

Effects of Emulsifier on Monolayer Structure and Evaporation Resistance

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Summary: In present paper, five non-ionic emulsifiers with different hydrophobic and hydrophilic groups were synthesized to discuss effects of emulsifier on monolayer structure and evaporation resistance. After testing the evaporation resistance, the dispersion rate and stability of the monolayers prepared from different emulsifiers were characterized. It could be inferred that compared with dispersion rate, stability seemed to be the more important factor which might control the monolayer performance, and emulsifier with small volume and strong interaction force between chains might be beneficial to decrease water evaporation.

Keywords: monolayer; emulsifier; dispersion; stability; evaporation.

Introduction

Though spreading monolayer at water/air surface had been thought to be an effective way to reduce water evaporation in open storage since 1950s, it had not been widely used in practical project. The reason of such condition is mainly due to the easily damaged properties of monolayer by wind, impurities and bacteria [1]. Methods have been tried to dissolve this problem by selection of better monolayer materials and improved application methods [2-4]. For example, amphiphilic polymers, such as poly(vinyl stearate) and poly(lauryl methacrylate), have been thought to be the promising materials due to their high molecular weight [4-5]. However, the low spreading rate of the polymer limits its extensive usage.

It is believed that the formation process might have great impact on monolayer structure and performance. Gentle discussed the relationship between spreading rates and monolayers performance with two different emulsifier Brij 78 and Tween 60 [6]. It was believed the improvement in spreading rate from Brij 78 lead to the high water evaporation resistance. According to early research, the emulsifier might exist in the final monolayer structure for its amphiphilic property, which had been proved by adsorption kinetics research of C₁₀E₈ [7]. So, the emulsifier might influence the monolayer performance not only from the monolayer dispersion, but in a more complicated way. However, to our knowledge, there is scarcely any systematic research about the relationship between the emulsifier structure and monolayer performance until now.

In this paper, five non-ionic emulsifiers with different hydrophobic and hydrophilic groups as shown in Fig. 1 were synthesized and the monolayer was formed by spraying mixture powder of

1-octadecanol and each emulsifier separately ($W_{1\text{-octadecanol}}/W_{\text{emulsifier}}=5/1$). The mixture powder was selected because there was less loss of materials dissolving into the bulk water compared with monolayer from emulsion, and it would be more accurate for characterization. The purpose of this paper is to reveal the effects of emulsifier on monolayer structure and evaporation resistance.

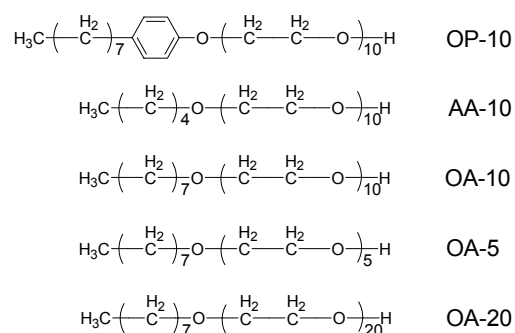


Fig. 1: Structure of non-ionic emulsifiers.

Results and Discussion

Effect of Emulsifier Structure on Evaporation Resistance

Emulsifiers (OP-10, OA-10 and AA-10) with same hydrophilic group were selected to discuss the influence of hydrophobic structure on water evaporation resistance. The results shown in Fig. 2 revealed that compared with the control experiment (without monolayer covering), all the monolayers could reduce water evaporation and the hydrophobic structure had great influence on monolayer performance. Compared with monolayer from OA-10, the amount of water evaporation from OP-10 was

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three times larger.

