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Study on the interfacial evaporation of aqueous solution of SDS surfactant self-assembly monolayer

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Abstract

Researches in chemical, biological and medical engineering consider that the self-assembly monolayer formed by SDS surfactants being to retard interfacial evaporation of aqueous solution. In heat transfer, the application of SDS surfactant in water is considered to enhance the boiling heat transfer. However, to our knowledge, the mechanism of interfacial evaporation in boiling heat transfer with the application of SDS surfactants has still not been clarified. The authors tried to give a new insight into this mechanism of the interfacial evaporation through the self-assembly monolayer of SDS surfactants by developing a model, which indicates that the accessible area and the hydrophobic interaction retard interfacial evaporation, while the decrease in the incipient temperature of phase change by SDS surfactants promotes interfacial evaporation. Thus, the effect of SDS surfactants in aqueous solution on interfacial evaporation is dual: as the concentration of SDS surfactant additives is lower than an optimal value and the interfacial superheat is not extremely high, the application of SDS surfactant promotes the interfacial evaporation; otherwise, retards the interfacial evaporation.

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1. Introduction

The interfacial evaporation from a self-assembly monolayer is of great importance due to its wide use in saving water, storing and protecting food, cooling electronic chips, and foaming, etc. The mechanism has been extensively investigated experimentally and theoretically for decades [1–5]. The common knowledge in physical chemistry, chemical and biology engineering is that the self-assembly monolayer would retard interfacial evaporation [6]. The studies reported in [2–4] demonstrated that the self-assembly monolayer could reduce the evaporation rate up to 50%, even 60–90%. Literature [1,7] reported that some biological materials, such as cholesterol, have a small retardation effect to interfacial evaporation. Barnes and Matsumoto [8,9] summarized that certain types of self-assembly monolayers spread on a liquid surface can reduce the evaporation rate of the liquid considerably. The experimental observations have shown that, generally, the self-assembly monolayer in the condensed state has a higher evaporation resistance than the expanded and gaseous state. Lunkenheimer and Zembala [10] pointed out that, for various classical soluble surfactants, most of them do not influence the water evaporation to a measurable degree, but not for very densely packed and compact monolayer. As indicated by Sadd et al. [11] the mass transfer resistance increases rapidly with the length of the surfactant's carbon chain, and always with increasing surfactant concentration, but not in a simple manner. At very low surfactant concentrations, there exists an initial undetectable resistance period, and the duration of this period would fall with increasing surfactant concentration, eventually disappear thereby. In summary, the surface occupation by surfactant molecules and the hydrophobic interaction of alkyl chains are two important causes for the resistance of interfacial evaporation.

SDS surfactants have been widely recognized to enhance boiling heat transfer [12–15], but without a unanimous theoretical explanation for the mechanism of

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Nomenclature

A	practical surface area of solution per surfactant molecule
a	fraction of accessible surface area
f	thermodynamic fugacity
G	free energy
h_{fg}	latent heat
J	rate of vaporization per unit area of liquid–vapor interface
M	molar weight
N_A	Avogadro number
N_o	site number occupied by surfactant molecules
P	pressure
Δq	extra evaporation rate
R	general gas constant
T	temperature
v	volume
π	energy of hydrophobic interaction per area

Subscripts

iv	liquid–vapor interface
l	liquid
s	solid phase
v	bulk vapor

boiling heat transfer enhancement. Frost and Charles [12] proclaimed by applying the high-speed film camera in the observations that 80% of the total heat flux was due to the latent heat transfer of the surfactant solution tested. By this reasoning, the interfacial evaporation associated with bubble formation was likely enhanced. The existence of an optimal concentration of SDS surfactants for the enhancement of boiling heat transfer has been reported [14,15], i.e. the boiling heat transfer will be enhanced as the concentration of applied SDS surfactants is lower than this optimal value.

The objective of this paper is to develop a model and try to give a reasonable description in the mechanism of the dual effect of the water interfacial evaporation through self-assembly monolayer.

