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STUDY ON THE INFLUENCING FACTORS OF DEMULSIFIER ON THE OIL-WATER INTERFACE VISCOELASTICITY

Abstract

Water flooding is a commonly used development method in oilfields, and the water cut of the output fluid of oil wells gradually increases with the increase of injected water in water wells. Due to the presence of natural surfactants such as gum, asphaltene and organic acid in crude oil, it is easy to form a high strength viscoelastic oil-water interfacial film and a stable emulsion. To facilitate the storage and transportation of crude oil, it is necessary to demulsify the crude oil emulsion. In this paper, the CQ crude oil was taken as the research object, and the effects of demulsifier type, concentration, demulsifier temperature and oil-water properties on the viscoelasticity of oil-water interfacial film were investigated by using rheometer and then the demulsification mechanism was explored. The results show that the lower the interfacial film strength, the better the demulsifier. In addition, with the increase of demulsifier concentration and temperature, the oil-water interfacial viscoelasticity decreases and the interfacial film strength further decreases. In general, the demulsification effect will be significantly improved with the increase of demulsifier concentration and temperature, and the dehydration effect will be better. The research results can provide theoretical guidance for the field application of demulsification.

Key words: interface viscoelasticity; interface film strength; demulsification effect; influencing factors.

Introduction

Crude oil demulsification is an important part in oil and gas gathering and transmission, and the key problem of demulsification lies in destroying the oil-water interfacial film, releasing the

dispersed-phase droplets, and achieving the effect of oil-water separation through agglomeration and flocculation [1]. The research of demulsifier has nearly 100 years of history so far. In 1914, Barnickel found that ferrous sulfate can break the emulsion and dewater crude oil emulsion, which opened a new era of demulsifier. The most widely used demulsifiers are ethylene oxide (EO) and propylene oxide (PO) block polyethers, which have excellent solubility properties, relatively simple synthesis conditions and less influence on demulsification performance by low temperature [2–4]. The demulsifier has amphiphilicity and the ability to destabilize the interfacial film. Demulsifier can be adsorbed at the oil-water interface to replace or react with natural surfactants to change the tension, viscoelasticity, and stability of the interfacial film [5].

Therefore, to obtain excellent demulsification and dehydration effects, it is necessary to understand the properties of the oil-water interfacial film and the influencing factors affecting the viscoelasticity of the oil-water interface. Interfacial rheology is an important property of oil-water interfacial film, which is closely related to the demulsification of crude oil emulsion [6–9]. Interfacial rheology mainly includes shear viscosity and viscoelasticity [10]. Due to the expandability and compressibility of the interfacial film, the strong interfacial viscoelasticity can make the film resist and quickly recover the deformation when it is damaged. Therefore, the interfacial film strength can be visually characterized [11]. In order to solve the problem, rheometer was used to measure the changes of oil-water interfacial viscoelasticity under different types of demulsifiers, concentrations, temperatures, and oil-water properties. Among them, the interfacial viscoelasticity can be characterized by two parameters, interfacial storage modulus and interfacial loss modulus, which represent the elasticity and viscosity of interfacial film, respectively.

Experiments

Materials and instruments

Dewatered crude oil and formation water were provided from CQ oilfield in China. Demulsifiers of AR101, AP301 and AR989 were purchased from Qingdao Changxing Hi-tech Development Co., Ltd. Sodium chloride (NaCl) and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) were all analytically pure and provided from Sinopharm Chemical Reagent Co. Ltd. Deionized water was self-made in the laboratory.

The interface rheological experiment was tested using the MCR 301 rheometer (Anton Paar, Austria).

Determination of interfacial viscoelasticity.

The oil-water interfacial film strength is characterized by the viscoelasticity, which was measured by the interfacial rheology system of the rheometer. Firstly, a suitable volume of water phase was added into the measuring cell to the scale line, heated to 30 °C, stabilized for 10 minutes to remove the gas. Then, the rotor was lowered to the specified height, and the interfacial distance testing system was run to ascertain the height of the rotor at point of contact with the gas-liquid interface. This was done to ensure that the edge of the rotor was in direct contact with the water surface. Finally, a specific volume of oil phase is added, and once equilibrium is reached the adsorption process at the oil-water interface, the test program is initiated to measure the changes in the interfacial elastic modulus (G') and the viscous modulus (G'') at the oil-water interface. This allows for the determination of the dynamic change in the interfacial film strength with the angular frequency.