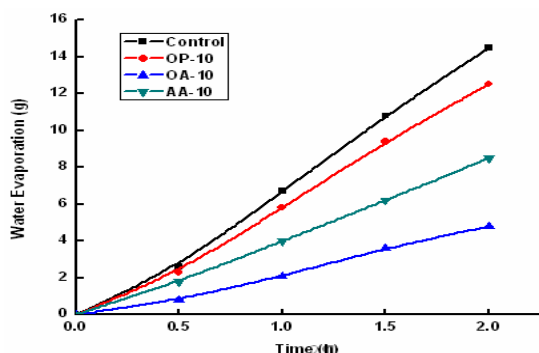


Fig. 2: Effect of emulsifier hydrophobic group on water evaporation

For the emulsifiers (OA-5, OA-10 and OA-20) with same hydrophobic group, but different hydrophilic structure (different amount of $-OCH_2CH_2-$ number), the results in Fig. 3 showed that the monolayers prepared from OA-5 and OA-10 had the same performance on evaporation resistance. Only when the $-OCH_2CH_2-$ number reached to 20, the water evaporation increased and the amount was about two times larger than monolayer prepared from OA-10. The reason of different monolayers performance from different hydrophobic and hydrophilic groups would be discussed in the following parts.

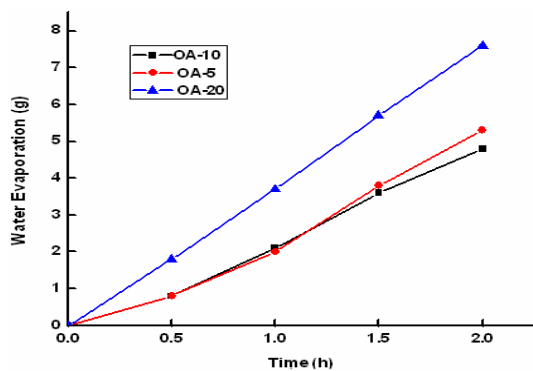


Fig. 3: Effect of emulsifier hydrophilic group on water evaporation

Effect of Emulsifier Structure on Monolayer Dispersion

Results of monolayer dispersion prepared from emulsifiers with different hydrophobic groups as shown in Fig. 4 revealed that the monolayer prepared from OP-10 had the quickest dispersion rate, but the monolayer would collapse after reaching the peak surface pressure. For OA-10 and AA-10, the dispersion rate was lower but more stable compared with OP-10. According to Gentle's results, the quicker

dispersion rate might lead to high water evaporation resistance [6]. However, the low surface pressure after collapsing which meant loose structure would lead to low evaporation resistance. Considering the monolayer performance, in present research the low surface pressure seemed to be the main control factor. If monolayers prepared from OA-10 and AA-10 was compared, the high dispersion rate and surface pressure might be the reason of the lower water evaporation.

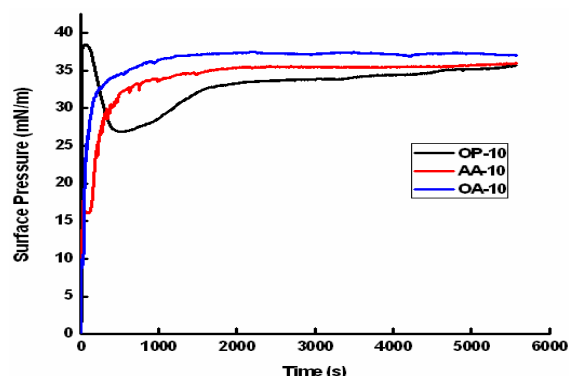


Fig. 4: Effect of emulsifier hydrophobic group on monolayer dispersion

For emulsifiers with different hydrophilic groups, as shown in Fig. 5, the hydrophilic structure seemed hardly had any effect on monolayer dispersion rate and the final surface pressure. Considering the water evaporation results in Fig. 3, it was hard to explain the obvious different performance between monolayers from OA-10 and OA-20. There might be some other mechanism for the hydrophilic structure to influence the monolayer performance.

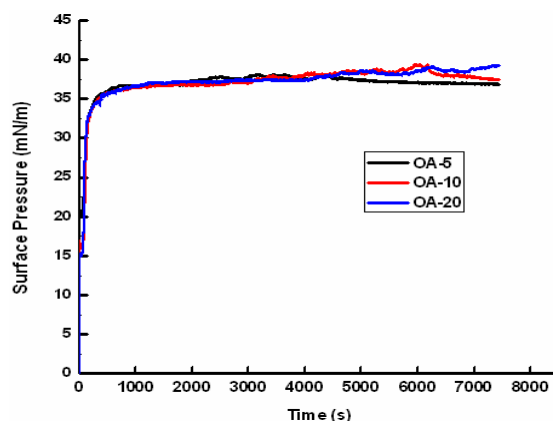


Fig. 5: Effect of emulsifier hydrophilic group on monolayer dispersion.