2. Thermodynamic analyses

2.1. Brief review on the existed models

Several theoretical models have been proposed in biological and medical engineering, for explaining the mechanism on the water interfacial evaporation through self-assembly monolayer, for instance, the energy barrier theory [3,4,8], the density fluctuation theory [16], and the accessible area theory [17]. These models try to present the effects of the interaction of occupation of accessible area and hydrophobic CH_2 groups, but do not consider the effect of superheat. As a result, these models cannot describe the possible mechanism of the water interfacial evaporation driven by superheat from self-assembly monolayer. We have analyzed previously [18] for the thermodynamic aspect of shifting liquid–vapor interfacial phase equilibrium, the change in surface tension would induce superheat of interfacial vapor and thus affect the interfacial evaporation. In the area of liquid–gas phase—change heat transfer, to our knowledge, no effective model for interfacial evaporation regards the actual effect of SDS surfactant self-assembly monolayer till now.

2.2. Theoretical consideration on the mechanism of the water interfacial evaporation through self-assembly monolayer

It is well known that SDS surfactants consist of either non-polarized water-dislike hydrophobic and polarized water-like hydrophilic function groups. This dual character is responsible for the spontaneous formation of self-assembly monolayers on water substrate, and the decrease of surface tension of aqueous solution. Referring to literature [19], surface tension has two types of definitions. One is in its usual meaning as related to “contact angle”, and the other one from the standpoint of free energy interaction, when two immiscible liquids 1 and 2 are in contact, the free energy change in expanding their interfacial area by unit area is known as their interfacial tension. Accordingly, a large free energy change leads to a big surface tension. Since the free energy is in its lowest value for thermodynamic equilibrium state, a water molecule evaporating from the interface needs to get over this free energy barrier. The change of free energy from a state of lower level to a higher one takes place in the evaporating process, for which an evaporating water molecule may escape from the interface by receiving energy from the outside, such as the heat from a heated wall. On this reasoning, reducing surface tension lowers the energy barrier for water molecules escaping from the interface so decreases the required outside inputting energy. From the acting force standpoint as usual, surface tension is recognized as one of those forces to hold molecules together while interfacial evaporation is a process for molecules to get out the hold of surface force, i.e. surface tension. Therefore, reducing surface tension by applying SDS surfactant may promote interfacial evaporation, meanwhile a self-assembly monolayer formed by applying SDS surfactant on aqueous substrate surely occupies part of the area of interfacial evaporation so to retard interfacial evaporation. In summary, the surfactant additives may have the dual effects to interfacial evaporation of water from self-assembly monolayers.

2.3. Theoretical model proposed

As stated by Plesset and Prosperetti [20], the direct driving force for interfacial evaporation is the difference between the ideal equilibrium and bulk vapor pressure, or between the ideal equilibrium and bulk vapor concentration. For the quasi-equilibrium interface, the pressure of the ideal equilibrium vapor is approximately that of the practical equilibrium vapor at the surface temperature. For the non-equilibrium evaporation, the pressure of the ideal equilibrium vapor is the thermodynamic fugacity at the surface temperature. The vaporization rate derived from the Hertz-Knudsen equation [8] by applying the kinetic theory of gas is

$$J = a\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}[P_{\mathrm{iv}}(T_{\mathrm{iv}}) - P_{\mathrm{v}}] \tag{1}$$

where a denotes the fraction of the accessible surface area, J the rate of vaporization per unit area of liquid–vapor interface, M the molar weight, R the universal gas constant, $P_{\mathrm{iv}}(T_{\mathrm{iv}})$ the ideal equilibrium vapor pressure corresponding to interfacial temperature T_{iv} and P_{v} the bulk vapor pressure. The fraction of accessible surface area is taken as unit for interfacial evaporation of pure liquid.

According to thermodynamics [21], the thermodynamic fugacity, f, is related to free energy, G, by

$$\mathrm{d}\ln f = \frac{\mathrm{d}G}{RT_{\mathrm{l}}} \tag{2}$$

For liquids of self-assembly monolayer, the change of free energy with regard of hydrophobic interaction is

$$\mathrm{d}G = v_{\mathrm{l}}\,\mathrm{d}P + \frac{Mh_{\mathrm{fg}}}{T_{\mathrm{l}}}\mathrm{d}T_{\mathrm{l}} + \pi N_{\mathrm{o}} N_{\mathrm{A}}\,\mathrm{d}A \tag{3}$$

where A denotes the surface area per surfactant molecule of self-assembly monolayer, h_{fg} the latent heat of liquid, N_{A} the Avogadro's number, N_{o} the number of sites occupied by surfactant molecules, v_{l} the liquid specific volume, and π the energy of hydrophobic interaction per area.