Results and discussion

The key to breaking the emulsion is to effectively reduce the oil-water interfacial film strength. A reduction in interfacial film strength results in an increased propensity for rupture, which in turn leads to a deterioration in emulsion stability. This ultimately facilitates the breakdown of the emulsion and the subsequent dewatering process. In the following, the effects of demulsifier type, concentration, temperature and oil-water properties on the interfacial viscoelasticity are investigated, respectively.

Effect of demulsifier type on the oil-water interface viscoelasticity.

The demulsifier can replace the natural active agent after adsorbing on the oil-water interfacial film, so as to achieve the purpose of destroying the film, as shown in Fig. 1. In the blank sample (no demulsifier), an interfacial film with certain viscoelasticity was gradually formed with the increase of time. In the oil-water system where a stable interfacial film had been formed, the demulsifier was added dropwise ($t = 10$ min).

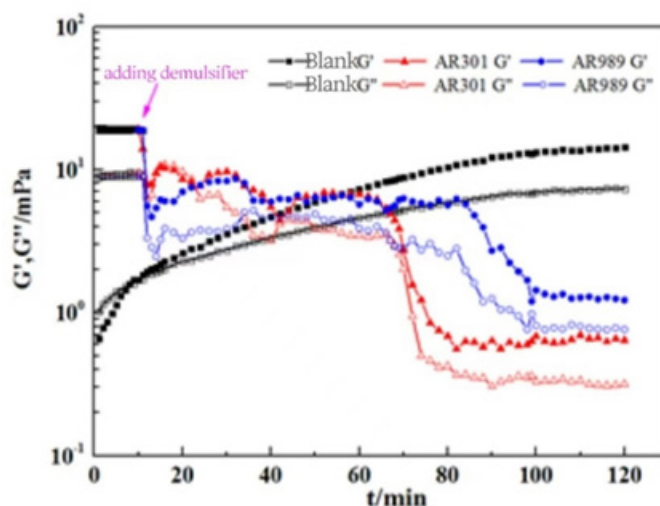


Figure1 – The change of oil-water interfacial viscoelasticity with different demulsifier

The addition of the demulsifier caused a perturbation to the stabilized system. The demulsifier spreads to the oil-water interface, destroying the rigid film formed by the natural active substance, constantly replacing the active substance and forming a looser interfacial film. When the demulsifier replaces the colloidal asphaltene completely adsorbed at the interface, the viscoelasticity of the oil-water interface decreases dramatically and gradually tends to be stabilized, and the newly formed interfacial film has a lower strength, which is more prone to rupture. Furthermore, it can also be seen that the diffusion and adsorption speed of AR301 is greater than that of AR989, and the time to reach stability is shorter and the stability value is lower. Therefore, the interfacial activity of AR301 is higher, the ability to reduce the viscoelasticity of the interfacial film is stronger and the effect of demulsification is better.

Effect of demulsifier concentration on the oil-water interface viscoelasticity.

The adsorption of the demulsifier AR101 in the interfacial film at different concentrations was explored, as shown in Fig. 2. It can be seen that, after adding the demulsifier at a concentration of 50 mg/L, the demulsifier molecules gradually diffused into the interfacial film and replaced the natural emulsifier, which made the strength of the interfacial film decrease. The decrease of the interfacial film strength was more and more obvious with the increase of the time until it stabilized. With the increase of the concentration of the demulsifier to 100 mg/L, the diffusion speed of the demulsifier was accelerated, the viscoelastic reduction rate was also obviously accelerated, and the stabilization time became shorter, and the stabilization value was even lower, which was consistent with the effect of the demulsifier.

