface of emulsion E_{Gs} can be expressed as[12]

$$E_{Gs} = \left(\frac{d\sigma}{d\ln S}\right)_{\Gamma} \quad (1)$$

where σ is interfacial tension, Mpa; S is the area of phase interface, m^2; Γ is the adsorption of emulsifiers, mol/m^2.

We can see from Equation (1) that the elasticity and tension of emulsion interface is positively correlated. On the other hand, water droplets containing supramolecular structure have fragile gel property to some extent, consequently, the addition of CFZTQ-1 will increase the elasticity of invert emulsion, turning the invert emulsion from viscous fluid to viscoelastic fluid.

The influence of CFZTQ-1 on the elasticity of invert emulsion has been investigated by monitoring the change of mean square displacement (MSD) of emulsion. A microrheometer Rheolaser™ was used to evaluate the influence of CFZTQ-1 on the MSD of invert emulsion with an oil-water ratio of 80 to 20 (Fig. 4). It can be seen from Fig. 4 that the MSD of pure invert emulsion under different standing time increases continuously with the decorrelation time; however, due to the binding effect of supramolecular structure on droplets in the