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Surfactants Improving the Wetting Behavior and Adhesion Mechanism of Pesticide Dilution Droplets on Jujube Leaf Surfaces

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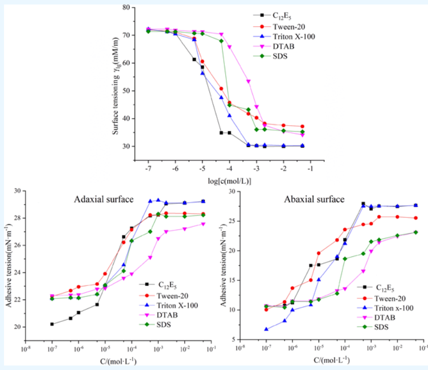
ABSTRACT: Fruit tree leaves have different chemical compositions and diverse wax layer structures that result in different patterns of wetting and pesticide solution spreading on their surface. Fruit development is a time when pests and diseases occur, during which a large number of pesticides are needed. The wetting and diffusion properties of pesticide droplets on fruit tree leaves were relatively poor. To solve this problem, the wetting characteristics of leaf surfaces with different surfactants were studied. The contact angle, surface tension, adhesive tension, adhesion work, and solid−liquid interfacial tension of five surfactant solution droplets on jujube leaf surfaces during fruit growth were studied by the sessile drop method. $C_{12}E_5$ and Triton X-100 have the best wetting effects. Two surfactants were added to a 3% beta-cyfluthrin emulsion in water, and field efficacy tests were carried out on peach fruit moths in a jujube orchard at different dilutions. The control effect is as high as 90%. During the initial stage when the concentration is low, due to the surface roughness of the leaves, the surfactant molecules adsorbed at the gas−liquid and solid−liquid interfaces reach an equilibrium, and the contact angle on the leaf surface changes slightly. With increasing surfactant concentration, the pinning effect in the spatial structure on the leaf surface is overcome by liquid droplets, thereby significantly decreasing the contact angle. When the concentration is further increased, the surfactant molecules form a saturated adsorption layer on the leaf surface. Due to the existence of a precursor water film in the droplets, surfactant molecules on the interface continuously move to the water film on the surface of jujube tree leaves, thus causing interactions between the droplets and the leaves. The conclusion of this study provides theoretical guidance for the wettability and adhesion of pesticides on jujube leaves, so as to achieve the purpose of reducing pesticide use and improving pesticide efficacy.



1. INTRODUCTION

The jujube (*Ziziphus jujuba*), a genus of plants in the Rhamnaceae family, is widely cultivated on five continents, with the top planting area being in Asia, where jujube trees are planted in 25 countries.[1] As one of the economic forest species in China, jujube trees have a history of more than 4000 years and more than 700 varieties widely planted, and it is an important source of income for farmers in many mountainous areas. At present, China has more than 98% of the world's jujube resources and a promising international trade market for jujube products.[2−5] The jujube tree is highly adaptable, has good resistance to stress, is simple to manage, is rich in fruit nutrients and functional compounds, has fast yield, and has significant economic benefits, which have an important impact on the current agricultural industry structure adjustment, poverty alleviation of farmers in mountainous areas, and export of agricultural products for foreign exchange.[6,7]

In recent years, the cultivation scale and yield of jujube in China have achieved the highest level in history; huge yield losses caused by the pests and diseases occur on jujube trees every year.[8−10] Conventional spraying of chemical pesticides is still the main application method for controlling diseases and insect pests of jujube trees. It is hard to believe that pesticides are sprayed on jujube trees over 12 times per year for the control of pests and diseases.[11] Pesticide spray droplets are easy to aggregate, bounce, and roll on the surface of jujube leaves, which leads to a low pesticide utilization rate. The wettability of the spray solution droplets on jujube leaves depends on the natural properties of leaves as well as the physicochemical properties of the spray solution. Previous studies have demonstrated that the addition of surfactants to pesticide spray solutions can decrease evaporation, bouncing and improves wetting ability, and helps to reduce droplet drift during application.[12,13] A better understanding of the wetting and adhesion mechanism of surfactants on jujube leaf surfaces

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is critical to improve pesticide utilization. However, there is little information on the wetting and adhesion mechanism of different surfactants on jujube leaf surfaces. In recent years, the prevention and control effects of many pesticides have been decreasing, and the wasteful use of pesticides has become more common. This is mainly due to uncertainty regarding the wetting mechanisms of pesticide solutions on jujube leaf surfaces, which result in their poor wetting and adhesion performances. Even if the pesticide solution reaches the leaf surface, the droplets can easily merge with each other and ultimately separate from the leaf surface. This lack of effectiveness wastes a large amount of pesticides and greatly increases the amount of pesticide residue in agricultural products. This has a serious impact on China's agricultural product export and causes economic losses.[14−16] Furthermore, the long-term use of common pesticides leads to pesticide resistance. Therefore, it is urgently necessary to develop new application forms to prevent and control jujube pests and diseases. In these design efforts, attention should be paid to selecting surfactants that improve pesticide performance and reduce the required pesticide concentrations to improve the prevention and control efficacies to the utmost extent and thereby slow the occurrence of pesticide resistance. With the improvement in jujube productivity levels in China, such advances are bound to have great significance for the promotion of economic development in rural areas.[17−20]

Jujube, as a major cash crop in most regions of China, is often affected by pests and diseases. How to use chemical pesticides highly efficient to control pests and diseases is an urgent problem during jujube cultivation in China. Herein, in this paper, contact angles, surface tension, and adhesional tension are studied to characterize wetting and adhesion behaviors of different surfactants on jujube leaf surfaces, and then the regulatory mechanisms of surfactant wetting and deposition on leaf surfaces are discussed. The results may provide a potential guide to practical application of pesticide spraying on jujube leaf surfaces, achieve the goal of reducing the application of chemical pesticides and increasing their effectiveness, and guarantee the safety of ecological environment and product quality of jujube.

