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Instant gel formation of viscoelastic surfactant fracturing fluids by diluting through lamellar liquid crystal

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ABSTRACT

In application of viscoelastic surfactants (VES) as hydraulic fracturing fluids, some VES fluids take a long time to dissolve and build up viscosity in the field operation when it is diluted from concentrate. Amphoteric surfactant is studied to understand the mechanism. The phase behavior of the surfactant–solvent–water was investigated. It was found that a three phase range consisted of liquid crystal gel was passed during diluting process. It consisted of a highly viscose hexagonal liquid crystal phase, which took a long time to dissolve and formed VES gel. A cosurfactant was added to concentrate, which increases the dissolving rate. The hexagonal liquid crystal gel is transformed to soft lamellar liquid crystal gel in the present of cosurfactant. The mixed surfactants form VES gel within 1 minute. Addition of cosurfactant also increases viscosity at higher temperature.

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1. Introduction

The viscoelastic surfactant (VES) fluids have been used in stimulation of low permeability oil and gas reservoir due to their low formation damage (Yang, 2002; Li et al., 2010; Gomma et al., 2011; Fontana et al., 2007). It was used as VES foam for treating ultralow-permeability reservoirs because of its low surface tension and reducing the amount of water and surfactant used in the fracturing fluid (Cawiezel and Gupta, 2010). VES was also used as diverting agent in self-diverting acid treatment (Taylor et al., 2003; Chang et al., 2007; Wang et al., 2012).

Conventional polysaccharide polymers are widely used as stimulation fluid in oil field application. However, they are known to have insoluble residue left in formation. These insoluble materials will plug pore throats, leading to impaired leak off and causing formation damage. Recovery of polysaccharide polymers after fracturing is also complicated. Enzymes or oxidizers have to be used. The physical association and entanglement of wormlike micelle gives viscoelastic properties in surfactant fluids, which gives similar properties as polymer. The wormlike micelles stimulation fluids contain virtually no insoluble residue and leak off very efficiently to the formation once mixed with hydrocarbon (Chase et al., 1997). Thus, they do not cause any formation damage. Compared with traditional polymer fluids, VES fluids used few

additives and were easy to prepare on the wellsite (Sullivan et al., 2007). The ultralong (> C18) hydrocarbon chain length surfactant was usually used in VES fracturing fluid. The van der waal attractive force of ultra long chain surfactant maintains the wormlike micelle and give viscoelasticity at higher temperature. However, longer chain VES concentrate fluids do take a long time to solubilize with formation of “fish eye” like gel clump during fluid preparation in the field. Thus, the fluids do not meet requirement by continuously mixing, “on the fly”, in the field.

In order to form VES gel rapidly, hot water or ultra high energy of mixing equipments had been used in some field applications. This will increase energy cost and require special equipment. Solvent can be also used to dissolve such “fish eye” like gel clump, however, solvent will decrease the upper temperature limit of VES fluid (Yang et al., 2013).

It is known that surfactant could form viscous liquid crystal structure in concentrate range. Its behavior has been studied with anionic surfactant in microemulsion EOR application (Levitt et al., 2009; Hackett and Miller, 1988). The microemulsion consists of oil–anionic surfactant–alcohol. To our knowledge, no studies have been done on ultra long hydrocarbon chain amphoteric and mixed surfactant system, especially related to increase the dissolution rate of VES fracturing fluid. The fundamental science of microstructural change related to the rate of dissolution has also not been studied.

Hence, we hereby systemically studied mechanism, microstructure of gelation and their rheological behavior through phase behavior of an ultra long chain surfactant. Amphoteric surfactant (AS) is selected to study. Since the amphoteric surfactant was

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disclosed as VES fluid (Dahayanaye and Yang, 2001), it has been widely used as fracturing fluid and self-diverting VES for its excellent salt and higher temperature tolerance (Sullivan et al., 2007). The phase behavior of system studied with no oil presence in the product itself is different from composition studied previous in EOR microemulsion application. Since the presence of oil in the VES product initially will destroy the wormlike micelle and lost the viscoelasticity for fracturing application. In addition, negative charged anionic cosurfactant was mixed with amphoteric surfactant. The effect of cosurfactant on VES dissolution rate and its mechanism was studied. In addition, the effect of cosurfactant on high-temperature performance of VES fluids was also investigated. The studies provide guidance to improve dissolution rate of VES in the field applications.

2. Experimental

2.1. Material

Amphoteric surfactant solution which contained 40% erucyl (C22) betaine in isopropanol and water mixture was obtained from Rhodia Inc. The product was further dried in a vacuum oven in order to determine its phase behavior in higher concentrate regions. Anionic cosurfactant, sodium dodecyl sulfate (SDS), was commercial materials with 99% in purity and used without further purification. Isopropanol is 99% in purity. Water was local water.

