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Effect of resins, waxes and asphaltenes on water-oil interfacial properties and emulsion stability

Juan Zhang, Dan Tian, Meiqin Lin*, Zihao Yang, Zhaoxia Dong

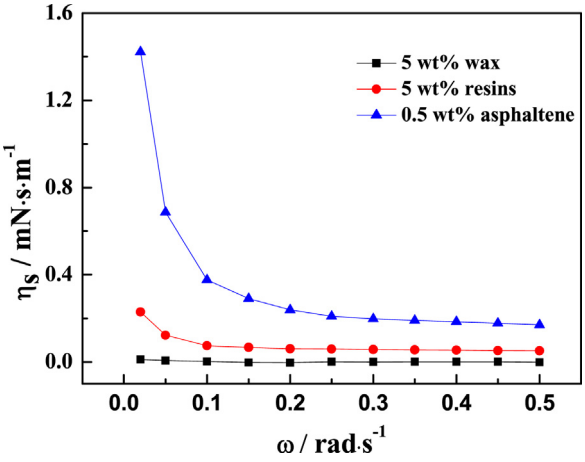
Enhanced Oil Recovery Research Institute, China University of Petroleum-Beijing, Beijing 102249, PR China

HIGHLIGHTS

- Research was carried out to compare the stability of O/W and W/O emulsion.
- The O/W emulsion with resins showed the highest stability.
- The stability of the W/O emulsion with asphaltenes was best.
- Emulsion stability depended on oil-water interfacial properties.

GRAPHICAL ABSTRACT

Influence of wax, resins and asphaltene on the interfacial shear viscosity between water and oil. ω is the angular velocity of the pallet rotating. The interfacial shear viscosity between model oil of the lowest concentration of asphaltene and simulated water was the largest, followed by resins and wax model oils. Besides, the interfacial shear viscosity between model oil of different components and simulated water decreased with the increasing of shear rate and eventually remained unchanged.



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ABSTRACT

In this paper, the interfacial properties of simulating water with different components of crude oil, including resins, waxes and asphaltenes, are investigated by interfacial tensiometer, surface viscoelasticity and zeta potential instruments and the results are then correlated with emulsion stability. The results show that the interfacial tension of the O/W (oil-in-water) emulsion formed by resins is lower and the interfacial shearing viscosity is higher than that formed by waxes. Besides, the O/W emulsion with resins has the largest absolute value of zeta potential and accordingly it shows the highest stability. And the O/W emulsion with waxes presents the lowest stability which has the lowest interfacial shearing viscosity. Differently, the stability of the W/O (water-in-oil) emulsion with asphaltenes is strongest, followed by that with resins or waxes. This is mainly because the interfacial shear viscosity of asphaltenes and water is the largest, resulting in the strongest strength of interfacial film. This work provides more insights into the mechanism of emulsion stability caused by resins and asphaltenes which can be useful for the petroleum science and industry.

* Corresponding author.
E-mail address: 13910509321@163.com (M. Lin).

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1. Introduction

In the petroleum industry, formation of stable emulsion is highly undesirable but ineluctable. The interfacial active fractions of crude oil play an important role in the formation and stability of oil emulsion. Stable emulsion can be formed in crude oil owing to natural interfacial active fractions existing in crude oil, such as resins, asphaltene, naphthenic acid, polar porpthyrin compounds, which could be adsorbed on the oil-water interface of emulsion to form strong interfacial film [1–6]. The stable interfacial film will prevent droplets from colliding with each other and coalescing, so that stabilizing the emulsion [7–15]. The increased crude viscosity owing to the emulsion formed in crude oil will decrease the flow ability of crude oil and increase the difficulty of demulsification. The influence of interfacial active fractions in crude oil on oil-water interfacial properties and emulsion stability is related to the nature of crude oil. Several techniques have been developed to study emulsion stability, including electric conductivity measurement [16–18], microscopic observation [19,20], light scattering methods [21], and ultrasound spectrometry [22,23]. Besides, nuclear magnetic resonance (NMR) self-diffusion can be used to detect the changing process of emulsions [24–26].