Substituting Eq. (3) into Eq. (2), yields

$$\mathrm{d}\ln f = \frac{v_{\mathrm{l}}}{RT_{\mathrm{l}}}\mathrm{d}P + \frac{Mh_{\mathrm{fg}}}{RT_{\mathrm{l}}^2}\mathrm{d}T_{\mathrm{l}} + \frac{\pi N_{\mathrm{o}} N_{\mathrm{A}}}{RT_{\mathrm{l}}}\mathrm{d}A \tag{4}$$

The specific volume for the liquid phase can be considered approximately as a constant. Therefore, integrating Eq. (4) through $(P_{\mathrm{iv}}, T_{\mathrm{iv}})$ to $(P_{\mathrm{v}}, T_{\mathrm{v}})$ results in

$$\ln\frac{f_{\mathrm{v}}}{f_{\mathrm{iv}}} = \frac{v_{\mathrm{l}}}{RT_{\mathrm{iv}}}(P_{\mathrm{v}} - P_{\mathrm{iv}}) + \frac{Mh_{\mathrm{fg}}}{RT_{\mathrm{v}}T_{\mathrm{iv}}}(T_{\mathrm{v}} - T_{\mathrm{iv}}) + \frac{\pi N_{\mathrm{o}} N_{\mathrm{A}}\Delta A}{RT_{\mathrm{iv}}} \tag{5}$$

where the subscript v and iv denotes respectively the bulk vapor and vapor interface, and f_{iv} and f_{v} denotes respectively the ideal equilibrium and bulk vapor pressure.

Supposing that the considered thermal non-equilibrium is not far from the equilibrium, the right-hand side of Eq. (5) is around zero, we have approximately

$$\frac{P_{\mathrm{iv}}(T_{\mathrm{iv}})}{P_{\mathrm{v}}} \cong 1 - \frac{v_{\mathrm{l}}}{RT_{\mathrm{iv}}}(P_{\mathrm{v}} - P_{\mathrm{iv}}) - \frac{Mh_{\mathrm{fg}}}{RT_{\mathrm{v}}T_{\mathrm{iv}}}(T_{\mathrm{v}} - T_{\mathrm{iv}}) - \frac{\pi N_{\mathrm{o}} N_{\mathrm{A}}\Delta A}{RT_{\mathrm{iv}}} \tag{6}$$

where P_{iv} is the practical interfacial pressure.

Hence, substituting Eq. (6) into Eq. (1) yields

$$J = a\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}\left[\frac{P_{\mathrm{v}}v_{\mathrm{l}}}{RT_{\mathrm{iv}}}(P_{\mathrm{iv}} - P_{\mathrm{v}}) + \frac{P_{\mathrm{v}}Mh_{\mathrm{fg}}}{RT_{\mathrm{v}}T_{\mathrm{iv}}}(T_{\mathrm{iv}} - T_{\mathrm{v}}) - \frac{P_{\mathrm{v}}\pi N_{\mathrm{o}} N_{\mathrm{A}}\Delta A}{RT_{\mathrm{iv}}}\right] \tag{7}$$

3. Discussion

The first two terms on the right-hand side of Eq. (7) are the same as that for pure liquids. The last term is new to consider the effect of self-assembly monolayers. Without heating the interface from the outside, self-assembly monolayers surely retard the interfacial evaporation of water by decreasing the accessible surface area and forming the hydrophobic interaction of n-CH$_2$ tails. The two terms π and ΔA in Eq. (7) are related to the chain length of CH$_2$ tails, the state of self-assembly monolayers and the structure of surfactant molecules [22], so that long CH$_2$ tails and dense self-assembly monolayers demonstrate stronger resistance against the interfacial evaporation than short and thin ones. Additionally, the fraction of accessible surface area in Eq. (7) is always less than one and decreases with increasing concentration of surfactant if a self-assembly monolayer is formed. The experimental results demonstrated that applying a surfactant in pure water eased the surface tension of the aqueous solution by forming self-monolayers [22]. As has been proclaimed in the above section about the definition of surface tension, the reduction in surface tension will ease the barrier for solute molecules escaping from the liquid phase to the vapor phase, so that the barrier for interfacial evaporation will be lowered. This is in accordance with the experimental observations [12–15]. For this reasoning, the coupling effect of the fraction of accessible with hydrophobic interactions and the decrease in surface tension may be one cause for the existence of an optimal concentration of SDS surfactant additives, for which the corresponding interfacial evaporation rate will reach its maximum value.