2.2. Methods

The phase diagram was determined by mixing of surfactant, solvent, cosurfactant and water at different weight ratio at 25 °C and equilibrated at 24 h. The presence of the liquid crystal in the sample is detected between a pair of cross polarizer, in which liquid crystal shows birefringence. The type of liquid crystal structure is characterized by polarized microscope and small angle X-ray diffraction (ANTON PAR SAXSess). Rheological properties at high temperature (> 100 °C) were measured by a HAAKE 6000 Rheometer with rotational cylinder in pressured cell. The viscosity was determined at shear rate of 100 s^{-1} , which is a common measurement rate in US oil industries. The dynamic rheological properties were measured with cone and plate geometry below 90 °C. The measurement errors are within 5%. All percentage was represented in weight. The pH of fluid is between 7 and 8.

3. Results and discussion

3.1. Dissolution rate of amphoteric surfactant and its mixture with anionic surfactant

The commercial surfactants are usually supplied as a concentrated isotropic liquid in which surfactant is dissolved by alcoholic solvent such as isopropanol, ethanol, methanol etc. In the field, 1–5% surfactant concentrate is crash diluted into water and formed the viscoelastic surfactant fracturing fluid. It can also be diluted with acid for VES acidizing.

However, ultralong chain surfactant took a long time to dissolve and form viscoelastic gel. Hence, such fluid cannot be prepared by continuously mixing and does not form gel in-situ in the field. In some field operation, hot water was used to reduce the dissolution time of the fluid.

The gel formation time and viscosity of the surfactant dissolved in water was shown in Table 1. The VES fluid was prepared by injection of 5% concentrate surfactant solution into water under mechanical mixing (700 rpm) at 25 °C. When the AS concentrate

solution was diluted into water, no viscose gel was formed after 60 minutes. The viscosity is very low and fluid cannot suspend the proppant. The photograph was shown in Fig. 1a. It can be seen that diluted solution has shining clump suspended in upper phase under cross polarized light (Fig. 1a), which indicates the presence of liquid crystal.

In order to increase the dissolution rate, addition of cosurfactant as solubilizer was studied. Anionic cosurfactant, SDS, was added at 16.7% by weight to concentrate solution of amphoteric surfactant, the dissolution rate was increased drastically and gel was formed within 1 minute as shown in Table 1, and appeared as homogenous with flow birefringence under crossed polarizer as shown in Fig. 1b, which is typical of wormlike micelle optical behavior (Shikata et al., 1994).

3.2. Phase behavior of surfactant–isopropanol–water

To understand mechanism of such different dissolution behavior, phase behavior and microstructure of surfactant, isopropanol and water system was studied as shown in Fig. 2.

It can be seen that there is a hexagonal liquid crystal phase (H_1) from 35% to 70% surfactant and up to 30% solvent. The hexagonal liquid crystal phase is characterized by highly viscose semi-solid and fan-shape texture as shown Fig. 3 under polarized microscope (Laughlin, 1994; Yang et al., 1995). The hexagonal structure is further confirmed for their long-range ordering in small angle X-ray diffraction peaks in the ratio $1:\sqrt{3}:\sqrt{4}$ (Laughlin, 1994). The model structure is illustrated at the right corner beside the phase diagram in Fig. 2. In the upper right corner of the phase diagram, there is an isotropic liquid area (L_1) in which the composition of the liquid concentrate product is located. When the VES fluid is prepared in the field, diluted path of the concentrate solution is passed through hexagonal liquid crystal phase region with composition changed along broken line arrow in Fig. 2. Hence, it forms a dispersion of the hexagonal liquid crystal as shown in Fig. 1a.

Table 1
Dissolution of amphoteric surfactant and its mixture with co-surfactant.

Surfactant	VES fluid at 1 min	VES fluid at 60 min	Viscosity at 1 min, mPa s (170 s^{-1})
Amphoteric	No gel	No gel	5
Amphoteric+anionic	Gel	Gel	85

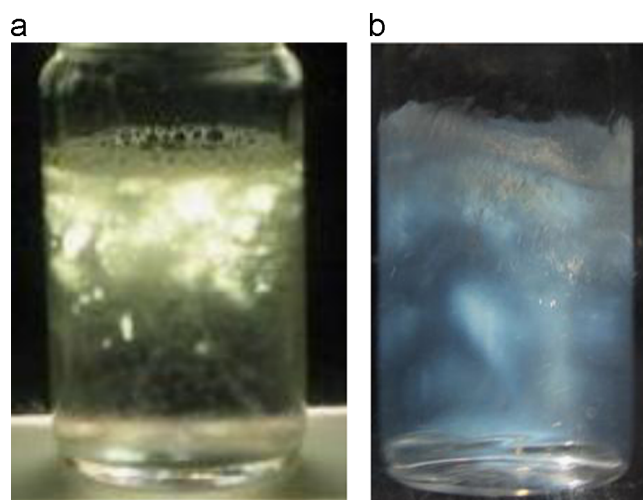


Fig. 1. Photographs of 5% concentrate surfactant solution in water under cross polarizer: (a) amphoteric surfactant (b) mixture of amphoteric and anionic surfactant.

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