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A New Approach to Simultaneously Enhancing Heavy Oil Recovery and Hindering Asphaltene Precipitation

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Abstract

A new chemical compound is developed at Petroleum University of Technology to enhance the recovery of the free imbibition process and simultaneously hinder asphaltene precipitation. The compound is tested on heavy oil samples from Marun oil field, Bangestan reservoir. The effects of the chemical compound on viscosity, hydrocarbon composition, and average molecular weight of the heavy oil are investigated. It is found that the substance dramatically reduces oil viscosity and molecular weight and hinders the precipitation of asphaltene in the heavy oil. The results of free imbibition tests demonstrate a significant recovery enhancement after oil reacts with the compound and is used in water in an Amott cell. Finally, the new chemical compound causes a significant reduction in surface tension and contact angle. This is verified by the molecular analysis of heavy oil after reacting with this ionic compound.

Keywords: Enhanced Heavy Oil Recovery, Asphaltene Precipitation, Recovery Factor, Free Imbibition Test

1. Introduction

By the depletion of conventional oil reservoirs, more and more attention is being paid to producing heavy oil and focusing on unconventional reservoirs. Under such circumstances, it is of utmost importance to devise methods to effectively exploit the discovered heavy oil reserves. Viscosity control is the key to many heavy oil production enhancement mechanisms. Aquathermolysis is the most effective method for reducing the viscosity of heavy oil and can decrease resins and asphaltene in heavy oil (Clark P D et al., 1984; Fan H F et al., 2001). Aquathermolysis operates at relatively high temperatures which can be well accommodated by the high reservoir temperatures.

Most of the current oil production in the world comes from mature fields. Thus, increasing oil recovery from the aging resources is a major concern for oil companies and authorities. In addition, the rate of the replacement of the produced reserves by new discoveries has steadily been declining in the last decades. Therefore, the recovery enhancement from mature fields under primary and secondary production will be critical to meet the growing energy demand in the coming years (Kharrat R. et al., 2008).

Asphaltene is the heaviest component of crude oil. Commonly, asphaltene is defined as a fraction that is soluble in toluene or benzene while it is insoluble in low boiling alkanes such as n-pentane or n-heptane. Under initial reservoir conditions, asphaltene is dissolved in crude oil. Asphaltene can be

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precipitated due to a change in specific reservoir conditions such as pressure, temperature, and composition. Asphaltene precipitates may deposit a layer on the surface of pores and plug the pore throat causing permeability reduction, wettability alteration, and formation damage. Asphaltene deposition in flow-lines is a severe operation problem, thereby significantly increasing the cost of production regardless of the onset pressure. There are various techniques to prevent and/or remove asphaltene from the wellbore, tubing, and surface facilities. They include inhibitor injection and chemical washing. Deposited asphaltene could also be removed by applying various remedial treatments such as solvent soaks with aromatic solvents and/or aromatic solvents blended with dispersants, and/or physical removal.

Over the past few years, several ionic liquids have been introduced and applied for upgrading and viscosity reduction of heavy crude oil. The common ionic liquids used for heavy oil recovery are the ones containing $[PF_6]^-$ and $[BF_4]^-$ that will produce HF gas when applied to heavy oil. Also, they are not inert toward various organic compounds in heavy oil, which might limit their applications. Therefore, these ionic liquids should be applied in an inert atmosphere and are not suitable to be applied under the reservoir conditions where it is difficult to control the moisture in the reservoir. Moreover, the synthesis costs and the precursors of these ionic liquids are expensive.

On the other hand, IRAN91 is a new ionic compound with an economic synthesis method; it is the aim of the current work to employ IRAN91 to enhance heavy oil recovery and inhibit asphaltene precipitation.