The experiments [14] showed that, the boiling of SDS aqueous solution occurred at a lower wall superheat as compared to pure water. With this consideration, an extra interfacial evaporation of SDS aqueous solution compared to pure water, ΔJ, could be yielded as

$$\Delta J = a\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}\left[\frac{P_{\mathrm{v}} M h_{\mathrm{fg}}}{R T_{\mathrm{v}} T_{\mathrm{iv}}}\Delta T - \frac{P_{\mathrm{v}} \pi N_{\mathrm{o}} N_{\mathrm{A}} \Delta A}{R T_{\mathrm{iv}}}\right] - \left(\frac{A_{\mathrm{s}}}{A}\right)\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}\left(\frac{P M h_{\mathrm{fg}}}{R T_{\mathrm{v}} T_{\mathrm{iv}}}\Delta T_{\mathrm{iv}}\right) \tag{8}$$

where ΔT is the extra superheat from the decrease of incipient temperature of interfacial evaporation, and ΔT_{iv} is the original interfacial superheat.

Then, the extra evaporation heat flux is

$$\Delta q = a h_{\mathrm{fg}}\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}\left[\frac{P_{\mathrm{v}} M h_{\mathrm{fg}}}{R T_{\mathrm{v}} T_{\mathrm{iv}}}\Delta T - \frac{P_{\mathrm{v}} \pi N_{\mathrm{o}} N_{\mathrm{A}} \Delta A}{R T_{\mathrm{iv}}}\right] - h_{\mathrm{fg}}\left(\frac{A_{\mathrm{s}}}{A}\right)\left(\frac{M}{2\pi R T_{\mathrm{iv}}}\right)^{1/2}\left(\frac{P M h_{\mathrm{fg}}}{R T_{\mathrm{v}} T_{\mathrm{iv}}}\Delta T_{\mathrm{iv}}\right) \tag{9}$$

The fraction of accessible surface area has been defined as [23]

$$a = 1 - A_{\mathrm{s}}/A \tag{10}$$

where A is the practical surface area of solution per surfactant molecules and A_{s} is the surface area of solution per surfactant molecules in solid phase of self-assembly monolayer. The value of A_{s} can be found from the π–A isothermal chart. The site number of SDS surfactant molecules on the surface can be obtained from the applied concentration of surfactant. As stated by literature [22] A_{s} is around 20.5 Å^2 for normal fatty alcohols and acids.

With the data quoted partly from literature [14], the variation of the incipient temperature shift or the extra superheat, ΔT, and the relative surface pressure, π, with the concentration of SDS surfactant additives have been presented in Table 1. The surface area of solution per surfactant molecule, A, was found from the state equation [22]:

$$\pi(A - A_{\mathrm{s}}) = kT \tag{11}$$

where A_{s} is the value in the solid phase of self-assembly monolayer. The calculated surface area, A, and the extra evaporation rate, Δq, according to Eq. (9) has been estimated and listed in Table 1 for $T_{\mathrm{v}} = 373$ K and the value of accessible area suggested by Barnes [23]. Compared to the effect of the incipient temperature shift of phase change presented in Table 1, the effect of hydrophobic interaction is so insignificant to be neglected here. Therefore, the fraction of accessible surface area and the extra superheat are the dominant factors for evaluation of Δq. Because of the limited experimental data in incipient temperature, the estimations were done only within the concentrations ranging from 0 to 200 ppm as illustrated in Figs. 1–6. These illustrations demonstrated that for the superheat, ΔT, below 0.3 K, the extra evaporation increased with increasing the SDS concentration, but the optimal concentration did not present because of the limited experimental data in incipient temperature. However, Eq. (9) indicates the existence of this optimal value. Fig. 4–6 illustrated that once the interfacial superheat, ΔT, exceeds 0.5 K, the use of SDS surfactant led to weaken interfacial evaporation. Relative to those large superheat, the heat flux of interfacial evaporation reached the level of 1×10^6 W/m^2, which fell into the range of developed nucleate boiling. As stated by the literature [12], the interfacial evaporation played the primary role in developed nucleation boiling heat transfer, the utilization of SDS surfactants may worsen the nucleation boiling heat transfer when approaching the boiling crisis where the superheat is