2. MATERIALS AND METHODS

2.1. Materials and Instruments. In this paper, the nonionic surfactants polyoxyethylene octyl phenyl ether (Triton X-100), pentaethylene glycol monododecyl ether ($C_{12}E_5$), and polysorbate 20 (Tween-20), the cationic surfactant dodecyltrimethylammonium bromide (DTAB) and the anionic surfactant sodium dodecyl sulphate (SDS) were selected for experiments. Table S1 shows the five surfactants used in this experiment and their manufacturers. The pesticide used in this study was a 3% beta-cyfluthrin emulsion made in the laboratory. The main instruments used in this experiment and their manufacturers are listed in Table S2.

2.2. Methods. *2.2.1. Preparation of Plant Leaves.* Jujube tree leaves were collected from Qi County, Jinzhong City, Shanxi Province, during the fruit growth period, and their adaxial and abaxial surfaces were distinguished. For plants of the same species and the same growth stage, the length and width of collected leaves were basically the same, and it was ensured that no damage, disease, insect bites, or other phenomena existed on the leaf surfaces. The time between collecting the jujube leaf and measuring the contact angle was less than 1 h. During tests, the leaf veins were avoided, and the middle segment was used. Double-sided adhesive tape was used to affix the leaves in a natural state onto glass slides. The glass slides were laid flat on the sample table of the video contact angle meter. During preparation, the leaf surface was not touched with hands or other foreign substances to prevent the leaf surfaces from being contaminated.

2.2.2. Preparation of Surfactant Solutions and Determination of Surface Tension. There are many differences in the molecular structures of surfactants, and different types of surfactants are categorized due to their charged properties, hydrophilic groups, carbon chain length, and branched chains. Therefore, their influences on wetting adhesion behavior are also widely different. After the surfactants were chosen, relevant preliminary experiments were carried out, and it was found that only using gradients including 12 concentrations from 1×10^{-7} to 5×10^{-2} mol/L the behavior of these five surfactants be determined completely, and more systematic experimental data analysis and trend determination could be carried out. These 12 concentrations were prepared using ultrapure water for dilutions. The surface tensions of the five surfactant solutions at different concentrations were measured by the drop-weight method at room temperature.[21] The surface tensions for solutions of each concentration were measured five times to ensure that the error did not exceed 0.2 mN/m.

2.2.3. Contact Angle Measurements. A micropipettor was used to pipette a drop (2 μL) of each diluted solution onto the leaf surfaces, and the dynamic and static contact angles of the drops were recorded using the video function of the optical video contact angle meter. The temperature was controlled at 25 ± 0.5 °C, and each treatment was repeated five times.

2.2.4. Calculations of Interfacial Tension, Adhesion Tension, and Adhesion Work. By measuring the contact angles of three pure liquids on a jujube leaf surface, the interfacial tension of each phase was divided into a polar component γ^p and a dispersion component γ^d according to the OWRK method.[22] The relationship between the interfacial free energy γ_{sl} of the solid and liquid phases and the polar and dispersion components of solid and liquid surface free energy can be expressed by the OWRK method as follows:

$$\gamma_{sl} = \gamma_{lg} + \gamma_{sg} - 2\,({\gamma_{lg}}^{d}{\gamma_{sg}}^{d})^{1/2} - 2\,({\gamma_{lg}}^{p}{\gamma_{sg}}^{p})^{1/2} \quad (1)$$

where ${\gamma_{sg}}^d$ and ${\gamma_{lg}}^d$ are the nonpolar components of the solid and liquid surface free energies, respectively, and ${\gamma_{sg}}^p$ and ${\gamma_{lg}}^p$ are the polar components of the solid and liquid surface free energies, respectively. Young's equation gives the following relationship between the contact angle of a liquid forming a droplet on a solid surface and the interfacial free energy of the three interfaces between solid, liquid, and gas:[23]

$$\gamma_{sg} - \gamma_{sl} = \gamma_{lg}\cos\theta \quad (2)$$

where γ_{lg}, γ_{sg}, and γ_{sl} are the interfacial free energies of liquid−gas, solid−gas, and solid−liquid, respectively; θ represents the contact angle; and $\gamma_{lg}\cos\theta$ represents the liquid adhesion tension. After substituting eq 1 into eq 2 and rearranging, the following is obtained:

$$\gamma_{lg}(1 + \cos\theta)/2({\gamma_{lg}}^{d})^{1/2} = ({\gamma_{sg}}^{d})^{1/2} + ({\gamma_{sg}}^{p})^{1/2}({\gamma_{lg}}^{p}/{\gamma_{lg}}^{d})^{1/2} \quad (3)$$

It can be seen from eqs 2 and 3 that if a series of liquids with known surface free energies γ_{lg}, polar components ${\gamma_{lg}}^p$, and nonpolar components γ_{lg}^{d} are used to measure the contact angle θ on the solid surface, plotting $(\gamma_{lg}^{P}/\gamma_{lg}^{d})^{1/2}$ using $\gamma_{lg}(1 + \cos\theta)/2(\gamma_{lg}^{d})^{1/2}$ allows γ_{sg}^{P} to be calculated from the slope of the obtained straight line and γ_{sg}^{d} to be calculated from the intercept. Deionized water, ethylene glycol, and formamide were selected as the liquids in this study.

