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Study on the relationships between the oil HLB value and emulsion stabilization

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In order to study the relationship between the HLB value of oil and emulsion stabilization, the optimal formation of emulsification system was determined, and then, the properties of emulsion, such as particle size, stability, interfacial tension and zeta potential, were tested by laser particle analyzer, stability analyzer, and interfacial tensiometer. Experimental results showed that the optimal ratio of emulsification was Tween 80 : Span 80 = 5 : 5. Meanwhile, when the HLB value of the emulsification system was close to that of oil, the emulsion exhibited the best stability. This phenomenon is due to the fact that when the HLB values are close, the surfactant molecules are arranged more closely on the oil–water interface, leading to smaller sized emulsion droplet, which is conducive to emulsion stability. This study provides new insights into the effective adjustment of emulsion stability.

1. Introduction

With the development of society, petroleum is consumed in a large quantity. Many scientists recognized this problem and focused to develop new energy resources, such as solar energy, wind energy, and tidal energy. Considering the progress in the new energy field, it will take a long time to replace petroleum; therefore, it is necessary to enhance oil recovery.

Nowadays, there are a lot of ways to enhance oil recovery, such as polymer flooding, surfactant flooding, alkaline flooding, and microbial flooding.^{1–3} In polymer flooding, improper injection blocks formation pores and causes reservoir damage.⁴ Alkali flooding can enhance oil recovery *via* generating surfactants through the reaction with petroleum acid.⁵ However, alkali can cause serious corrosion to pipelines. Although microbial flooding has great performance, the high cost limits its large-scale use.^{6,7}

Owing to its low cost and great performance, surfactant flooding is attracting people's interest.^{8–11} Surfactant flooding enhances oil recovery *via* four main aspects: interfacial tension reduction, wettability alteration, foam generation, and emulsification.^{12,13} Several petroleum researchers have conducted excellent studies on surfactant flooding. Wu *et al.* investigated the possibility of sodium dodecyl sulfate (SDS) to enhance oil recovery. The core flooding experimental result showed that 0.2 wt% SDS can enhance oil recovery by 4.43%.¹⁴ Jia *et al.* studied SDS and 1-dodecyl-3-methylimidazolium chloride compound system's enhanced oil recovery ability.¹⁵ The experimental result showed that the combined system can enhance oil recovery by

10% under high temperature and saline reservoir. Zhang *et al.* using acid amidopropyl betaine (EDAB) and SDS constructed a compound surfactant system.¹⁶ Core flooding experiment was carried out under the conditions of X reservoir. Experimental results showed that the compound surfactant system have great oil displacement performance. The enhanced oil recovery ability of surfactant flooding and subsequent water flooding reached 22.6%. Recently, nanoparticles have attracted considerable attractions from petroleum researchers.^{17,18} Cheraghian formed a nano-TiO₂/SDS compound surfactant system.¹⁹ Compared with SDS, this compound surfactant system enhanced oil recovery by 4.85%.

In surfactant flooding, emulsification is the most important among the above-mentioned four enhanced oil recovery mechanisms.²⁰ Now surfactant flooding used in oilfields have good performance;²¹ however, their application range is narrow and only suitable for specific oilfields and it needs a long time to adjust for different reservoir condition. How to obtain the surfactant's screening standard for surfactant flooding with good emulsification ability is of great significance for the further use of surfactant flooding in oilfield.²² HLB value was proposed by W. C. Griffin in 1949.²³ It is used to represent the balance of the magnitude and strength of hydrophilic and lipophilic groups in molecules.²⁴ HLB value can be used to filter surfactant systems and crude oil with good matching relationship? According to the literature, a series of different HLB value surfactant solutions were prepared and emulsion was formed with crude oil. When the stability of the emulsion is the best, the HLB value of the corresponding surfactant is the HLB value of the crude oil.