The effect of demulsification temperature on the adsorption process of demulsifier molecules is explored, as shown in Fig. 3. It can be seen that the interfacial viscoelasticity decreased significantly with the increase of temperature, and the rate of decrease of interfacial viscoelasticity accelerated significantly. Because, the increase of temperature increased the diffusion speed of demulsifier, which

is conducive to the faster reduction of interfacial film viscoelasticity. So, the increase of temperature is conducive to improving the efficiency of demulsification.

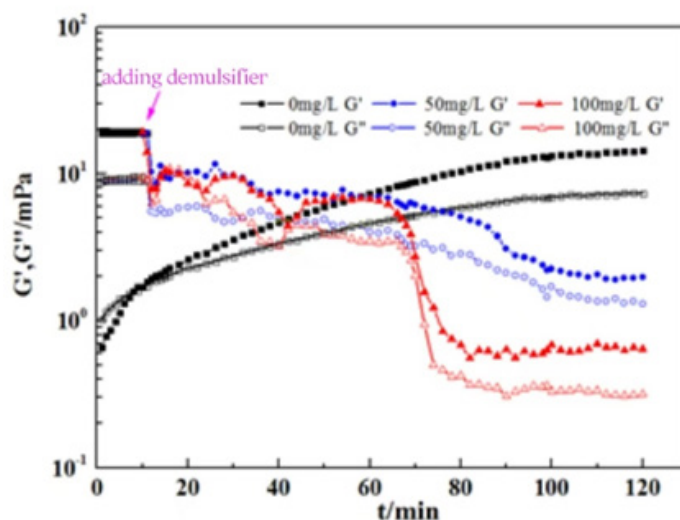


Figure 2 – as of oil-water interfacial viscoelasticity with different demulsifier concentration

Effect of demulsification temperature on the oil-water interface viscoelasticity.

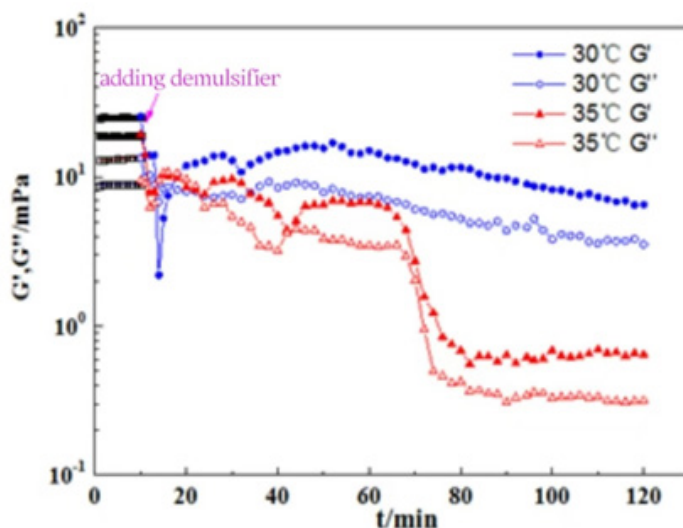


Figure 3 – Curves of oil-water interfacial viscoelasticity at different temperatures

Influence of oil-water properties on the oil-water interface viscoelasticity

As the interfacial film is formed between the oil and water phases, in addition to the demulsifier type, temperature and concentration, the oil-water properties also have a certain impact on the interfacial viscoelasticity.

(1) Gum and asphaltene content

To clarify the influence of gum and asphaltene on the oil-water interface viscoelasticity, simulated oil was prepared using crude oil and paraffin in different ratios, and the interfacial viscoelasticity of the emulsion was investigated at 30°C with different crude oil contents, as shown in Fig. 4.

