Interfacial properties of Daqing crude oil-alkaline system

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Abstract: The oil/water interfacial properties of crude oil emulsions formed by alkaline/surfactant/polymer (ASP) flooding in the Daqing Oilfield were investigated in this paper by the measurement of interfacial tension, interfacial shear viscosity and Zeta potential of the oil/water system. The result showed that both NaOH and Na₂CO₃ could react with acid substances in the crude oil to produce interfacially active components, which are adsorbed on the interfaces between the aqueous phase and oil phase, resulting in a decrease of the interfacial tension, negatively charging the surface of oil droplets, but making little change in the interfacial shear viscosity. For the same ionic strength of NaOH and Na₂CO₃, the interfacial tension of NaOH solution-crude oil system is lower, but the interfacial shear viscosity of NaOH solution-crude oil system is higher, than that of Na₂CO₃ solution-crude oil system. The negative value of the Zeta potential on the surface of the oil droplets is large. Accordingly, the O/W emulsion of NaOH solution-crude oil system is more stable than that of Na₂CO₃ solution-crude oil system.

Key words: Alkali, interfacial tension, interfacial shear viscosity, Zeta potential, turbidity

1 Introduction

In recent years, alkali/surfactant/polymer (ASP) flooding has been used to enhance oil recovery in China (Shen and Yu, 2001; Wan, 1996). ASP flooding can significantly improve the oil recovery but the produced fluids form more stable oil-in-water (O/W) emulsion than simple water flooding. As a result, the dehydration rate of the produced fluids by ASP flooding is low, resulting in high oil content in waste water and making waste water treatment more difficult (Deng et al, 2002; Zhang et al, 2006). Among the three components of ASP, alkali has a great effect on the emulsification of oil and stability of the emulsion. Alkali in ASP flooding could react with some crude oil components, forming soap with sodium ions (Lakatos-Szabo and Lakatos, 1999; Acevedo et al, 1999). This soap is surface-active and can emulsify crude oil to form a stable emulsion (Guo et al, 2006; Wu et al, 2001; Luo et al, 2003). The reaction between alkali and crude oil can generate both oil soluble surfactants and water soluble surfactants. It is easy for water-soluble surfactants to emulsify crude oil to O/W emulsion, which made the produced fluids more stable and difficult to be treated. The stability of produced fluids is related to interfacial properties (Li et al, 2002; Dicharry et

al, 2006; Opawale and Burgess, 1998), so this paper focuses on the effect of NaOH, or Na₂CO₃, with Daqing crude oil on water/oil interfacial properties.

2 Experimental

2.1 Materials

The crude oil used in the experiment has an acid number of 0.05 mg(KOH)/g(crude oil) and was provided by Daqing oilfield, Northeast China. The composition of synthesized Daqing oilfield formation water is listed in Table 1. NaCl, NaOH, Na₂CO₃, NaHCO₃, CaCl₂, MgSO₄ were all analytically pure. Kerosene used for preparing model oil was provided by Beijing Yanshan Petrochemical Co. Ltd., China. The kerosene was repeatedly purified with activated silica gel. After the adsorption treatment, the interfacial tension between kerosene and redistilled water is more than 48 mN·m⁻¹.

Table 1 Major ion composition of formation water from the Daqing oilfield

Ion	Na ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻	CO ₃ ²⁻	HCO ₃ ⁻	Salinity
Concentration mg/L	1686.89	0.72	0.83	0.68	1214.37	96.79	2196	5196.28

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2.2 Measurement of interfacial tension

The interfacial tension between model oil and aqueous alkali was measured at 30 °C by the Wilhelmy method, using a Tensiometer DCAT-21 made by Dataphysics Instruments Ltd, Germany.

2.3 Measurement of interfacial shear viscosity

The interfacial shear viscosity between model oil and aqueous alkali was measured at 30 °C by biconical bob method, using a SVR-S interfacial viscoelastic meter (Kyowa Kagaku Co. Ltd., Japan).

2.4 Zeta potential on the surface of oil droplets

The Zeta potential on the surface of oil droplets in O/W emulsion was measured at 30 °C with a Zetasizer Nano-ZS and Zeta potentiometric analyzer made by Malvern Instruments Ltd. (United Kingdom).

