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Demulsification performance, behavior and mechanism of different demulsifiers on the light crude oil emulsions

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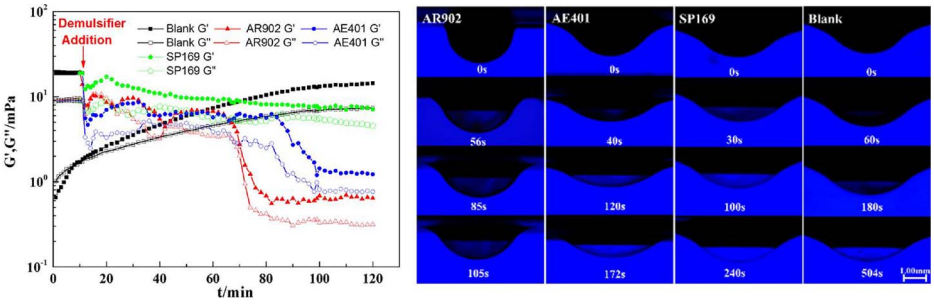
GRAPHICAL ABSTRACT

The storage modulus and loss modulus of water-oil interface and microscopic changes during the oil film rupture process with 100 mg/L demulsifiers at 40 °C.



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ABSTRACT

Chemical demulsifiers were widely applied for demulsification of crude oil emulsions which were generally formed with natural stabilizers during the extraction. Based on our previous study of the light crude oil emulsions stability, the demulsification performance of four classes of nonionic poly(ethylene oxide) poly(propylene oxide) copolymer demulsifiers and sodium dodecyl sulfate (SDS) as well as their dynamic demulsification process on the W/O light crude oil emulsion were analyzed by the multiple light scattering method. The demulsification mechanism of these demulsifiers were illuminated by the measurement of dynamic interfacial tension (IFT), dynamic interfacial viscoelasticity, rupture rate and microscopic changes of oil film by single droplet method. The results have shown that demulsification performance doesn't depend on IFT, though effective demulsifiers could have a lower IFT around 1 mN/m. Multiple light scattering data and dynamic IFT clarified the demulsification process of efficient demulsifiers, quick diffusion and adsorption of demulsifiers, palpable change in interfacial property, droplet coalescence and sedimentation. The capacities of demulsifiers to penetrate into the interface and to decrease the interfacial viscoelasticity were the dominating demulsification mechanisms. The quantitative interpretation of multiple light scattering data associated with the dynamic IFT and interfacial viscoelasticity illuminated the demulsification mechanism of different demulsifiers. The rupture rate and dynamic rupture process of the oil film between the aqueous phases also vividly showed the differences in demulsification process. The nonionic demulsifiers AR902 and PR929 with aromatic groups has the highest speed and best performance due to the similar aromatic groups with those in asphaltenes, which produced the

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least stable oil film. This study provides a valuable guideline for the selection of demulsifier for light crude oil emulsions and enhanced demulsification mechanism studies.

1. Introduction

Demulsification process was of great significance before transportation or refinery in order to decrease the energy cost, pipeline corrosion and scaling since emulsion formed naturally during crude oil extraction in which asphaltenes, resins, wax and clay act as emulsifiers [1–3]. Chemical, electrical, and mechanical methods are commonly used in order to promote water and oil phase separation [2,4,5]. Chemical demulsifiers (e.g. ionic and nonionic demulsifying surfactants, bio-demulsifiers and recently reported Janus or magnetic particles) were the most economic and widely applied methods for the demulsification [6–10]. However, due to the complicated components of the oil, the principles for the selection of effective demulsifiers were still in dimness [1,2], which resulted in a time consuming screening of demulsifiers process for different crude oil. Furthermore, though some researchers found that demulsification was closely related with the alteration of the interfacial rheology [11–14], a detailed and quantitative evaluation on its mechanism has not been reported. Therefore, a clarified demulsification mechanism and demulsifier selection principles for light crude oil emulsions are of great importance for the guideline of the application of chemical demulsifiers.

In our previous study, five W/O light crude oil emulsions from CQ oilfield were studied and the main stabilizing mechanism was concluded that the strong viscoelastic interfacial network with asphaltenes inhibited the coalescence of droplets and enhanced the emulsion stability [15]. Meanwhile, the solubility of asphaltenes and viscosity of crude oil might also played some role in the stabilizing mechanism [15]. Overall, the presence and concentration of the asphaltenes in the oil were the dominating factors of the emulsion stability. The comparison among the interfacial rheological properties of the oil samples emphasized the importance of high interfacial viscoelasticity in the emulsion stability [15].