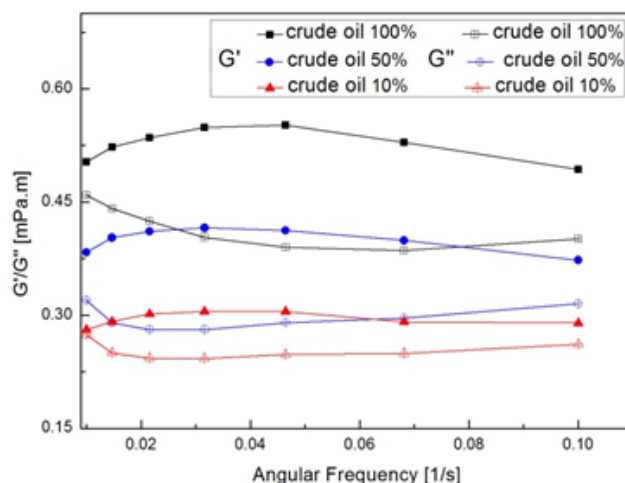


Figure 4 – The effect of colloid asphalt on interfacial viscoelasticity

With the increase of crude oil content in the simulated oil, the interfacial viscoelasticity increases and the interfacial film strength increases. This is due to the crude oil contains gum, asphaltene and other natural film-forming substances that are easy to adsorb on the oil-water interface to form a rigid film, increasing the stability of the emulsion. The higher the content of crude oil, the greater the adsorption, the greater the strength of the interfacial film formed and the stronger the stability of the corresponding emulsion.

(2) Salt ions

Salt ions in the water phase are also important factors affecting the interface viscoelasticity. The interfacial viscoelasticity of emulsions formed by simulated formation water and crude oil with different salinity was investigated, as shown in Fig. 5.

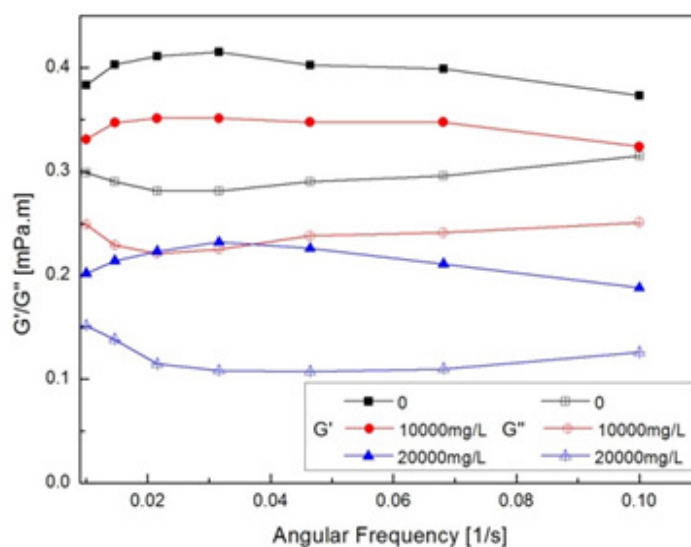


Figure 5 – Effect of salt concentration on interfacial viscoelasticity

The interfacial viscoelasticity decreases and the film strength decreases as the increase of salinity. As the higher concentration of salt ions affects the adsorption of gum and asphaltene in the oil phase on the oil-water interface, thus reducing the interfacial film strength.

In addition, the salt ion valence state also has a certain effect on the interfacial viscoelasticity, respectively test the conditions of Na^+ and Mg^{2+} presence of the oil-water interface viscoelasticity change rule, as shown in Fig. 6.

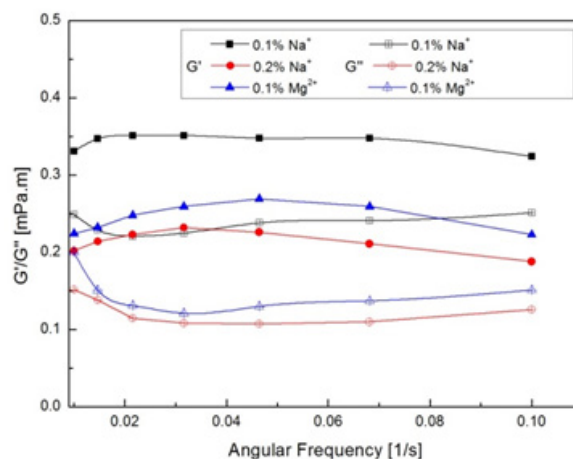


Figure 6 – Effect of ionic valence on interfacial viscoelasticity

Both Na^+ and Mg^{2+} can effectively reduce the interfacial viscoelasticity and thus the interfacial film strength. Under the same concentration, the Mg^{2+} has a higher valence than the Na^+ , which reduces the interfacial film to a greater extent. That is, high valence state salt ions can reduce the interfacial viscoelasticity more effectively than low valence state salt ions, thus effectively reducing the film strength.