Based on the change in free energy when a liquid wets a solid, the equation for calculating the adhesion work W_A of the liquid on the solid surface can take the form $W_A = \gamma_{lg} + \gamma_{sg} - \gamma_{sl}$. If the measured contact angle is substituted into this equation, the final equation for calculating the adhesion work is as follows:[24]

$$W_A = \gamma_{lg}(1 + \cos\theta) \tag{4}$$

2.2.5. Field Control Effect Experiment. The experimental site was in a jujube orchard in Qi County, Jinzhong City, Shanxi Province. Fertilizer and water conditions were consistent, and the trees were 10 years of age. The pesticide was sprayed on the morning of July 22 to carry out a field efficacy experiment on peach fruit moths. $C_{12}E_5$ and Triton X-100 (0.15, 0.3, and 0.6%) were added to a beta-cyfluthrin emulsion (3%) in water, and the mixtures were diluted (2000, 3000, and 4000 fold) with tap water. The plots were arranged in random blocks with protective rows around each plot. The experiment was carried out under the condition that the pests (*Carposina sasakii* Matsumura) were evenly distributed and densely populated on the jujube leaves. The experimental area was no less than 1/3 hm^2. With each jujube tree sprayed with ultrapure water as a blank control, the initial numbers of fruits containing pests and pest eggs were determined 1 day before application, and the number of fruits containing pests was determined 7 and 14 days after application. Three trees were randomly investigated for each treatment. More than 100 fruits were randomly investigated around the canopy and the middle and upper parts of the inner chamber of each investigated tree, resulting in the investigation of more than 200 fruits, and the number of fruits containing pests was counted.

$$\begin{aligned}&\text{Increase rate of fruits containing pests (\%)}\\&= (\text{The number of fruits containing pests after pesticide}\\&\quad \text{application} - \text{The number of fruits containing pests}\\&\quad \text{before pesticide application})/(\text{The number of fruits}\\&\quad \text{containing pests after pesticide application}) \times 100\end{aligned} \tag{5}$$

$$\begin{aligned}&\text{Control effect (\%)}\\&= [\text{CK increase rate of fruits containing pests (\%)}\\&\quad - \text{Pt increase rate of fruits containing pests (\%)}]\\&\quad /[\text{CK increase rate of fruits containing pests (\%)}]\\&\quad \times 100\end{aligned} \tag{6}$$

2.2.6. Data Analysis. The statistical data are presented as the mean ± standard deviation, and all statistical analyses were carried out using SPSS. Differences between groups were compared using the Duncan's multiple range test. Significance was set at the $P < 0.05$.

3. RESULTS

3.1. Surfactant Surface Tension Determination. Studies on crop leaves show that the surface free energy of the adaxial and abaxial surface consists of polar and nonpolar components and that the wetting and spreading of liquid droplets on the solid−liquid surface occurs mainly through weak interactions such as dispersion.[25] Unlike the solid surfaces of polymers, surfactants can dissolve or solubilize the wax layer on the leaf surface, thus affecting its three-dimensional structure.[9] Through this mechanism, surfactants can promote the wetting and adhesion by droplets on the leaf surface, resulting in a gradual decrease in the contact angle. Therefore, the surface tensions of the five surfactants used in this paper were measured.

As shown in Figure 1, the surface tensions of the five surfactants decreased with increasing concentration. With the

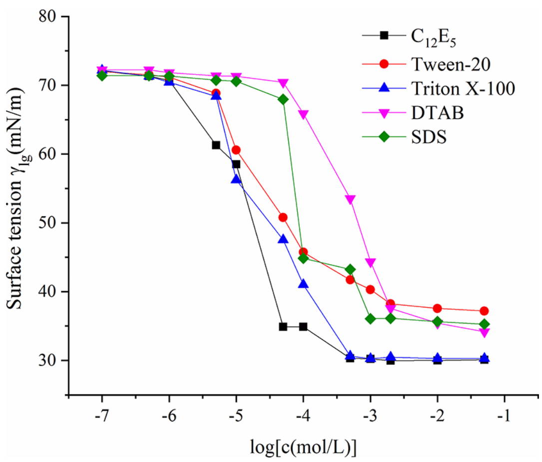

Figure 1. Surface tension (γ_{lg}) of aqueous surfactant solutions versus log *C* (*C* is surfactant concentration).

formation of a saturated adsorption layer of surfactant molecules at the gas−liquid interface, the surface tension gradually stabilized. $C_{12}E_5$ and Triton X-100 caused the greatest reduction in liquid surface tension, and there was no significant difference between them. Although the remaining three surfactants also caused significant reductions, their lowest stable values were lower than those of $C_{12}E_5$ and Triton X-100. The results showed that these surfactants have different wetting abilities due to their different structures.

3.2. Contact Angles of Five Surfactants on the Adaxial and Abaxial Surfaces of Jujube Leaves during Fruit Inflating Growth. Contact angle trends of the surfactants at different concentrations on the adaxial and abaxial leaf surfaces during fruit inflating growth are shown in Table 1. The contact angles of the liquid drops were relatively high at low concentrations, approximately 70° on the adaxial surface and approximately 80° on the abaxial surface. As the concentration increased, the contact angles decreased sharply up to a concentration of 5 × 10^{-3} mol/L, where the contact angle rates of change began to decrease. At the concentration of 5 × 10^{-2} mol/L, the contact angles of $C_{12}E_5$ and Triton X-100 on the adaxial surface were relatively small, whereas the contact angle of Triton X-100 on the abaxial surface was the smallest (Table 1), indicating that it had a stronger ability to reduce the liquid surface tension. This also suggests that the different molecular structures of the surfactants lead to

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Table 1. Contact Angles of Five Surfactants on the Adaxial and Abaxial Surfaces of Jujube Leaves during Fruit Inflating Growth[a]

