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Research paper

The synergetic effect between heavy oil components and emulsifier in heavy oil-in-water emulsion

Jinmei Bai [a,*], Tongyao Zhang [b], Weiyu Fan [c]

[a] E-tech Oilfield Technology Development Co., Ltd. Tianjin, 300384, China
[b] Institute of Oil Recovery Engineering CNOOC, Tanggu, Tianjin, 300452, China
[c] State Key Laboratory of Heavy Oil Processing in China University of Petroleum, Shandong, 257061, China

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ABSTRACT

Resin and asphaltene were extracted from Gudao and Liaohe heavy oil by using the adsorption chromatography. Toluene and *n*-dodecane were selected as model oil, sodium dodecylbenzene sulfonate was selected as emulsifier. The interfacial tension (IFT) was investigated without emulsifier and adding emulsifier, the effect of pH value on the interfacial tension was also investigated. The results show that the interaction between component and emulsifier lies on the interfacial activity of components, and the higher interfacial activity is, the stronger interaction is. And the influence of pH on IFT is great at acid and base conditions, but little at neutral condition. The synergetic effect between polar component and emulsifier is stronger in the neutral condition and weak acid and base conditions.

1. Introduction

Emulsification–viscosity–reduction is an important area of exploitation, pipeline transportation and processing of heavy oil. Researchers have studied the preparation and application of heavy oil-in-water emulsion (Zaki, 1997; Ahmed and Amal, 1999), but they did little research about the mechanism of emulsification and stabilization of heavy oil-in-water emulsion (Fan et al., 2001). They were only interested in the stability of heavy oil emulsion (McLean and Kilpatrick, 1997; Yang and Lu, 1998; Li, 1998). In order to widely apply emulsification–viscosity–reduction technology, research about the mechanism of emulsification and stabilization of heavy oil-in-water emulsion should be studied in-depth. The bad adaptability of emulsifiers and the unmanageable stabilization were caused by the differences of heavy oil components. The interaction between heavy oil components and emulsifiers is the core of heavy oil-in-water emulsion's formation and stabilization.

In this paper, resin and asphaltene was extracted from Gudao and Liaohe heavy oil with the method of adsorption chromatography. Toluene and *n*-dodecane were selected as model oil, sodium dodecylbenzene sulfonate(LAS) was selected as emulsifier. The interfacial tension was investigated. When emulsifier was added and before it was added, the effect of pH value on the interfacial tension was investigated separately.

2. Experimental

Table 1 gives basic properties of Liaohe Du-84 heavy oil and Shengli Gudao heavy oil.

Isolate heavy oil to polar components: the method to obtain polar components (saturate, aromatic, resin and asphaltene) is based on the Chinese petroleum industry standard method (SH/T 0509-92).The main conditions are as follows:

Isolation of asphaltene: heavy oil:*n*-heptane = 1 g:50 mL; isolation of soluble fractions: 75–150 μm neutral Al_2O_3 columns.

Acid number: using 0.1 M KOH/ethanol as titrant, V(toluene):V(hexamethylene):V(anhydrous ethanol):V(water) = 100:50:49:1 as titration solvent, pHS-3C pH value meter.

Base nitrogen number: using perchloric acid/caproic acid as titrant, V(toluene):V(caproic acid) = 10:20 as titration solvent, then determining variation of electric potential (mV) with the volume of titrant (V), the point whose derivatives are the largest on the graph of mV versus V is the terminal point of titration.

Ultimate analysis: Elementar Analy Sensysteme GmbH Vario Elc III ultimate analysis instrument (German).

Determination of interfacial tension: interfacial tension of oil–water is measured by spinning drop method at 50 °C, using XZD-3 interfacial tension apparatus.

Preparation of oil/water system: heavy oil, resin and asphaltene were regarded as solute; toluene and *n*-dodecane (W(toluene):W(*n*-dodecane) = 1:1) were selected as mix solvent, a series of model

* Corresponding author.
E-mail address: baijinmei_1982@hotmail.com (J. Bai).

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Table 1
Basic properties of Liaohe and Gudao heavy oil.

Heavy oil	Density (20 °C)ρ/ (g cm^{-3})	Viscosity (80 °C) ν/(mm^2 s^{-1})	Solidification point/ °C	Acid number/ mg KOH g^{-1}
Gudao*	0.9934	810.38	8.5	3.25
LiaoheDu-84*	1.0001	4898.92	42	9.05

*Gudao is a production base of heavy oil in Shengli Oil field which is the second oil field of China.
*Liaohe Oil field is the third oil field of China, most of its reserve is heavy oil.

oil containing 0.5–5% (w/w) solute were prepared. Sodium dodecylbenzene sulfonate was selected as emulsifier. According to the experimental demand, the variational aqueous phase was de-ionized water, de-ionized water in different pH value, or emulsifier aqueous solution.