2.5 Measurement of emulsion stability

The O/W emulsions were prepared from the model oil and synthesized formation water (with a volume ratio of 1:4) in an emulsifier (IKA-18, Germany) and then stirred at 6,000 r/min for 5 min. The relationship of turbidity vs. time was obtained at 25 °C with a Turb 550 turbidity meter made by WTW company (Germany) and the turbidity was used for judging the stability of the O/W emulsion.

3 Results and discussion

3.1 Effect of sodium hydroxide on interfacial properties

3.1.1 Effect of sodium hydroxide on interfacial tension

Fig. 1 shows the relationship of interfacial tension vs. time between different mass concentrations of NaOH solution and 10% Daqing model oil. It can be seen that for a concentration of NaOH solution, the oil/water interfacial tension decreased gradually with time and tended to stabilize, and that with the increase of NaOH concentrations, the oil/water interfacial

Fig. 1 Influence of NaOH concentration on the interfacial tension between model oil and water

tension declined. At an NaOH concentration of 1.2 wt%, the oil/water interfacial tension rose again because the ionic strength increased. The higher the NaOH concentrations, the shorter the time for NaOH solution-Daqing model oil system to reach stability. This is because with the increase of NaOH concentration and ionic strength, the diffusion rate of NaOH molecules and adsorption rate increases, and NaOH quickly reacts with acidic substances and esters in crude oil to generate interfacial surfactants. As a result, the oil/water interfacial tension declined and tended to stabilize quickly.

3.1.2 Effect of sodium hydroxide on interfacial shear viscosity

Fig. 2 shows the changes of interfacial shear viscosity of the NaOH solution (with different NaOH concentrations)/model oil systems with shear rate. It is shown that the interfacial shear viscosities of the model oil/NaOH solution system with different NaOH concentrations were all small and almost the same, indicating that the reaction between NaOH and Daqing model oil in a short time hardly influenced the oil/water interfacial shear viscosity.

Interfacially active agents stay on interface forming an interfacial film. The tighter and more intense the interfacial film, the larger the oil/water interfacial viscosity. The crude oil from Daqing oilfield is a paraffin-based oil with a content of asphaltene less than 1% and a content of saturates and aromatics more than 90%, and has a small acid number. The interfacially active agents formed by oil and NaOH were absorbed on the oil-water interface as molecules. The intensity of the interfacial film was relatively weak. As a result, the interfacial shear viscosity was small.

Fig. 2 Influence of NaOH concentration on the interfacial shear viscosity between model oil and water

3.1.3 Effect of sodium hydroxide on Zeta potential

Because of the limits of the Zeta potentiometric analyzer, the ionic strength in the measurement of Zeta potential could not exceed 0.3 mol/kg, the NaOH solution/Daqing model oil system with different mass concentrations of NaOH was diluted two-fold with synthesized formation water after it was homogenized and kept for 5 hours. Fig. 3 shows the influence of NaOH concentration on the Zeta potential on the surface of oil droplets in O/W emulsion.

Fig. 3 Influence of NaOH concentration on the Zeta potential of O/W emulsion

Fig. 3 shows that the absolute value of Zeta potential on the surface of oil droplets first increased and then declined with increasing concentrations of NaOH. NaOH had two functions: firstly, as a strong alkali NaOH reacted with acidic components in the model oil and produced compounds with a high degree of ionization. In this process, the acidic components in the model oil were neutralized to salts, improving the degree of ionization and leading to the increase of the absolute value of Zeta potential; secondly, when the concentration of NaOH was high, the surplus NaOH played the role of an electrolyte, enhancing the ionic strength of the aqueous phase and hence leading to the compression of the electric double layer around the oil droplets. As a result, the absolute value of the Zeta potential on the surface of oil droplets decreased. The change of Zeta potential on the surface of oil droplets with the concentration of NaOH was the result of a combination of the two factors.

3.2 Effect of sodium carbonate

3.2.1 Effect of Na_2CO_3 on interfacial tension

Fig. 4 shows the interfacial tension between the 10% Daqing model oil and Na_2CO_3 solution with different Na_2CO_3 concentrations vs. reaction time. It is seen that the interfacial tension decreased gradually with an increase of Na_2CO_3 concentration. This is because with the increase of Na_2CO_3 concentration and ionic strength, the diffusion rate of Na_2CO_3 from water to interface and adsorption rate all increased. Na_2CO_3 reacted with acidic substances to generate interfacial surfactants. With more and more interfacial surfactants being produced, the interfacial tension first declined and then tended to stabilize.