2. Experimental procedures

2.1. Preparation of chemical substances

183.6 grams (1.375 mol) of $AlCl_3$ were slowly added into a 500-ml round bottom flask containing 126.4 grams (0.919 mol) of $[Et_3N]HCl$. This reaction mixture was slowly stirred and cooled by an ice bath. When half of $AlCl_3$ was added, the mixture became completely liquid. After the addition process was completed, the ice bath was removed and the reaction mixture was stirred at room temperature for 5 min and then at 80 °C for 7 hours. As a result, a light yellow liquid was formed. Next, 6.84 grams (0.0688 mol) of CuCl were added and the resulting mixture was stirred for 2 hours, which finally produced a dark yellow product. This substance was named IRAN91 in National Iranian South Oil Company and was used for enhancing heavy oil recovery.

2.2. Reaction with heavy oil

120 grams of the heavy oil sample (Bangestan oil sample) and 3 grams of $[Et_3NH]Cl/1.5\ AlCl_3$ (X=0.6) modified with CuCl (IRAN91) were added to an autoclave and the system was heated at 95 °C for approximately 24 hrs. Upon the completion of the reaction, the system was allowed to cool down. Then, the viscosity, average molecular weights, and the asphaltene precipitation of the oil sample were measured according to the procedures described below.

2.3. Viscosity determination

Viscosity was determined using a Cannon-Fenske viscometer. It was charged with oil sample and mounted in a water bath at a constant temperature. When thermal equilibrium was achieved, the flow times were measured. The kinematic viscosity from the viscometer constant and the flow times were then computed.

2.4. Average molecular weight

The average molecular weight of the heavy oil sample was measured before and after upgrading. First 70 cc of benzene was poured in a two-wall tube and then the tube was sealed with a cork. Next, the set up apparatus was placed in an ice bath to lower the temperature of benzene. The temperature of benzene was recorded at 30-second intervals until the temperature remained unchanged. The freezing point of pure benzene was recorded as T_{f1}. The same procedure was followed using the same amount of benzene and 1-2 mgr. of the oil sample. The freezing point of the mixture was recorded as T_{f2}. Finally, the molecular weight of the oil sample was calculated according to Equation 1:

$$\Delta T_f = mK_f \tag{1}$$

where, m is the molality.

2.5. Asphaltene precipitation

The analyzer was composed of a glass boiler, a stainless steel set including filter holder, reflux distributor, an upper boiler, and a condenser. The extraction apparatus consisted of an efficient form of condenser with a coil or double surface, a reflux extractor, and a conical flask. A valve and system allowed making various stages of the analysis including deposition, filtration, washing, dissolution, and recovering of solvents. This test method specified a procedure for the determination of the heptane-insoluble asphaltene content of oil, lubricating bitumen, and crude petroleum which have been heated to a temperature of 260 °C. However, this method was a time-consuming process and seemed difficult to be used with chemicals produced in breaking and hydro treating processes.

2.6. Recovery factor

Recovery factor was measured in a free imbibition test. Initially, the porosity and permeability of the core sample were measured. The sample was a carbonate from Asmari formation and had a porosity and permeability of 18% and 54 mD respectively. Next, the sample was saturated with oil. Then, the oil saturated sample was placed in a water-filled Amott cell. The oil recovery was subsequently monitored on a daily basis.

3. Results and discussions

3.1. Effect of IRAN91 on viscosity, molecular weight and asphaltene precipitation

After oil reaction with IRAN91, the viscosity, molecular weight, and asphaltene precipitation of the heavy oil are examined; the results are presented in Table 1. The results show that IRAN91 can reduce the viscosity of heavy oil. The viscosity of the untreated oil can be reduced by 64% from 1800.2 cP to 644 cP by adding IRAN91. The average molecular weight of the treated heavy oil sample drops from the original value of 2840 to 384 gr.(gr.mol)$^{-1}$. The asphaltene content of the untreated heavy oil is 15%, while that of the treated oil is 7%.