3. Results and discussion

3.1. Elemental properties of two kinds of heavy oil and their polar components

The elemental properties of two kinds of heavy oil and their polar components as shown in Table 2 can reveal the following results:

The sequence of fractions content is: resin > aromatic > saturate > asphaltene. Compared with Gudao heavy oil, there are more resins and less asphaltenes in Liaohe heavy oil.
The acid number of two kinds of heavy oil and their fractions suggests that they are different in the distribution of acid number and the composition of acidic substance. The nitrogen number of two kinds of heavy oil and their fractions indicates that they are different in the composition of basic nitride.
The results of ultimate analysis got the conclusion that: compared with Gudao heavy oil and its corresponding components, the Liaohe heavy oil and its polar components have higher degree of unsaturation, higher content of nitrogen and oxygen, and higher acid number. And most of nitrogen and oxygen atoms consist in resin and asphaltene.
Basic properties showed that there are more differences between two kinds of heavy oil and their polar components, which make it easy to review the influence of component difference on interfacial property in the study.

3.2. Comparison of interfacial activities of two kinds of heavy oil and their polar components

Interfacial tension is the most important parameter of oil–water interfacial property. It affects the adsorption rata and adsorbed amount of polar components in oil/water interface and also affects the interfacial structure. It is the appearance of interaction between polar components and emulsifier.

In order to compare two kinds of heavy oil and their polar components' interfacial activity, the influence of dosage of heavy oil and its polar components in simulated oil on oil–water interfacial tension was studied. Table 3 shows the results.

Blank interfacial tension is the oil/water interfacial tension of blank model oil and de-ionized water without components. The data of Table 3 show that the existence of heavy oil and polar components reduce the oil/water interfacial tension of model oil, and the tendency of oil/water interfacial tension reduces with the increasing of polar components' contents. Results indicate that the adsorbed amount of natural surfactant existing in crude oil increases with the increasing of polar components' contents, it goes into saturation under certain concentrations. Interfacial pressure is the variation of the oil/water interfacial tension with and without surfactant.

$$\pi = \gamma - \gamma'$$

π is the symbol for interfacial pressure, γ stands for the oil/water interfacial tension without surfactant, γ' stands for the oil/water interfacial tension with surfactant. Interfacial pressure is the symbol of interfacial activity. Interfacial pressure increases with the adsorbate amount of surfactant in surface. The larger interfacial pressure in the same concentration, the stronger the ability of reducing interfacial tension will be.

Table 4 gives the influences of heavy oil and its components amount in model oil on oil–water interfacial pressure. The data of Table 4 show that the interfacial pressure of two kinds of heavy oil and their polar components are different in the same concentration, that is, their interfacial activities are different. The sequence of the interfacial activity (IFA) of Gudao heavy oil and its polar components is IFA (heavy oil) > IFA(resin) > IFA (asphaltene). The sequence of the IFA of Liaohe heavy oil and its polar components is IFA (asphaltene) > IFA(heavy oil) > IFA (resin). The interfacial activity of Liaohe heavy oil and its polar fractions is superior to that of Gudao.

From elemental properties and the IR spectrum of asphaltene, we can know there are hydroxide radical, amidocyanogen, carbonyl group and carboxyl in asphaltene molecule, and Liaohe asphaltene has more than others, so there is more hydrogen bond in asphaltene which leads to stronger interfacial activity of asphaltene (Fig. 1).

3.3. Effects of the interaction of heavy oil components and emulsifiers on interfacial tension

In order to review the influences of the interaction between components and emulsifier on interfacial tension, the variation of interfacial tension with the concentration of fractions in the model oil with 1% emulsifier was studied. Table 5 gives the results.

Table 2
Elemental properties of two kinds of heavy oil and their polar components.

Heavy oil fractions	Distribution/%	Acid number/mg KOH g^{-1}	Nitrogen number/μg g^{-1}	Element fractions/%					n(H)/n(C)
				C	H	N	O	S	
Gudao heavy oil	–	3.25	13441	84.01	10.92	0.57	0.64	3.31	1.56
Liaohe heavy oil	–	9.05	8106	86.50	10.91	0.81	1.33	0.42	1.51
Gudao saturates	25.08	–	–	86.73	13.12	0	0	0	1.82
Liaohe saturates	26.07	–	–	87.07	12.87	0	0	0	1.77
Gudao aromatics	31.39	–	–	84.25	10.70	0.24	0.19	4.16	1.52
Liaohe aromatics	28.49	–	–	87.87	10.57	0.34	0.19	4.16	1.44
Gudao resins*	34.88	0.23	13671	82.97	9.85	1.39	1.40	3.99	1.42
Liaohe resins*	41.65	0.22	13149	85.53	9.93	1.74	1.57	0.55	1.39
Gudao asphaltenes	6.65	2.79	13212	80.62	8.72	1.21	1.96	6.37	1.30
Liaohe asphaltenes	3.38	9.74	20830	81.92	8.65	1.71	3.13	0.51	1.26

*The amount of resins is calculated according to difference; the amount of oxygen is the actual value examined.