In this study, we focused on the most stable emulsion E5 in the light crude oil emulsions, and the demulsification performance of four classes of nonionic poly(ethylene oxide) poly(propylene oxide) copolymer demulsifiers and SDS were evaluated and compared. The dynamic demulsifying process and mechanism were analyzed in detail by the multiple light scattering method, IFT, rheology of the interface, oil film rupture rate and microscopic changes. The quantitative interpretation of multiple light scattering data associated with the dynamic IFT and interfacial viscoelasticity illuminated the demulsification mechanism. Based on these results, the correlation between the demulsifier chemical structure and its demulsification performance of light oil emulsion were proposed and explained. The conclusions provided a valuable guideline for the selection of demulsifier for light crude oil emulsions and enhanced understanding of its demulsification mechanism.

2. Material and methods

2.1. Material

Chemical demulsifiers AR902, PR929, AE401, and SP169 were purchased at Changxing Chemicals Co. (Shandong, China), and sodium dodecyl sulfate (SDS) was purchased at Sinopharm. China, (AR, purity ≥ 99.9%). Those characteristic demulsifiers were selected according to the mass screening. The chemical structures of the demulsifiers were illustrated in Fig.1. Deionized water was obtained by double distillation in the lab (resistance = 18.4 MΩ cm). The dehydrated and degassed light crude oil named as X5 from CQ oilfield, China was used in this research. The basic properties of these oils could be referred in our previous study [15].

2.2. Methods

2.2.1. Preparation of artificial emulsions and demulsifier solution

The emulsions E5 were prepared with the oil samples X5 respectively and deionized water [15]. The crude oil in a beaker covered with cap was first stirred at 6000 rpm for 3 min by IKA Eurostar 20 high speed digital electronic stirrer (IKA Works GmbH & Co., Staufen, Germany) to avoid any early formed aggregation or precipitation. 60mL of the pre-treated oil sample and 40 mL deionized water was added in the beaker (preheated at 40 °C for 30 min), then stirred the mixture at 200 rpm for 1 min at 40 °C by the electronic stirrer to form the W/O emulsion. 20 mL of the freshly prepared emulsion was put into the test bottle for further investigation by Turbiscan Stability Analyzer.

The 10,000 mg/L demulsifier original solution was prepared with certain amount of demulsifier and 1:1 v./v. methanol and deionized water. In the process of demulsification evaluation, 20 mL emulsion E5 were mixed with 200 μL 10,000 mg/L demulsifier solution at 40 °C, thus, the concentration of the demulsifier in the emulsion was 100 mg/L. In the case of blank, the same amount of solvent (1:1 v./v. methanol and deionized water) were mixed with the emulsion.

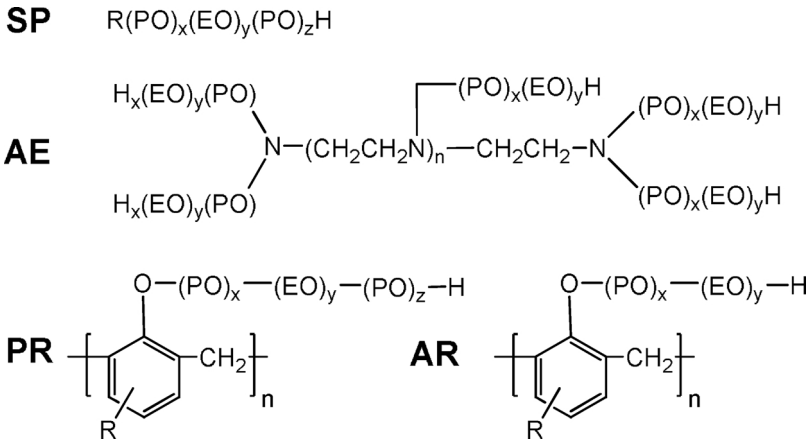

Fig. 1. Chemical structure of demulsifiers AR, PR, AE and SP classes (x, y, z and n are independent integrates for different demulsifiers, and R represents the alkyl group).