In this study, the HLB value of crude oil was determined. Tween 80 and Span 80 were used to form various emulsification systems with different HLB values. Experiments such as

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Table 3 The formation of simulated formation water

Ionic	Na ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Total salinity
Concentration (mg L ⁻¹)	1394.375	6.08	120.24	1010.325	18.0113	3706.965	6255.996

Table 4 Composition and HLB value of emulsification systems

Span 80 : Tween 80	Span 80 (wt%)	Tween 80 (wt%)	HLB value
2 : 8	0.06	0.24	12.86
4 : 6	0.12	0.18	10.72
5 : 5	0.18	0.12	9.65
8 : 2	0.24	0.06	6.44
9 : 1	0.27	0.03	5.37

2.7. Zeta potential

The zeta potential of emulsion was measured by Zetasizer Nano (Malvern, UK). The experiment temperature was 50 °C.

2.8. Interfacial tension

Oil-water interfacial tension between various emulsification systems and crude oil was measured at 50 °C based on spinning drop method using a TX-500C interfacial tensiometer (Bowing Industry Corp., USA) with a measuring range of 10⁻⁵ to 10² mN m⁻¹.

3. Result and discussion

3.1. HLB value of crude oil

Fig. 3 depicts the morphology image of the dewatering of emulsions with different HLB values. When the HLB value of

compound system reached 9.65, the emulsion had best stability after 90 min. At the same time, Fig. 4 shows the dewatering rate of emulsions with the variation in the HLB value of the compound system. It can be clearly seen from Fig. 4 that with the increased in the HLB value of compound system, the dewatering rate first decreased and then increased. When the HLB value of compound system was 9.65, the dewatering rate was the

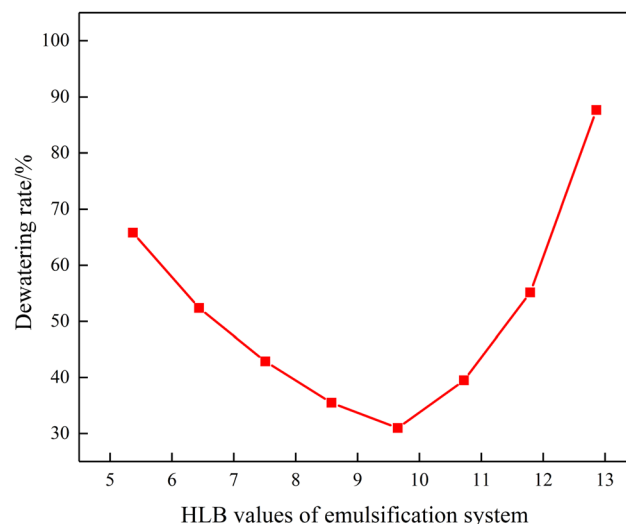


Fig. 4 Dewatering rate of emulsion with the variation of HLB values of compound system after 90 min ($T = 50$ °C).