Effect of Emulsifier Structure on Monolayer Stability

Besides dispersion rate, monolayer stability was thought to be another important factor which could affect the monolayer performance. The stability was characterized by surface pressure measurement under oscillation condition. From Fig. 6, it was indicated that monolayers prepared from OA-10 and OA-5 might have the most stable structure, because the peak and valley surface pressure kept stable during the oscillation. But for OP-10 and OA-20, the peak value of the surface pressure became larger and the valley peak value became lower during the oscillation, which meant the unstable structure of the monolayer. The unstable structure of monolayer from OA-20 might be the reason of the lower evaporation resistance compared with OA-10, though both of the

monolayer had the same dispersion process.

Mechanism of Emulsifier on Monolayer Structure and Performance

In the above mentioned results, it seemed the mechanism of emulsifier on monolayer structure and performance was more complicate than it had been thought. For example, monolayer from OP-10 had quicker dispersion rate, but higher water evaporation compared with monolayer from OA-10, and monolayer from OA-10 and OA-20 had the same dispersion rate, but different performance. When the results from monolayer dispersion and stability were considered together, it could be inferred that the stability might be the more important factor which would influence the monolayer performance.

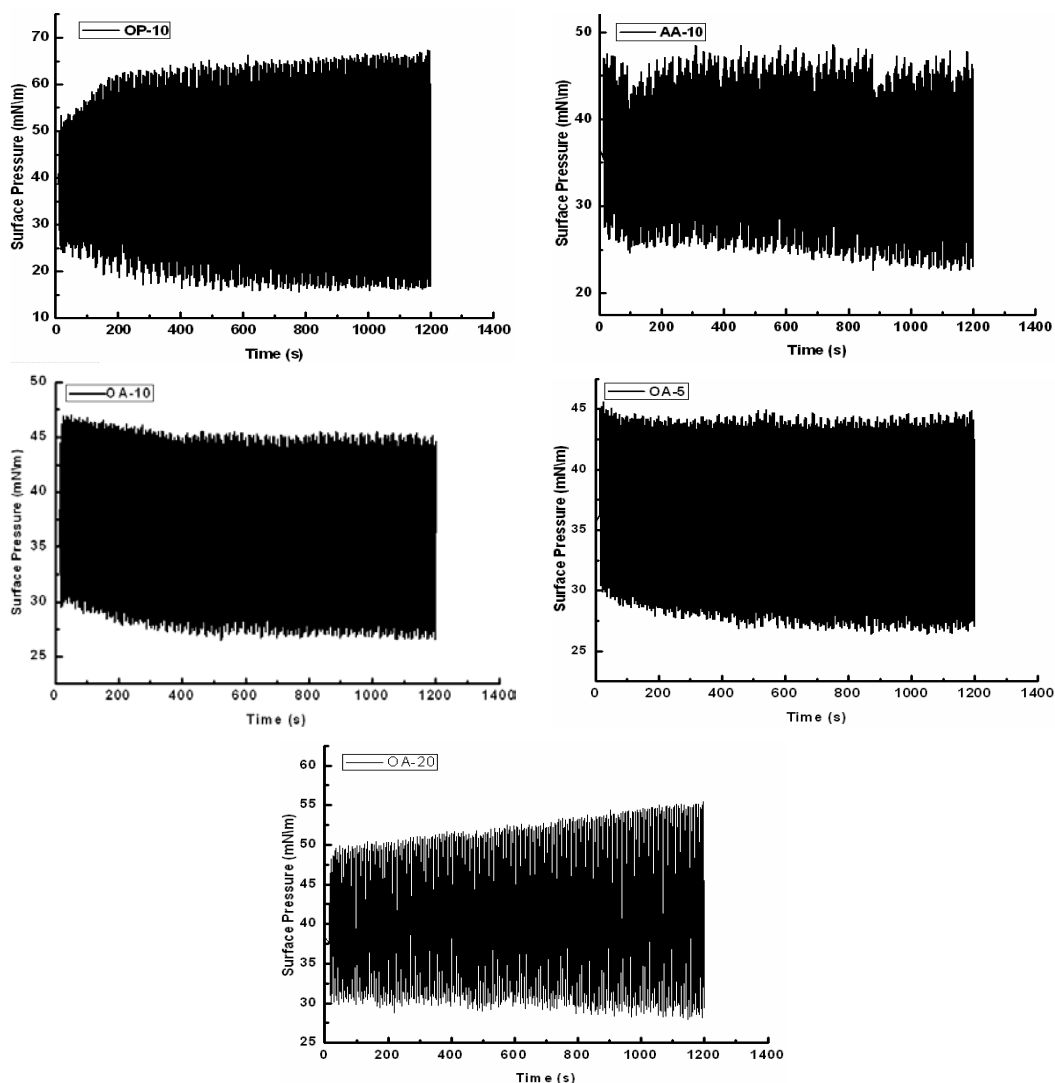


Fig. 6: Effect of emulsifier structure on monolayer stability.

Considering that the monolayer was formed by emulsifier and 1-octadecanol together, the volume of emulsifier head group might influence the monolayer structure. As revealed by Marszall, the volume of hydrophilic group would increase as the $-OCH_2CH_2-$ number increase, especially when the number was larger than 10 [10]. The large volume of OA-20 (20 $-OCH_2CH_2-$ groups) and OP-10 (benzene ring) would lead to looser and more unstable monolayer structure compared with the other emulsifiers as shown in Fig. 7. According to Henry's research, the long alkyl chain with strong van der Waals force was beneficial to monolayer surface packing density and stability, which might be the main reason of the high evaporation resistance from OA-10 [11].

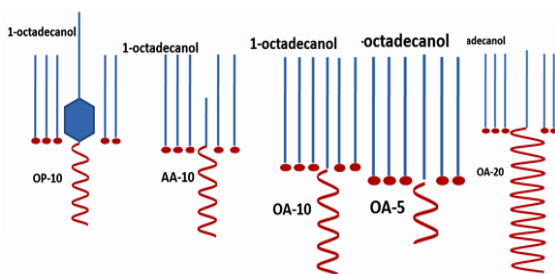