Comparing Fig. 1 with Fig. 4, it is seen that the interfacially active agents generated by acidic components in crude oil and different alkaline substances had considerably different influences on the interfacial tension. At the same mass concentration of Na_2CO_3 solution and NaOH solution, the NaOH solution-Daqing model oil system had lower interfacial tension than Na_2CO_3 solution-Daqing model oil

system, and the time to reach stable interfacial tension was shorter.

Fig. 4 Influence of Na_2CO_3 concentration on the interfacial tension between model oil and water

3.2.2 Effect of Na_2CO_3 on interfacial shear viscosity

Fig. 5 shows the interfacial shear viscosity of Na_2CO_3 solution-Daqing model oil system with different Na_2CO_3 concentrations vs. shear rate. It can be seen that Na_2CO_3 -Daqing model oil system had low interfacial shear viscosity. Comparing with Fig. 2, the difference of the interfacial shear viscosity between NaOH (strong alkali) solution-model oil system and Na_2CO_3 (weak alkali) solution-model oil system was not significant, indicating that the type and mass concentration of alkali had little influence on the formation of interfacial film and its strength.

Fig. 5 Influence of Na_2CO_3 concentration on the interfacial shear viscosity between model oil and water

3.2.3 Effect of Na_2CO_3 on Zeta potential

The Na_2CO_3 solution-Daqing model oil system with different Na_2CO_3 mass concentrations was diluted one-fold using synthesized formation water which had already been emulsified and kept for 5 hours. Fig. 6 shows the Zeta potential on the surface of oil droplets of the system.

It is shown that with increasing Na_2CO_3 concentration, the absolute value of the Zeta potential on the surface of oil droplets first increased and then decreased. Comparing Fig. 3 with Fig. 6, at the same alkali concentration, the Na_2CO_3 solution-model oil system had a lower Zeta potential than the NaOH solution-model oil system. The reason is that Na_2CO_3 is weak alkali and could only react with acidic components of crude oil, but not with esters. Hence little interfacially active agents were produced and only a small amount of electric charge was adsorbed on the surface of oil droplets, resulting in the Na_2CO_3 solution-model oil system having a smaller absolute value of the Zeta potential than the NaOH solution-model oil system.

Fig. 6 Influence of Na_2CO_3 concentration on the Zeta potential of O/W emulsion

3.3 Oil/water interfacial properties at the same ionic strength of NaOH and Na_2CO_3

Even though the mass concentration of NaOH and Na_2CO_3 was the same, the ionic strength of the two system was different, which would influence the interfacial properties between oil and water. At the same ionic strength of 0.375 mol/kg, the interfacial properties between Daqing model oil and NaOH or Na_2CO_3 aqueous solution were investigated.

3.3.1 Interfacial tension at the same ionic strength

Fig. 7 shows the relationship of interfacial tension vs. reaction time for NaOH solution-model oil and Na_2CO_3 solution-model oil systems, at the same ionic strength.

It can be seen that at the same ionic strength, the NaOH solution-model oil system had lower interfacial tension than the Na_2CO_3 solution-model oil system. Moreover, it took a shorter time for the NaOH solution-model oil system to reach a stable interfacial tension than the Na_2CO_3 solution-model oil system. The reason is that the reaction rate of NaOH (as a strong alkali) with the acidic components in Daqing model oil was fast, and a large amount of interfacially active agents were generated and adsorbed on oil/water interface and reach a stable state sooner. As a result, the interfacial tension between water and oil decreased steeply and became stable soon. The reaction rate of Na_2CO_3 (as a weak alkali) with the

Fig. 7 Interfacial tension between NaOH or Na_2CO_3 solution and Daqing model oil

acidic components in Daqing model oil was slow. Therefore, a small amount of interfacially active agents were generated. The Na_2CO_3 solution-Daqing model oil system had a higher interfacial tension than NaOH solution-model oil system, and it took longer time for the Na_2CO_3 solution-Daqing model oil system to reach a stable state.