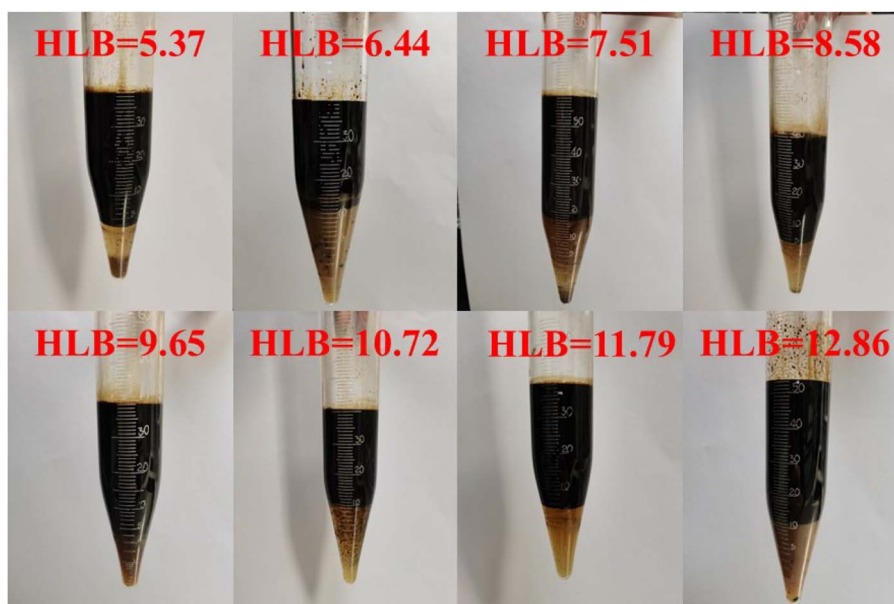


Fig. 3 Morphology images of emulsions at different HLB values after 90 min ($T = 50$ °C).



lowest. Based on the experimental method and HLB value of crude oil proposed by He *et al.*,²⁵ the HLB value of crude oil used in this study was 9.65.

3.2. Stability comparison of emulsions

Fig. 5 shows the emulsion stability as a function of the HLB values of emulsification systems using a TURBISCAN Lab Expert stability analyzer. The TSI curves of four emulsions with different HLB values of emulsification systems increased with time. As we all know, emulsion is a thermodynamically unstable system.²⁶ This phenomenon means these four kinds of emulsions were demulsified over time. When the experiment was completed, the TSI values of these four emulsions were 5.5, 3.4, 1.7, 2.7, and 2.1, respectively. Compared with other emulsions, the emulsion formed by the emulsification system with HLB = 9.65 was more stable. From the perspective of HLB value, when

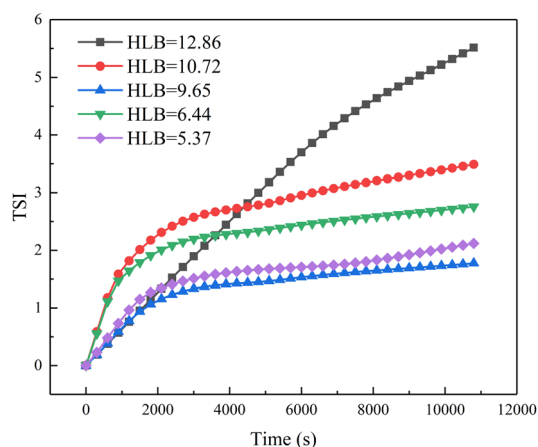


Fig. 5 TSI curves of emulsion under different emulsification system's HLB value ($T = 50\text{ }^{\circ}\text{C}$).

the HLB value of crude oil and emulsification system is close, the emulsion has better stability. Fig. 6 shows the morphology images of emulsion as a function of the HLB values of emulsification systems. It can be clearly seen that the formed emulsion was a water-in-oil emulsion. At the same time, when the HLB value of the emulsification systems reached 9.65, the emulsion has smaller particle size. Because the emulsion is water-in-oil emulsion and Span 80 in the emulsification system is a lipophilic surfactant, when the proportion of Span 80 in the emulsification system increases, it exhibits good emulsifying effect.

3.3. Droplet size distribution of emulsions

The droplet size of emulsions is critical to the emulsion stability.²⁷ Fig. 7 shows the droplet size distributions as a function of the HLB values of the emulsification systems. The average droplet size of HLB = 5.37, HLB = 6.44, HLB = 9.65, HLB = 10.72, and HLB = 12.86 were 475.9 nm, 333.4 nm, 319.7 nm, 659.7 nm, and 1276.1 nm, respectively. Meanwhile, the emulsion formed by emulsification system with HLB = 9.65 has narrow particle size distribution range. The same results as TSI experiment, the average droplet size was smallest when the HLB value of the emulsification system was 9.65. That is, when the HLB value of the emulsification system is close to the HLB value of oil, the average droplet size is smallest and the particle size distribution is narrower. When an appropriate HLB value emulsifier existed, crude oil can form a relatively stable emulsion. Meanwhile, compared with low HLB value emulsification system, the average droplet size of high HLB value emulsification is higher. This phenomenon can be explained as follows. When the HLB value of the emulsification system is high, the proportion of Tween 80 is high. On the oil-water interface, the volume and cross-sectional area of Tween 80 are larger than Span 80, so the emulsion has a larger radius of curvature, which means larger average droplet size. In addition, due to different