Table 1

Changes of fluid properties in the treated oil, compared to the original values

Property	Before Treatment	After Treatment
Viscosity (cP)	1800.2	644
Molecular weight (gr.(gr.mol)$^{-1}$)	2840	384
Asphaltene precipitation (%)	15	7

3.2. Effect of IRAN91 on recovery factor

The effect of IRAN91 on the recovery factor of the free imbibition process demonstrates a significant recovery enhancement after adding the chemical compound to the heavy oil sample and using it in the Amott cell. IRAN91 improves the recovery factor from 41% to 74% which is a significant enhancement in recovery factor. The reduction in molecular weight and viscosity of the sample, results in a drop in oil density and thereby an increase in the difference between densities of the fluids will be occurred. Subsequently, this heightens the capillary effects according to Equation 2:

$$P_c = \Delta \rho g h \qquad (2)$$

where, P_c is the capillary pressure; $\Delta\rho$ stands for density difference between the phases; g and h represent gravitational acceleration and height of capillary rise respectively. Therefore, an increase in $\Delta\rho$ causes the increase in capillary pressure (P_c).According to Laplace equation of capillary pressure (Equation 3), heightened capillary effects mean greater $\sigma \times \cos\theta$ values, because r is constant.

$$P_c = 2\sigma \cos\theta / r \qquad (3)$$

where, σ is the interfacial tension and θ stands for contact angle; r represents the inner radius of capillary. Since interfacial tension (because of the viscosity drop) falls after the treatment, contact angle definitely decreases, which changes the wettability alteration toward the water-wet state. This induced water-wetness is the main reason for the observed recovery improvement.

3.3. Reaction mechanism

It can be seen that after treating oil with IRAN91, the sulfur content of the heavy oil sample is decreased. Thus, reduction of the viscosity and average molecular weight of the heavy oil might be attributed to the breakup of C-S bonds. According to the reaction of thiophenic sulfur with transition metal salts, the reaction mechanism of the upgrading and viscosity reduction of heavy oil in the presence of IRAN91 can be described as displayed in Figure 1. It is seen that the content of sulfur in heavy oil decreases. On the other hand, an increase in the amount of the saturate and aromatics of the heavy oil treated by IRAN91 can also favor the viscosity reduction of the heavy oil (Fan H F et al., 2001; Zou C J et al., 2004).

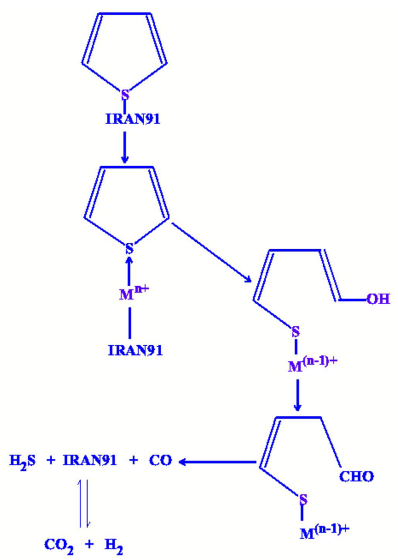

Figure 1
Reaction mechanism of IRAN91 and heavy oil

4. Conclusions

In accordance with the experimental results, the following conclusions can be drawn:

1. IRAN91 can dramatically reduce the asphaltene content, viscosity, and average molecular weight of heavy oil.
2. IRAN91 can produce considerably high recovery factors in free imbibition processes and is suitable for enhanced oil recovery purposes.
3. A complex is formed between IRAN91 and the organic sulfur in heavy oil, which weakens the C-S bonds. Thus, the average molecular weight drops, and the amount of asphaltene decreases; the amount of saturates and aromatics increases in the modified heavy oil, which results in viscosity reduction. The ionic compound has a strong attraction toward sulfur due to its cationic nature. Therefore, a high sulfur content in oil is beneficial to oil upgrading and the viscosity reduction of heavy oil.

The practical applications of IRAN91 in the petroleum industry are very appreciable. Finally, the facts that developing of this substance does not incur much initial and maintenance costs alongside its ability for recovery enhancement and asphaltene content reduction aspects, make it a proper candidate for further consideration and studies.

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Nomenclature

T_{f1}	: Freezing point of pure benzene
T_{f2}	: Freezing point of the mixture
ΔT_f	: Freezing point depression
m	: Molality
K_f	: Freezing point depression constant
P_c	: Capillary pressure
$\Delta\rho$	: Density difference between the phases
g	: Gravitational acceleration
h	: Height of capillary rise
σ	: Interfacial tension
θ	: Contact angle
r	: Inner radius of capillary

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