All the results showed that alkali could react with crude oil to produce interfacially active substances, which were adsorbed on the oil/water interface and lower the oil/water interfacial tension in a short time. At the same ionic strength, the strong alkali-Daqing model oil system reacted more quickly. As a result, more interfacially active substances were formed. The oil/water interfacial tension decreased steeply and reach a stable state sooner.

3.3.2 Interfacial shear viscosity at the same ionic strength

Fig. 8 shows the interfacial shear viscosity of NaOH solution-model oil system and Na_2CO_3 solution-model oil system with the shear rate, at the same ionic strength.

It is shown that at the same ionic strength, the NaOH solution-model oil system had a higher interfacial shear

Fig. 8 Interfacial shear viscosity between NaOH or Na_2CO_3 solution and Daqing model oil

viscosity than the Na_2CO_3 solution-model oil system. This is because Na_2CO_3 could only react with small acidic molecules in the oil. But for strong alkali NaOH , they could react with not only small molecules but also long-chain macromolecules, resulting in that more interfacially active substances were produced and adsorbed on the interface to form strong films.

3.3.3 Zeta potential on the surface of oil droplets at the same ionic strength

At the same ionic strength of 0.375 mol/kg, the Zeta potentials on the surface of oil droplets in NaOH , or Na_2CO_3 , solution-Daqing crude oil systems are shown in Table 2. It can be seen that the absolute value of Zeta potential on the oil droplets' surface in the NaOH solution-model oil system was larger than that in the Na_2CO_3 solution-model oil system. The main reason was that the strong alkali reacted with acidic substances of the crude oil, making the adsorption and ionization on the interface easy, and resulting in the absolute value of Zeta potential on the surface of oil droplets become larger.

Table 2 The Zeta potential of O/W emulsion formed by NaOH or Na_2CO_3 solution with Daqing model oil

Alkali	NaOH	Na_2CO_3
-1.5×10^{-3} V	-1.5×10^{-3} V	-1.5×10^{-3} V

3.3.4 Stability of emulsion at the same ionic strength

Fig. 9 shows the turbidity of the emulsions, formed by 10% Daqing model oil in NaOH or Na_2CO_3 solution, with time, with the same ionic strength. It is seen the emulsion formed by NaOH solution and model oil had a higher turbidity than that formed by Na_2CO_3 solution-model oil, indicating that the O/W emulsion formed by strong alkali NaOH solution and model oil was more stable. This is because that strong alkali NaOH reacted with model oil and produced more interfacially active substances being adsorbed on oil/water interface, leading to a steep decrease in the oil/water interfacial tension (see Fig. 7), an increase of interfacial shear viscosity (see Fig. 8), and a rise in negative value of

Zeta potential on the surface of the oil droplets (see Table 2). Under the condition of constant interfacial area, the interfacial energy decreased with the decrease of oil/water interfacial tension. The increase of interfacial shear viscosity made the oil/water interfacial film stronger, so it was more difficult for oil droplets in the emulsions to aggregate. The increase of the negative value of Zeta potential made the electrostatic repulsive force between the oil droplets in the emulsion stronger. The cooperation of the above three actions made O/W emulsion formed by NaOH solution-model oil system more stable than that by Na_2CO_3 solution-model oil system.

4 Conclusions

(1) NaOH or Na_2CO_3 reacted with acidic components in Daqing oil and produced interfacially active agents, which could adsorb on the interface between oil and water, then reduced the interfacial tension. With an increase of NaOH and Na_2CO_3 mass concentrations, more interfacially active components were generated. As a result, the oil/water interfacial tension decreased gradually. Meanwhile, the absolute value of the Zeta potential on the oil droplets decreased gradually because of increase in the ionic strength of the aqueous phase.

(2) NaOH , as a strong alkali, compared with Na_2CO_3 , with the same ionic strength, could react with neutral and acidic substances, esters in the crude oil quickly. More interfacially active agents produced by the reaction led to a decrease in the interfacial tension of the NaOH solution-Daqing crude oil system.

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Fig. 9 The turbidity of O/W emulsion formed by NaOH or Na_2CO_3 solution and model oil vs. time

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