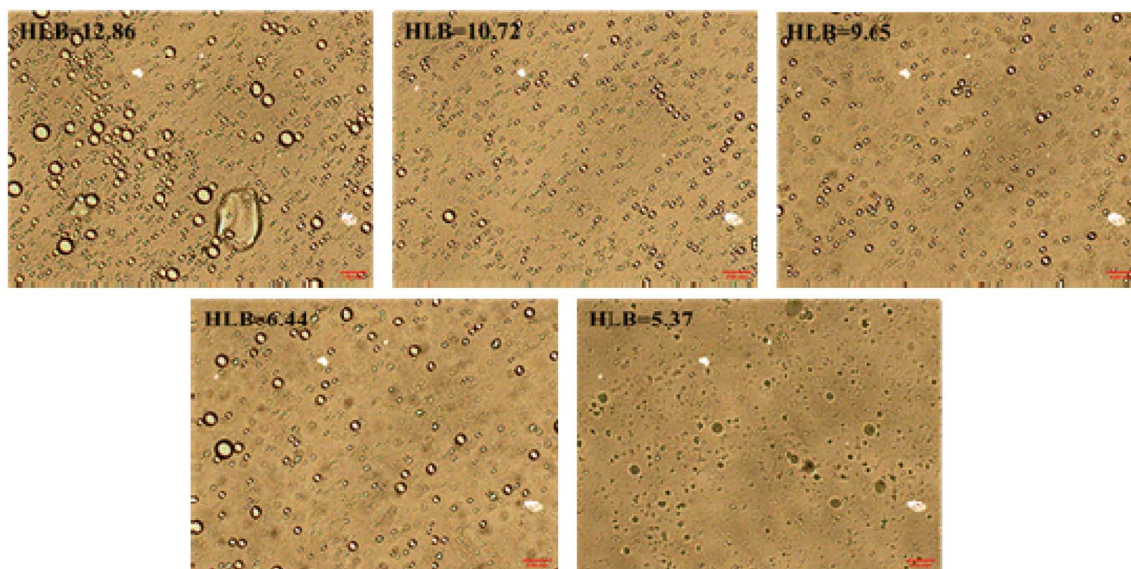


Fig. 6 Emulsion morphology images under different emulsification system's HLB value.



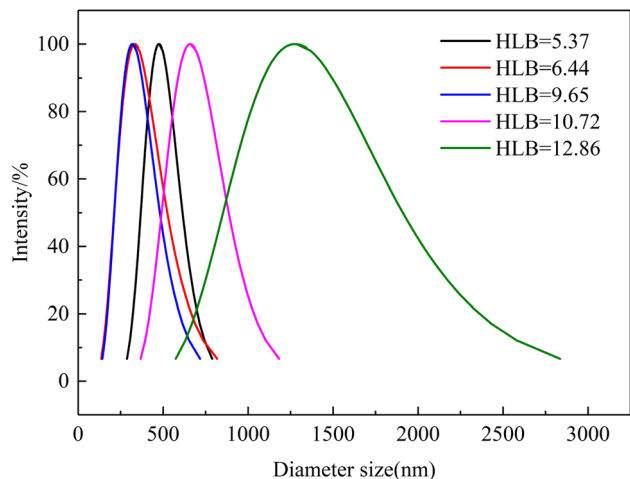


Fig. 7 Droplet size distributions of emulsion as a function of emulsification system's HLB value ($T = 50\text{ }^{\circ}\text{C}$).

molecular sizes of Tween 80 and Span 80, the adsorption kinetics on the oil–water interface are different.²⁸ During the homogenization process, Span 80 (smaller molecular weight) has faster adsorption speed than Tween 80 (higher molecular weight).