Table 1
Data for superheat and surface pressure

C (ppm)	ΔT_{wall} (K)	ΔT (K)	$\pi \times 10^3$ (N m^{-1})	$A \times 10^3$ (N m^2)
0.0	10.3	0.0	0.0	∞
20.0	10.2	0.1	10.0	72.0
50.0	9.9	0.4	23.0	42.9
100.0	9.8	0.5	27.0	39.6
200.0	9.6	0.7	36.0	34.8

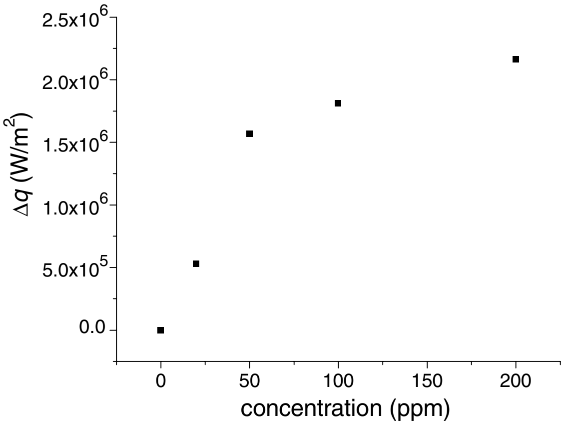

Fig. 1. Estimated extra interfacial evaporation heat for $\Delta T = 0.01$ K by Eq. (9).

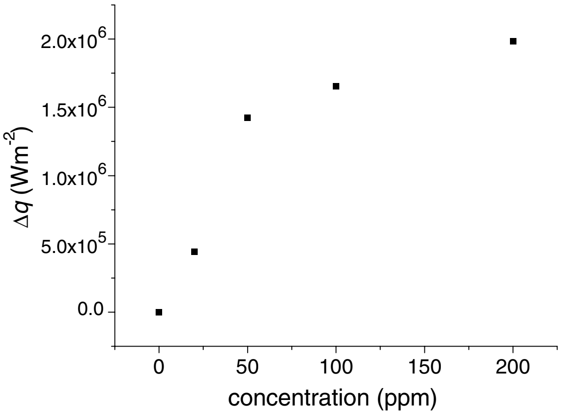

Fig. 2. Estimated extra interfacial evaporation heat for $\Delta T = 0.1$ K by Eq. (9).

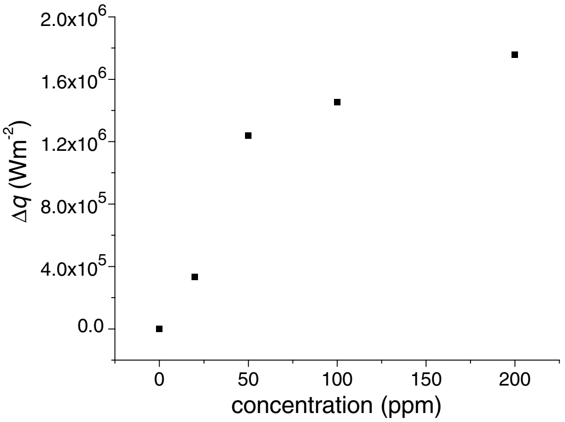

Fig. 3. Estimated extra interfacial evaporation heat for $\Delta T = 0.3$ K by Eq. (9).