Conclusion

The interfacial viscoelasticity directly reflects the interfacial film strength, the lower the interfacial film strength, the better the demulsification effect. The demulsifier with excellent effect can adsorb and replace the interfacial active material, reduce the interfacial viscoelasticity, decrease the liquid film strength, thus destroying the stability of the emulsion, and achieve better oil-water separation effect.

As the concentration of demulsifier and temperature increase, the interfacial viscoelasticity decreases, the better the effect of demulsification. In other words, increasing the dosage of demulsifier and increasing the demulsification temperature can effectively improve the demulsification effect.

In addition, the oil-water properties also have some influence on the interfacial viscoelasticity. The more gum and asphaltene content in the oil phase, the higher the interfacial viscoelasticity. The higher the concentration of salt ions in the water phase, the lower the interfacial viscoelasticity. And the high valence salt ions can reduce the interfacial viscoelasticity more effectively compared with the low valence salt ions.

REFERENCES

- 1 Ding Y., Li H., Jia J., et al. Synthesis of a demulsifier for treating crude oil-in-water emulsion through a straightforward low-temperature process. *Journal of Molecular Liquids*, 2024, vol. 410, p.125635.
- 2 Wang H., Wu Y., Wu Z., et al. Preparation of a low-temperature poly (amino acids) demulsifier and its demulsification mechanism. *Fuel*, 2024, vol. 365, p.131237.
- 3 Jiang S., Li Q., Ma Q., et al. Efficient Demulsification Performance of Emulsified Condensate Oil by Hyperbranched Low-Temperature Demulsifiers. *Molecules*, 2023, vol. 28, p. 7524.

4 Li M., Huang H., Liu J., et al. A gemini ionic liquid and its low-temperature demulsification performance in water-in-crude oil emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2023, vol. 671, p. 131696.

5 Feng X., Liu S., Liu H., et al. A low temperature demulsifier with double hydrophobic chains was prepared by a one-step method. *Geoenergy Science and Engineering*, 2023, vol. 226, p. 211573.

6 Li Z., Fuentes J., Chakraborty A., et al. Dehydration of water-in-crude oil emulsions using polymeric demulsifiers: A model for water removal based on the viscoelastic properties of the oil–water interfacial film. *Fuel*, 2023, vol. 332, p. 126185.

7 Keita A., Furitsu S., Yoshihiro Y., et al. Relationship between air-water interfacial dilational viscoelasticity and foam property in aqueous solutions of sodium alkylsulfates with different hydrocarbon chains. *Journal of Dispersion Science and Technology*, 2020, vol. 42, pp. 1218–1224.

8 Fan Y., Simon S., Sjöblom J. Interfacial shear rheology of asphaltenes at oil-water interface and its relation to emulsion stability : Influence of concentration, solvent aromaticity and nonionic surfactant. *J. Colloids and Surfaces A : Physicochemical and Engineering Aspects*, 2010, vol. 366, pp. 120–128.

9 Vincent J.V., Rosemary K.L., Peter K.K. Adsorption and molecular rearrangement of amphoteric species at oil-water interfaces. *Journal of Physical Chemistry B*, 2009, vol. 113, pp. 13788–13799.

10 Kendra A.E., Jeffrey D.M., Jonathan T.S., et al. Shear and dilational interfacial rheology of surfactant-stabilized droplets. *Journal of Colloid and Interface Science*, 2012, vol. 377, pp. 442–449.

11 Qiao X., Miller R., Schneck E., et al. Effect of surfactants on the interfacial viscoelasticity and stability of silk fibroin at different oil/water interfaces. *Journal of the science of food and agriculture*, 2023, vol. 104, pp. 2928–2936.