Fig. 7: Module of emulsifier and monolayer structure.

Experimental

Materials

1-octadecanol ($C_{18}OH$) was purchased from Fluka and purified by recrystallizing with hexane. Five emulsifiers OP-10, OA-10, OA-5, OA-20 and AA-10 were synthesized in our lab by addition reaction of ethylene oxide with different alcohol or phenol. All the emulsifiers were characterized by GPC and H-NMR, and the purity >95%.

Water Evaporation Measurement

The water evaporation was tested by the method as early research described [3]. Desiccant of lithium chloride in round vessel was positioned on the monolayer surface at the distance of 5mm. The water evaporation amount was tested by the change of desiccant with or without monolayer covering.

Dispersion process

The dispersion process of the monolayer was measured by spreading powder (1mg) on the water/air

interface directly, then the change of surface pressure versus the given periods (π -t curves) was recorded without compression.

Monolayer Stability under Oscillation Condition

Methods to characterize monolayer stability under dynamic oscillation had been described in detail elsewhere [8-9]. When the barrier reached the pre-designed position during the monolayer compression, the barrier was automatically switched to sinusoidal oscillate with the given relative amplitude ($\Delta A/A=1\%$) and frequency ($f=100\text{mHz}$). The surface pressure was record two times during the oscillation to ensure good reproducibility.

Conclusions

In present research, five non-ionic emulsifiers with different hydrophobic and hydrophilic groups were selected to discuss the effects of emulsifier on monolayer structure and performance. It seemed the mechanism of emulsifier on monolayer structure and performance was more complicated than it had been revealed previously. There was no direct relationship among emulsifier structure, monolayer dispersion rate and evaporation resistance. However, the emulsifier with small volume and strong interaction force between chains, such as OA-10, seemed be beneficial to increase the monolayer packing density and stability, which would lead to high water evaporation resistance. This research would help to improve the monolayer performance by selecting or synthesizing novel amphiphilic molecules and emulsifier in the future.

Acknowledgements

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