surfactant concentration (mol/L)	contact angle (°)									
	adaxial surfaces					abaxial surfaces				
	$C_{12}E_5$	Tween-20	TritonX-100	DTAB	SDS	$C_{12}E_5$	Tween-20	TritonX-100	DTAB	SDS
1×10^{-7}	73.70 ± 0.96	78.50 ± 0.46	72.39 ± 0.63	75.24 ± 2.16	74.18 ± 1.30	81.80 ± 1.83	82.98 ± 0.75	84.04 ± 1.15	83.56 ± 0.96	83.64 ± 1.06
5×10^{-7}	72.89 ± 0.65	75.52 ± 1.06	70.49 ± 1.14	72.69 ± 0.99	73.74 ± 1.23	81.41 ± 1.24	81.85 ± 1.06	83.33 ± 0.54	81.63 ± 1.17	81.43 ± 0.67
1×10^{-6}	71.77 ± 0.94	72.19 ± 0.79	69.74 ± 0.43	71.67 ± 0.67	71.79 ± 1.35	80.66 ± 0.82	79.92 ± 0.77	81.05 ± 0.76	80.87 ± 0.95	80.87 ± 1.05
5×10^{-6}	68.58 ± 0.73	69.42 ± 0.38	68.04 ± 0.85	71.08 ± 0.68	69.21 ± 0.86	73.87 ± 1.35	77.78 ± 0.87	79.88 ± 0.82	80.51 ± 0.85	80.01 ± 1.17
1×10^{-5}	66.61 ± 1.34	67.78 ± 1.23	61.08 ± 1.07	70.31 ± 0.75	65.58 ± 0.68	65.54 ± 0.86	75.03 ± 0.76	73.36 ± 0.87	80.00 ± 0.74	79.39 ± 0.85
5×10^{-5}	40.25 ± 3.34	52.51 ± 0.78	53.39 ± 0.52	68.93 ± 0.98	62.27 ± 1.15	57.63 ± 1.53	59.24 ± 0.98	66.53 ± 0.74	79.65 ± 1.06	74.15 ± 1.33
1×10^{-4}	35.65 ± 0.98	46.21 ± 1.17	41.51 ± 0.74	66.80 ± 1.14	44.81 ± 1.43	49.42 ± 1.25	52.65 ± 0.94	54.89 ± 0.77	76.04 ± 0.84	68.48 ± 0.77
5×10^{-4}	21.68 ± 0.86	39.92 ± 1.27	17.16 ± 2.26	57.84 ± 1.06	39.89 ± 2.20	28.86 ± 0.83	47.53 ± 0.86	39.53 ± 0.94	71.45 ± 0.86	60.38 ± 0.75
1×10^{-3}	17.81 ± 1.81	33.65 ± 0.53	11.25 ± 1.81	44.28 ± 1.98	24.89 ± 1.53	24.44 ± 1.06	44.67 ± 0.74	33.72 ± 0.98	65.33 ± 1.13	56.82 ± 0.84
5×10^{-3}	14.35 ± 1.01	27.40 ± 1.13	9.66 ± 0.76	31.32 ± 1.29	20.64 ± 1.55	24.08 ± 0.994	37.58 ± 1.07	30.71 ± 1.03	55.49 ± 1.06	53.09 ± 0.77
1×10^{-2}	14.17 ± 0.78	24.05 ± 1.36	9.22 ± 1.13	28.38 ± 1.15	18.15 ± 2.23	23.85 ± 0.85	33.01 ± 1.04	20.77 ± 0.77	50.34 ± 0.83	50.63 ± 0.83
5×10^{-2}	13.83 ± 1.10	23.24 ± 0.55	7.85 ± 0.68	27.86 ± 1.03	17.84 ± 1.56	23.38 ± 0.87	29.32 ± 1.58	19.31 ± 1.14	47.85 ± 1.16	48.32 ± 0.66
CK	93.34 ± 0.64					96.83 ± 0.89				

[a]Values with different letters in the same column are significantly different at $P < 0.05$.

different minimum contact angles on jujube tree leaves and thus different effects on wetting behavior. The contact angles of the five surfactants on the abaxial surface were all larger than those on the adaxial surface, which was attributed to the greater surface roughness of the abaxial surface, which results in a smaller surface free energy and a greater wetting difficulty.

During the fruit growth period of jujube trees, when the concentrations of the five surfactants exceeded the critical micelle concentrations, their surface contact angles on all jujube tree leaves also reached their minimum stable values. The contact angles formed by $C_{12}E_5$ and Triton X-100 were significantly different from those formed by the other three surfactants. The minimum contact angles of $C_{12}E_5$ and Triton X-100 on the adaxial surface were approximately 10°, whereas those of the other three surfactants were approximately 20°. The minimum contact angles of $C_{12}E_5$ and Triton X-100 on the abaxial surface were approximately 20°, whereas those of the other three surfactants were 30−50°. As shown in Table 1, the surfactant contact angles on the leaves were not significantly different at low concentrations. As the concentrations increased, the difference between the contact angles of $C_{12}E_5$ and Triton X-100 and those of the other groups became increasingly significant. In addition, Triton X-100 had the smallest contact angles on the adaxial and abaxial surfaces of jujube tree leaves. In the concentration range of 1×10^{-7} to 5×10^{-6} mol/L, the five surfactants showed partial wetting on the adaxial and abaxial surfaces of jujube tree leaves (Table 1). Their contact areas were the wax layer and the air layer of the leaf epidermis, and they showed a certain composite wetting state and a certain roughness due to the existence of folds and other elements on the leaf surface. In the high concentration range, the non-ionic surfactants $C_{12}E_5$ and Triton X-100 had better wetting effects.

3.3. Wetting Behavior of Surfactant Droplets on Jujube Leaf Surfaces. As shown in Figure 2, the surface adhesive tension of the surfactants on the adaxial and abaxial surfaces of the jujube tree leaves gradually increased with increasing concentration, and the adhesive tension on the adaxial surface was greater than that on the abaxial surface. With increasing concentration, $C_{12}E_5$ and Triton X-100 droplets adhered and deposited on jujube leaf surfaces more easily. When the concentration of surfactant reached the critical micelle concentration, the adhesive tension of the solution also reached the stable value, which proved that the adhesion of the solution reached the highest level.