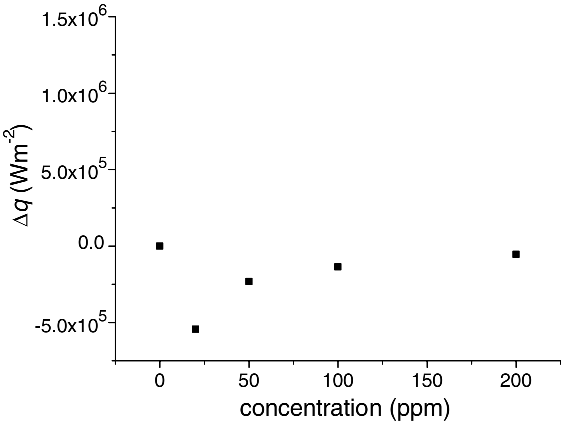

Fig. 4. Estimated extra interfacial evaporation heat for $\Delta T = 0.5$ K by Eq. (9).

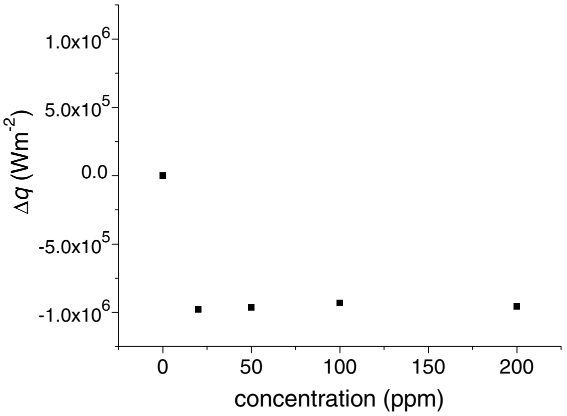

Fig. 5. Estimated extra interfacial evaporation heat for $\Delta T = 0.7$ K by Eq. (9).

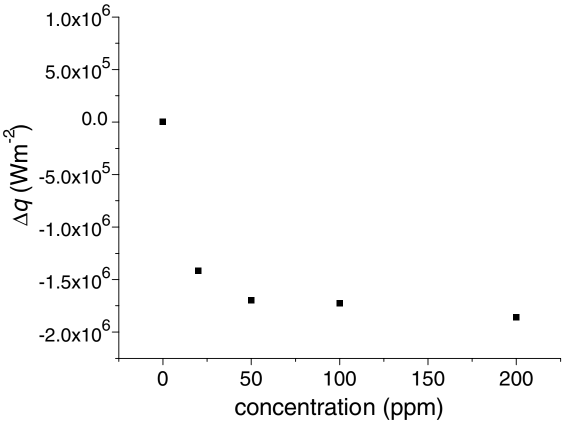

Fig. 6. Estimated extra interfacial evaporation heat for $\Delta T = 0.9$ K by Eq. (9).

close to the limited value. This consequence is in accordance with those experimental observations that the heat flux of boiling crisis of pure water is larger than that of aqueous solutions of SDS surfactants.

The new proposed model indicates that increasing the concentration of surfactant surely decreases the interfacial evaporation rate. The review on the work of Hedestrand [1] and Rideal [2] showed that the concentration of surfactant additives applied in the two different experiments was quite different. This difference may be the cause for the very different conclusions of the two works.

4. Conclusion

The new model developed by the authors demonstrated that there are two contradictive factors influencing the performance of water interfacial evaporation through the self-assembly monolayer of SDS surfactants. The decrease in surface tension by forming the self-assembly monolayer promotes the interfacial evaporation, and meanwhile the formed self-assembly monolayer resists this interfacial evaporation. For this reasoning an optimal concentration of SDS surfactant application may exist. Once the concentration of SDS surfactant additives exceeds the optimal value or the original superheat is extremely high as near the boiling critical heat flux, SDS surfactant additives will be as the inhibitors to the interfacial evaporation of aqueous solution.

For the case of zero interfacial superheat, the fractions of accessible area, the pressure difference and the hydrophobic interaction play the dominant role in the interfacial evaporation. The new model indicates that, in this case, the interfacial evaporation is certainly inhibited by forming the self-assembly monolayer because of the decrease in the accessible area and the enhancement in the hydrophobic interaction. Because the hydrophobic interaction relates to the chain length of CH_2 tails, the structure of hydrophobic tails, and the concentration of surfactant application, etc., different surfactant additives shall perform differently on the interfacial evaporation.

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