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МҰНАЙ – СУ АРАЛЫҚ ҚАБЫҚШАСЫНЫҢ ТҮТҚЫР СЕРПІМДІЛІГІНЕ ДЕЭМУЛЬГАТОРДЫҢ ӘСЕР ЕТУШІ ФАКТОРЛАРЫН ЗЕРТТЕУ

Аңдатпа

Мұнай кен орындарын игеруде су айдау әдісі кеңінен қолданылады, бұл кезде су айдау көлемінің ұлғаюына байланысты мұнай ұңғымаларынан алынатын өнімнің сулануы біртіндеп артады. Шикі

мұнайдың құрамында шайырлар, асфальтендер және органикалық қышқылдар сияқты табиғи беттік белсенді заттардың болуы салдарынан мұнай – су шекарасында тұтқырлығы жоғары, серпімді қабықша мен тұрақты эмульсия оңай түзіледі. Шикі мұнайды сақтау мен тасымалдауды жеңілдету үшін шикі мұнай эмульсиясын деэмульсиялау қажет. Бұл жұмыста CQ шикі мұнайы зерттеу нысаны ретінде алынды және деэмульгатор түрі, концентрациясы, деэмульгатор температурасы және мұнай – су аралық қабықшаның тұтқыр серпімділігіне әсері реометрмен зерттеліп, содан кейін деэмульгациялау механизмі арқылы зерттелді. Нәтижелер фазааралық қабықшаның беріктігі неғұрлым төмен болса, деэмульгатордың соғұрлым жақсы екенін көрсетеді. Сонымен қатар, деэмульгатордың концентрациясы мен температурасының жоғарылауымен мұнай – су аралық тұтқырлығы төмендейді және фазааралық пленка беріктігі одан әрі төмендейді. Тұтастай алғанда, деэмульгатор концентрациясы мен температурасының жоғарылауымен деэмульгаторлық әсер айтарлықтай жақсарады, ал сусыздандыру әсері жақсырақ болады. Зерттеу нәтижелері деэмульсификацияны далалық қолдану үшін теориялық басшылықты қамтамасыз ете алады.

Тірек сөздер: аралық қабықшаның тұтқыр серпімділігі, аралық қабықша пленка беріктігі, деэмульгаторлық әсер, әсер етуші факторлар.

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ИССЛЕДОВАНИЕ ФАКТОРОВ ВЛИЯНИЯ ДЕЭМУЛЬГАТОРА НА ВЯЗКОУПРУГОСТЬ НА ГРАНИЦЕ РАЗДЕЛА НЕФТЬ – ВОДА

Аннотация

Заводнение является широко используемым методом разработки на нефтяных месторождениях, и обводненность выходной жидкости нефтяных скважин постепенно увеличивается с увеличением закачиваемой воды в водяные скважины. Из-за присутствия в сырой нефти природных поверхностно-активных веществ, таких как смола, асфальтены и органические кислоты, легко образуется высокопрочная вязкоупругая пленка на границе раздела нефть – вода и стабильная эмульсия. Для облегчения хранения и транспортировки сырой нефти необходимо деэмульгировать эмульсию сырой нефти. В этой статье сырая нефть CQ была взята в качестве объекта исследования, и влияние типа деэмульгатора, концентрации, температуры деэмульгатора и свойств нефти – воды на вязкоупругость пленки на границе раздела нефть – вода было ис-

следовано с помощью реометра, а затем был исследован механизм деэмульгирования. Результаты показывают, что чем ниже прочность пленки на границе раздела нефть – вода, тем лучше деэмульгатор. Кроме того, с увеличением концентрации деэмульгатора и температуры вязкоупругость на границе раздела нефть – вода уменьшается, а прочность межфазной пленки еще больше уменьшается. В целом эффект деэмульгирования будет значительно улучшен с увеличением концентрации деэмульгатора и температуры, а эффект дегидратации будет лучше. Результаты исследований могут предоставить теоретические рекомендации для полевого применения деэмульгирования.

Ключевые слова: вязкоупругость границы раздела, прочность пленки границы раздела, деэмульгирующий эффект, влияющие факторы.

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