The variation in adhesion tension with changing surfactant surface tension on the adaxial and abaxial leaf surfaces (Figure 3A,B). No linear relationship between surface tension and adhesion tension was present across the tested surfactant concentration range. There was an inflection point in $C_{12}E_5$ and Triton X-100 adhesion tension versus surface tension curves. Dividing these curves into two stages yielded linear relationships in the concentration ranges on either side of the inflection point, whereas no inflection point occurred for the other three surfactants. Some points did not align with the linear fits due to errors in the measurement process, but the correlation coefficient of each linear relationship was greater than 0.9, indicating a definite linear relationship in each concentration range. The amounts of surfactant adsorbed at the gas−liquid interface were greater than those at the solid−liquid interface. This illustrates a certain hydrophobicity, which is consistent with the theoretical results of previous studies on the surface free energy of tree leaves.[25]

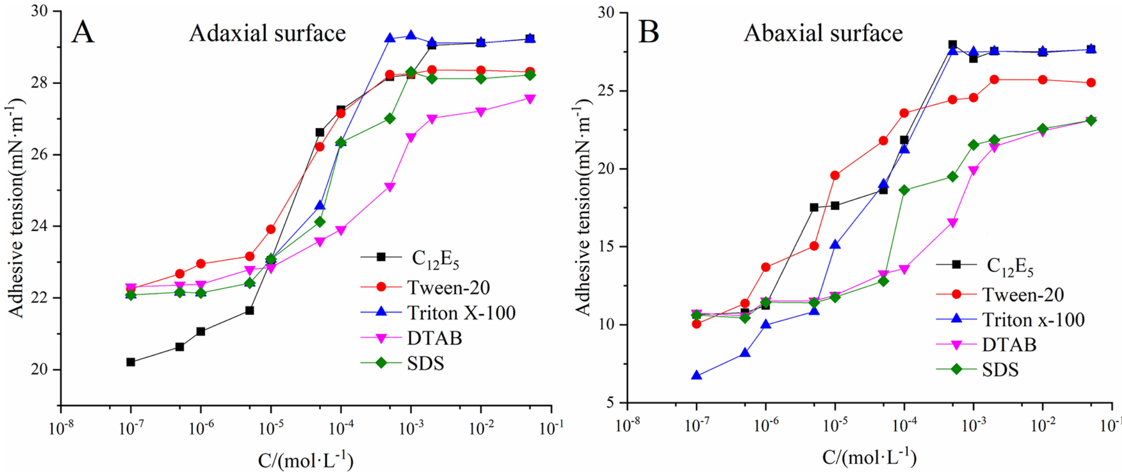

Figure 2. Effect of different surfactant droplets on the adhesive tension (γ_{lg} cos θ) of (A) adaxial and (B) abaxial jujube leaf surfaces at fruit inflating growth.

The surfactant solid−liquid interfacial tension on the surface of jujube tree leaves gradually decreased with increasing concentration (Figure 3C,D). Micelles were formed when the adsorption approached saturation, and the magnitude of the decrease was greatly reduced. The five surfactant molecules mainly caused hydrophilic groups to face the bulk phase through van der Waals forces and hydrophobic action, whereas hydrophobic groups were adsorbed onto the leaves, thus reducing the solid−liquid interfacial tension. The surfactants displayed differing interfacial tension behavior on the adaxial surface, $C_{12}E_5$ and Triton X-100 had the greatest adsorption capacities, the strongest abilities to reduce solid−liquid interfacial tension, and DTAB had the weakest adsorption capacity. With regard to the abaxial surface, the solid−liquid interfacial tension behavior of the five surfactant molecules were also different, with $C_{12}E_5$ and Triton X-100 having the strongest abilities. These solid−liquid interfacial tension values obtained from eqs 1 and 2 provide a theoretical basis for the application of these five surfactants to jujube tree leaves in the future.

As shown in Figure 3C,D, the concentrations between 1×10^{-7} and 5×10^{-2} mol/L, when the concentration was lower than the critical micelle concentration, the decrease in solid−liquid interfacial tension with the increase in concentration was smaller than the corresponding decrease in surface tension. Therefore, the adhesion work decreased with increasing concentration. The adhesion work trends of the five surfactants were the same for both the adaxial and abaxial surfaces (Figure 3E,F).

3.4. Adhesion Mechanism of Surfactant Droplets on the Jujube Leaf Surface. The systematic study of the adsorption behavior of the five surfactant molecules on the gas−liquid and solid−liquid interfaces of jujube tree leaves during the fruit growth period allowed the main mechanisms by which the surface tension and contact angle were related to the wetting behavior to be explored. To facilitate analysis and discussion of the results, the behavior of the adsorption parameters was mainly divided into three processes according to surfactant concentration, as described below and shown in Figure 4. In the first process, due to the low surfactant concentration, molecules were adsorbed at the gas−liquid and solid−liquid interfaces to form unsaturated adsorption layers. At this point, the changes in surface tension, adhesion tension, and contact angle were not significant. Here, the contact angles changed slightly due to antagonism between adhesion tension and surface tension, and the two forces balanced each other. The surface tension of the liquid drops was relatively high in the low concentration range, and the air layer in the three-dimensional structure of the jujube tree leaves could not be replaced, resulting in a semi-wet state.

In the second process, as the surfactant concentration gradually increased, the number of surfactant molecules adsorbed on the interface increased continuously. As a result, the adhesion tension also increased continuously, but the rate of change in surface tension gradually decreased (Figure 4). As the surface tension of the drops continued to decrease, the surfactant drops began to overcome the pinning effect resulting from the three-dimensional structure of the leaves, and as the retention resistance was overcome, the contact angle decreased continuously, resulting in a fully wet state. The contact angle formed by the droplets on the leaf surface was approximately 80°, which was mainly due to hydrophilization of the leaves by the surfactant molecules. In this process, a synergistic effect between the reduced surface tension and increased adhesion tension led to a sharp decrease in contact angle. When the concentrations of $C_{12}E_5$ and Tween-20 were 1×10^{-6} mol/L, their contact angles began to decrease (Figure 4A−D). At 5×10^{-6} mol/L, the contact angles of Triton X-100 and SDS began to decrease (Figure 4E,F,I,J), and that of DTAB began to decrease at 5×10^{-5} mol/L (Figure 4G,H). This indicated that the wetting effects of the different surfactant molecules differed at the same concentrations. In the third process, the concentration of the surfactant solution exceeded the critical micelle concentration, and finally, a saturated adsorption layer was formed on the leaf surface. Due to the roughness of the leaf surface and other factors, the amount of surfactant adsorbed and the adsorption area increased. At this stage, the contact angle rate of change was small, and thus, the surface tension and adhesion tension also remained basically unchanged. The concentrations of the different surfactants required to reach a stable, fully wetted state differed. Micelles of surfactant molecules formed in the bulk phase, and capillary action in the spatial three-dimensional structure enabled surfactant droplets to be in a semipermeable state on the jujube leaf surface.