3.4. Effect of HLB value on emulsion's zeta potential

Zeta potential represents the surface electrical properties of suspended particles, and the value can be used to determine electrical attraction or repulsion between the particle and surface.^{29,30} Xu *et al.* proposed zeta potential is one of the main factors affecting the emulsion stability.³¹ In this part, the zeta potential of emulsion under different emulsification systems was measured.

Fig. 8 shows the zeta potential of emulsion as a function of the HLB values of emulsification systems. The zeta potential of the emulsion was negative irrespective of the HLB value of the

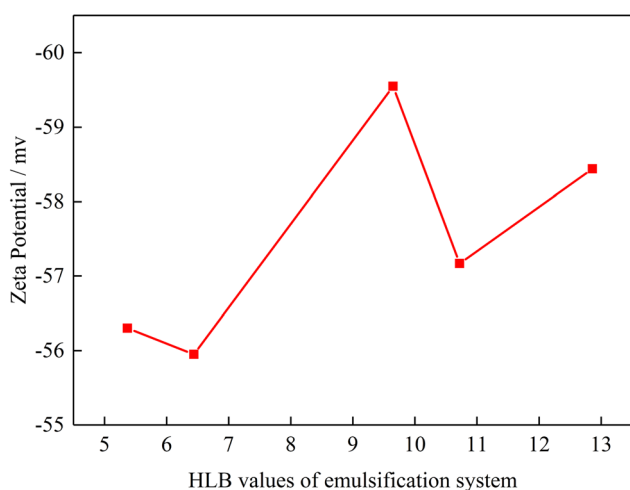


Fig. 8 Zeta potential of emulsion as a function of emulsification system's HLB value ($T = 50\text{ }^{\circ}\text{C}$).

emulsification system. The absolute value of emulsion's zeta potential was in the order of $\text{HLB} = 9.65 > \text{HLB} = 12.86 > \text{HLB} = 10.72 > \text{HLB} = 5.37 > \text{HLB} = 6.44$. This result indicates when the HLB value of the emulsification system is close to the HLB value of oil, the absolute value of emulsion's zeta potential is highest. Meanwhile, high HLB value emulsification system has high absolute value of emulsion's zeta potential. This phenomenon occurred due to the presence of polyoxymethylene in emulsification system. When polyoxymethylene exists, hydrogen bonding is formed between polyoxymethylene and water and then hydroxide is generated. Therefore, when polyoxymethylene concentration is increased, the absolute value of emulsion's zeta potential is increased. When zeta potential is largest, the emulsion droplets have the best stability. However, when the polyoxymethylene concentration increased to a certain value, the polyoxymethylene gets closer to emulsion surface, which produces a shielding effect, and the zeta potential value decreases due to crowding effect.

3.5. Effect of HLB value on interfacial tension

Interfacial tension plays an important role on the emulsion stability.^{32,33} In order to explore the effect of the HLB value of the emulsification system on surface tension, interfacial tension experiments were conducted. The experimental results are shown in Fig. 9. With an increase in the HLB value of the emulsification system, interfacial tension first decreased and then increased. It reached a minimum value at $\text{HLB} = 9.65$ ($3.99 \times 10^{-1} \text{ mN m}^{-1}$). Combined with emulsion stability experiments, the interfacial tension experiment can be explained as follows. When an emulsification system has a suitable HLB value, surfactant molecules can arrange in an oil–water interface film more reasonably, which reduces the free energy of the oil–water interface film and can improve emulsion stability significantly. When the HLB value of the emulsification system increases, the proportion of Tween 80 in the system increases and the lipophilicity of the system is stronger, and hence it has a lower