It is generally recognized that the stability of emulsion is mainly determined by asphaltenes among the all components of crude/heavy oil. Although a large number of studies support this view, the molecular mechanisms that govern the stability of emulsions in petroleum industry remain unsolved. Lin et al. [27] separate Daqing crude oil into asphaltene, polar compounds and raffinate oil. They find that all of these components have certain interfacial activity. Asphaltene has a weaker W/O emulsifying ability while raffinate oil has a better W/O emulsifying ability, which is the main component causing W/O emulsification of Daqing crude oil. However the polar compounds are the main components causing O/W emulsification of Daqing crude oil. Fang et al. [28] study the influence of each component of Shengli crude oil on dilatational rheology of interfacial film, but the relationship between interfacial dilatational rheology and the stability of emulsion formed by each component is not given. After development of Shengli Gudong oil field over more than 30 years, most of oil fields come into the mid and later stage of water flooding when the components and properties of crude oil have changed and crude oil can be easily emulsified and then the stable emulsion will be formed, which would bring great trouble to oil-water separation and sewage treatment.

Therefore, in this paper, the influence of interfacial active fractions in Shengli Gudong crude oil on oil-water interfacial properties and emulsion stability is investigated. The results show that the O/W emulsion with resins shows the highest stability as the interfacial tension of the O/W emulsion formed by resins is lower and the interfacial shearing viscosity is higher than that formed by waxes. Whereas the stability of the W/O emulsion with asphaltene is strongest compared to that with resins or waxes.

2. Experimental

2.1. Materials

The crude oil used in this investigation is a Gudong crude oil obtained from Shengli oilfield, with density of 0.9215 g/cm^3 (50 °C) and viscosity of 232.0 mPa s (50 °C). The kerosene used in preparing simulated oil is kerosene distillate distilled under atmospheric pressure, which is produced by Yanshan petrochemical company. In order to remove the impurities with interfacial activity, the kerosene is treated by silica gel adsorption for 24 h under room temperature before use. Pentane, sodium chloride, magnesium chloride, calcium chloride, sodium bicarbonate, potassium chloride are analytical grade. The ion composition of simulated formation water used in the study is given in Table 1.

Table 1
The component of Gudong oil field stimulation water.

Ion	Cl^-	SO_4^{2-}	HCO^-_3	Mg^{2+}	Ca^{2+}	Na^+, K^+
Concentration (mg/L)	2988.0	87.3	619.0	30.1	34.3	2120.8

2.2. Separation method of three fractions of crude oil

The *n*-pentane is added into 200.0 g dehydrated crude oil at a volume ratio of 30:1 and the mixed solution is stirred for 20 min and then stored at room temperature for 3 days. The precipitated asphaltene is filtered out and washed with *n*-pentane for three times. Finally, the asphaltene component is obtained after being dried in a vacuum oven at 50 °C. The activated silica gel is added into residual mixed solution without asphaltene at a mass ratio of 20:1 by three times, and the mixed solution is stirred and adsorbed for 60 h each time until the solution becomes colorless. The mixed solution is distilled using a rotatory evaporator until a small amount of solvent is left and then dried to constant mass in a vacuum oven at 50 °C and the wax component is obtained. The silica gel after adsorption is washed with mixed solution of benzene and ethanol (v/v = 1:1) and the volume ratio of the mixed solution to crude is 25:1. The silica gel is removed from mixed solution after stirring for 60 h and then the mixed solution is distilled using a rotatory evaporator until a small amount of solvent is left. After distilling the system, the benzene and ethanol which have been distilled out is added into the mixed solution and then distilled again. This step is repeated until the silica gel is light in color. The resins component is obtained when the mixed solution is distilled being dried to constant mass in a vacuum oven at 50 °C.

2.3. Simulated oil preparatipon

A certain amount of resin or wax is put into and dissolved fully in a certain amount of refined kerosene. The weight concentration of resin or wax is defined as: weight concentration of resin or wax = $m_{resinorwax}/(m_{resinorwax} + m_{kerosene}) \times 100\%$.

For asphaltene, because it can not be dissolved in pure kerosene, a certain amount of asphaltene is first put into and dissolved in a certain amount of dimethylbenzene and then a certain amount of refined kerosene is added and mixed well. The weight concentration of asphaltene is defined as: weight concentration of resin or wax = $m_{asphaltene}/(m_{asphaltene} + m_{dimethylbenzene} = +m_{kerosene}) \times 100\%$.

2.4. Interfacial tension measurements

SVT20N video spinning drop tensiometer is used to measure the interfacial tension between the simulated oil and the simulated formation water at 30 °C.

2.5. Interfacial shear viscosity measurements

The interfacial shear viscosity between the model oil and the simulated formation water is measured by SVR.S interfacial shear viscosity meter made by Kyowa Scientific Co., Ltd. (Japan) at 30 °C. The angular velocity of the pallet rotating is defined as ω. The meter mainly contains a turnplate, a measurement cell, a subuliform measuring head, a thermostat, a torsion wire and a swing angle scaleplate. The diameter of the measurement cell is 5.335 cm. A series of swing angles are recorded by changing ω.