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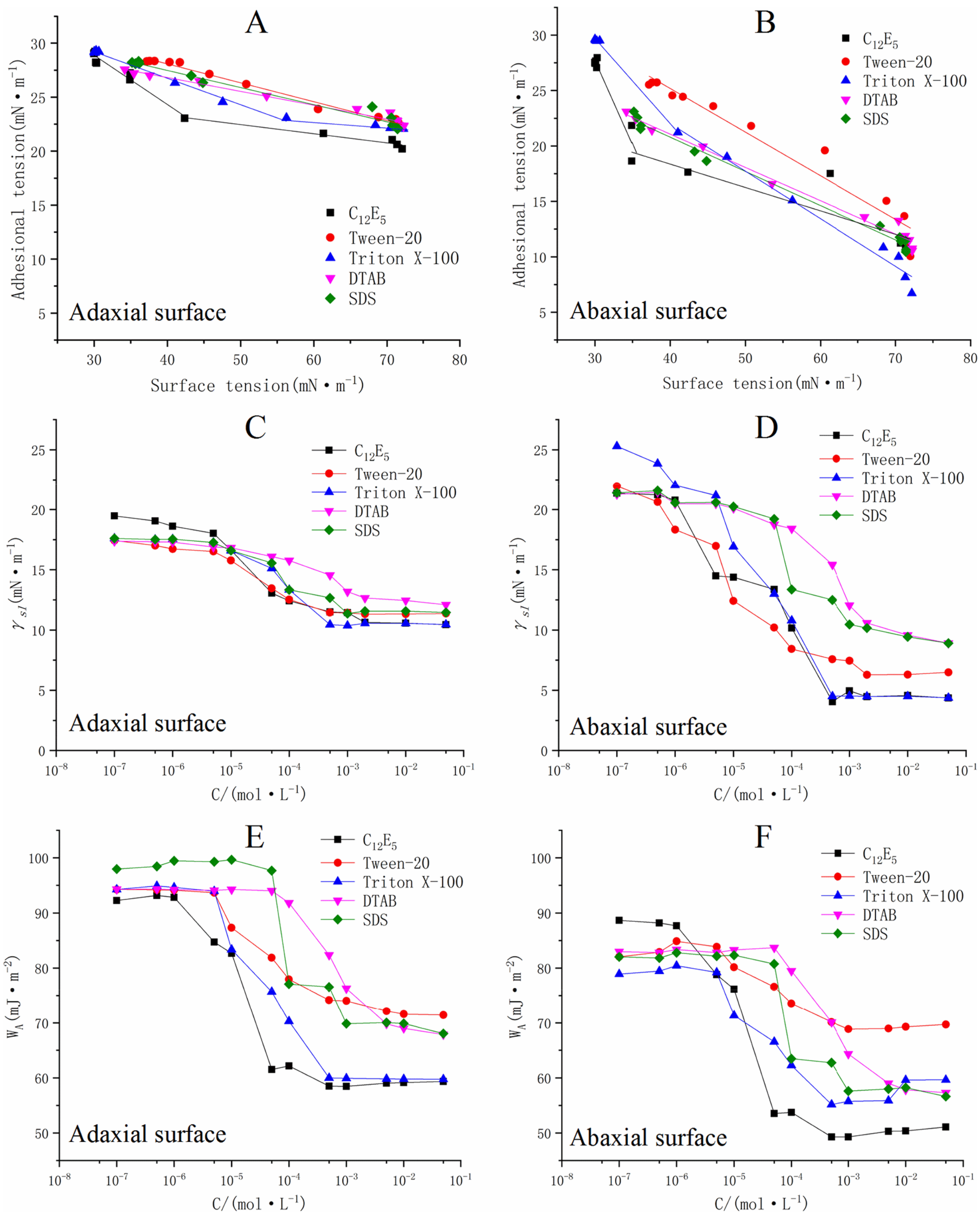

Figure 3. (A, B) Relationship between surface tension and adhesional tension of surfactants on adaxial and abaxial leaf surfaces at fruit inflating growth. (C, D) Relationship between interfacial tension (γ_{sl}) and C (C is surfactant concentration) of surfactants on adaxial and abaxial leaf surfaces at fruit inflating growth. (E, F) Relationship between adhesion work and C of surfactants on adaxial and abaxial leaf surfaces at fruit inflating growth.

Characterization of the leaf surface adaxial and abaxial the interaction without and with the surfactants by scanning electron microscopy (SEM) and optical photographs is showed in Figure 5. In SEM images, we can find that the pores on the abaxial of the leaves treated with surfactants are open, which is more conducive to the transport and conduction of pesticides (Figure 5D). Combining SEM and optical photographs of the leaves, we can see that there is a certain thickness of the waxy layer on the adaxial and abaxial of the leaves, and the waxy layer on the adaxial surface is thicker than that on the abaxial surface. After the treatment of surfactants, the waxy layer on both sides of the leaves is dissolved to some extent, and the waxy layer on the abaxial surface of the leaves is completely dissolved, which is conducive to the spread of pesticides (Figure 5G,H). The results showed that when the waxy layer on the leaf is dissolved, the surface roughness would be reduced, which is conducive to the wetting expansion of the liquid droplets.