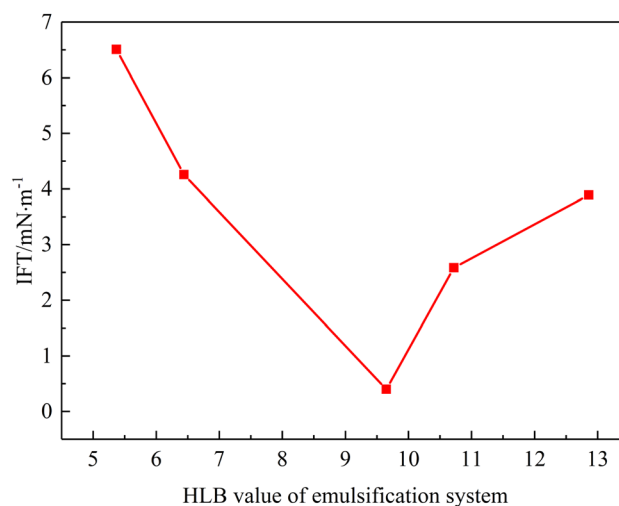


Fig. 9 Interfacial tension of emulsion as a function of emulsification system's HLB value ($T = 50\text{ }^{\circ}\text{C}$).



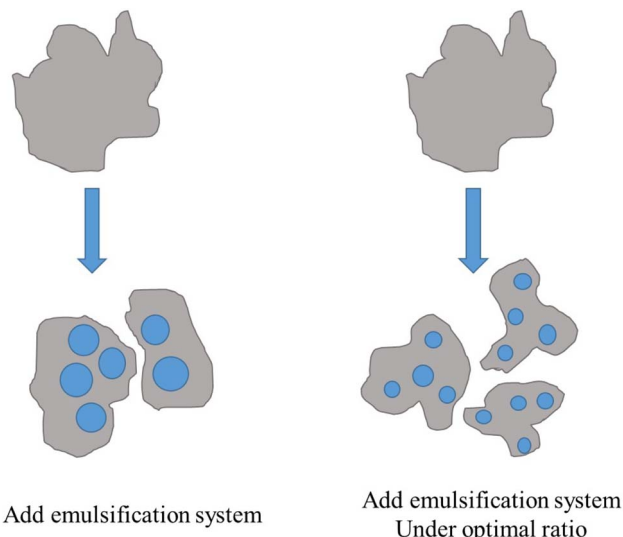


Fig. 10 The mechanism of HLB value on emulsion stability.

interfacial tension compared with an emulsified system with a low HLB value.

3.6. The mechanism of HLB value on emulsion stability

Based on the above results, the mechanism of HLB value on emulsion stability is illustrated in Fig. 10. When a surfactant interacts with oil, the surfactant molecules gather on the oil–water interface film spontaneously, reducing the interfacial tension and improving emulsion stability. When the HLB value of the emulsification system is close to that of crude oil, surfactant molecules arranged more closely on oil–water interface film, which leads to greater interfacial film strength. At the same time, the electrical repulsion between emulsion droplets is increased. Therefore, emulsion has better stability when the HLB value of the emulsification system is close to that of oil.

4. Conclusion

Various emulsification systems were constructed using Tween 80 and Span 80 with different ratios. The HLB value of crude oil was 9.65. The relationship between the HLB value of oil and emulsion stability was proposed. When the HLB value of the emulsification system is close to that of oil, surfactant molecules are arranged more closely on the oil–water interface, leading to smaller sized emulsion droplet. At the same time, electrical repulsion between emulsion droplets is increased, through these aspects, emulsion had better stability.

Conflicts of interest

No conflict of interest exists in the submission of this manuscript, and manuscript is approved by all authors for publication. I would like to declare on behalf of my co-authors that the work described was original research that has not been published previously, and not under consideration for publication

elsewhere, in whole or in part. All the authors listed have approved the manuscript that is enclosed.

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