3.5. Control Effect of 3% Beta-Cyfluthrin Added with $C_{12}E_5$ and Triton X-100 to Peach Fruit Moth.

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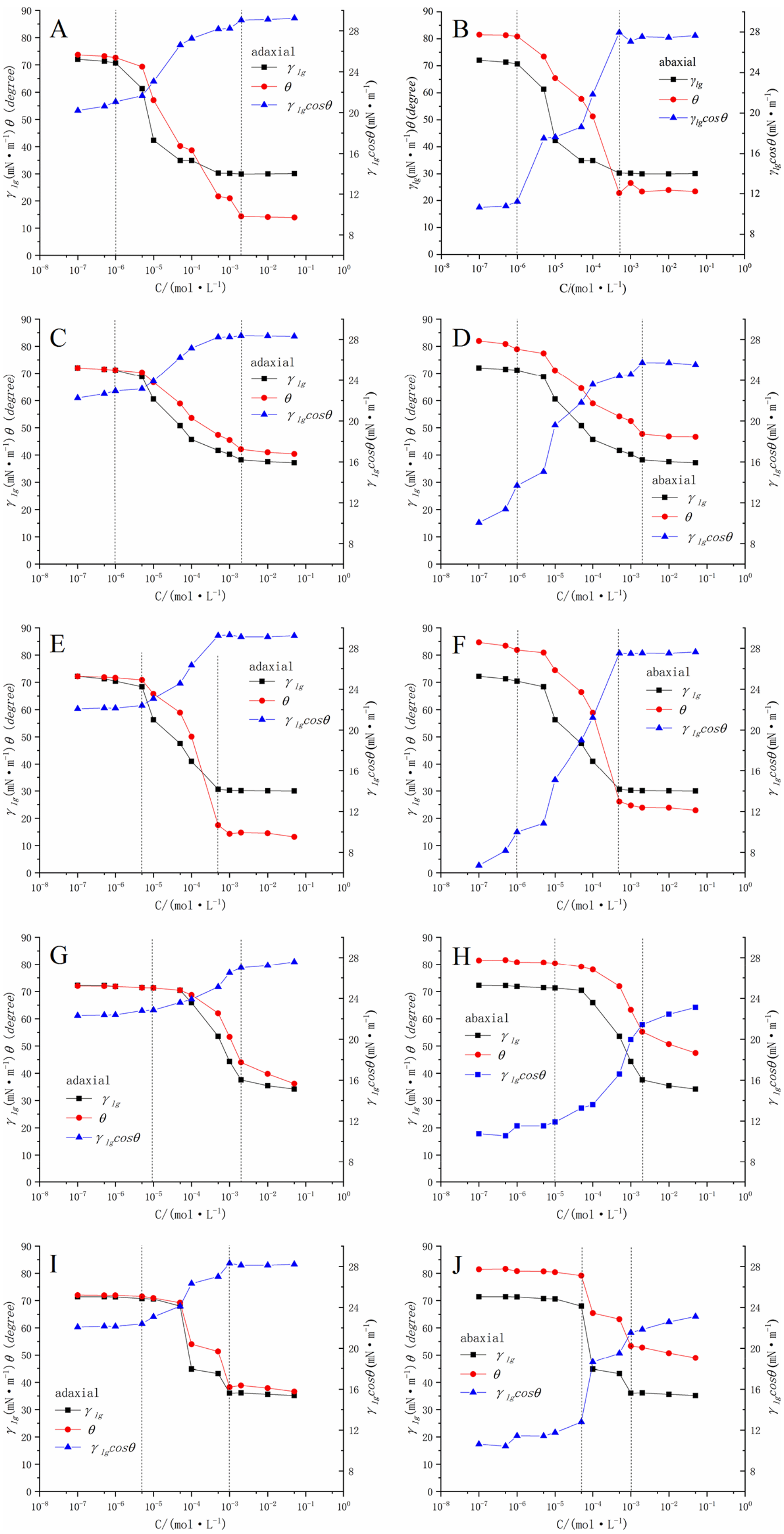

Figure 4. Concentration dependence of adhesion parameters of surfactants (A, B: $C_{12}E_5$; C, D: Tween-20; E, F: Triton X-100; G, H: DTAB; I, J: SDS) on (A, C, E, G, I) adaxial and (B, D, F, H, J) abaxial leaf surfaces during fruit inflating growth.

experiments, different percentages of surfactants were added to a beta-cyfluthrin emulsion in water, and the surface tension behavior, contact angles, and wetting adhesion of the pesticide solutions on the leaves were explored.[37] It was found that the

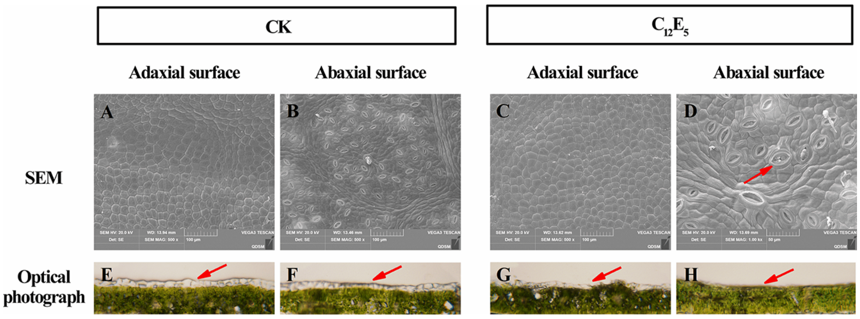

Figure 5. SEM images of (A, C) adaxial and (B, D) abaxial leaf surfaces; optical photographs of (E, G) adaxial and (F, H) abaxial leaf surfaces. (A, B, E, F) Leaf surface characteristics without surfactant treatment, (C, D, G, H) leaf surface characteristics treated with the $C_{12}E_5$ surfactant.

Table 2. Control Effect of 3% Beta-Cyfluthrin Added with $C_{12}E_5$ and Triton X-100 to Peach Fruit Moth[a]

				time			
				7 days		14 days	
surfactant	content (%)	pesticide dilution multiple	before application insect fruit rate (%)	after application insect fruit rate (%)	control effect (%)	after application insect fruit rate (%)	control effect (%)
$C_{12}E_5$	0	2000	1.13	3.25	82.48 ± 2.10c	5.13	83.88 ± 1.10c
	0.15		1.38	2.63	85.78 ± 2.40bc	3.75	88.12 ± 2.10b
	0.3		1.25	2.00	89.27 ± 3.70ab	2.88	91.04 ± 1.20b
	0.6		1.00	1.63	91.43 ± 3.40a	1.50	95.33 ± 3.10a
	0	3000	1.00	4.63	75.12 ± 2.60c	6.63	78.82 ± 4.10c
	0.15		0.75	3.25	82.35 ± 4.00b	5.50	82.55 ± 2.60bc
	0.3		1.13	3.00	83.44 ± 9.20b	4.63	85.23 ± 2.70b
	0.6		1.25	1.50	91.91 ± 2.30a	2.13	93.33 ± 1.40a
	0	4000	1.63	4.88	73.78 ± 2.40b	7.88	75.13 ± 3.40c
	0.15		0.88	3.88	78.99 ± 5.80ab	7.00	77.61 ± 6.10bc
	0.3		1.38	3.38	81.54 ± 6.10a	5.00	83.87 ± 4.70ab
	0.6		1.75	2.63	85.97 ± 2.60a	3.50	88.85 ± 2.80a
	water	CK	0.88	18.63		31.88	
Triton X-100	0	2000	1.38	3.50	81.30 ± 2.60c	4.63	85.98 ± 4.50b
	0.15		2.25	2.50	86.66 ± 3.30bc	3.13	89.88 ± 2.40ab
	0.3		1.50	1.88	90.29 ± 3.00ab	2.63	92.03 ± 2.90a
	0.6		2.63	1.25	93.15 ± 5.80a	1.75	94.21 ± 3.30a
	0	3000	2.13	4.63	75.32 ± 3.20c	7.00	77.83 ± 2.60c
	0.15		2.38	3.63	80.19 ± 8.50bc	5.63	81.83 ± 4.10bc
	0.3		1.38	2.88	84.48 ± 4.80b	4.63	85.15 ± 2.70b
	0.6		1.75	1.5	91.97 ± 3.70a	2.88	90.94 ± 2.10a
	0	4000	1.88	5.25	72.02 ± 5.10b	8.50	73.77 ± 2.10b
	0.15		1.63	4.13	77.78 ± 6.00ab	6.38	79.89 ± 2.20ab
	0.3		2.25	3.00	83.54 ± 9.20ab	5.13	82.63 ± 8.40ab
	0.6		1.63	2.50	86.26 ± 9.50a	3.13	89.22 ± 8.10a
	water	CK	1.38	18.88		32.13	

[a]Values with different letters in the same column are significantly different at $P < 0.05$.

addition of surfactants significantly improved the wetting adhesion of the original pesticide. Therefore, in this experiment, we further verified the effects of adding a surfactant to the original pesticide on its field efficacy for peach fruit moths. It can be seen from Table 2 that the control effect of three different dilutions of pesticide solutions with surfactants was significantly different from those without surfactants. With the increase of the surfactant concentration, the control effect of pesticides also increases. However, when the surfactant reaches the critical micellar concentration, it is added to the fixed-concentration solution. At this time, even if the surfactant concentration is increased, the control effect of pesticide solution remains in a certain range. When the pesticide was diluted 4000 times, the minimum control effect reached more than 70%, and the control effect reached more than 80% when the surfactant was added (the concentration reached the critical micelle concentration). At 2000-fold dilution, the control effect of pesticide with surfactants reached the highest values (more than 85%). The above results indicated that the pesticide could be used in reduced quantities with suitable surfactants, and a higher control effect could be achieved.

4. DISCUSSION

Wetting and adhesion processes of five surfactant droplets on jujube tree leaf surfaces during the fruit growth period were studied in this paper, and the mechanisms of action were investigated. The wetting behavior of five surfactants with

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different molecular structures was studied. $C_{12}E_5$ and Triton X-100 had the best wetting effects. Both form micelles in solution, resulting in a solubilization effect on the leaf wax layer that improved the wetting performance of the solution.[13,26] Non-ionic surfactants do not dissociate in water and are stable in nature, making them the main emulsifiers used for pesticides. However, among these surfactants we investigated, the steric hindrance effect caused by molecular structures was found to possibly affect the adsorption capacity of the solid−liquid interface, and thus, their wetting effect was poorer than that of non-ionic surfactants.[23] On different solid surfaces, the structure of the adsorption layer formed by surfactant molecules is related not only to the properties of the solid surface itself but also to the structure of the surfactant molecule and the pH and temperature of the surrounding environment. If the molecular structure of the hydrophobic surfactant is branched, micelles can form on the solid surface through hydrophobic interactions between molecules at high concentrations. This greatly reduces the solid−liquid interfacial tension, thus increasing the solid−liquid interfacial adsorption capacity and providing better wetting performance than other types of surfactants exhibit.[27,28] However, inorganic salts and organic small molecules in ionic surfactant solutions can interact with surfactant molecules to change the surface molecular structure of the complex solution, thus affecting its interfacial tension and greatly affecting its wetting and adhesion behavior.[29,30]

Due to the differences in the molecular structures of $C_{12}E_5$ and Triton X-100, the contents of chemical substances on the jujube leaf surface and the thickness of the wax layer on the surface, their wetting behaviors are significantly different. The two surfactants $C_{12}E_5$ and Triton X-100, with the best experimental results in this paper, and Tween-20, with relatively good effects, are all polyether surfactants. They are characterized by low levels of dissociation in water, high stability, resistance to water with high hardness, strong electrolytes, acids, and alkalis, and good miscibility with other types of surfactants. In addition, polyether surfactants also have very high surface activity. Their aqueous solutions have relatively low surface tension and critical micelle concentration compared with those of ionic surfactants and good emulsification, bubble inhibition, and washing functions.[31] The oxygen atom, benzene ring, and ethoxy group in anionic surfactants are adsorbed on the surfaces of the particles, providing a negative charge, and the dispersion systems are stabilized by electrostatic repulsion and steric hindrance. They are adsorbed on the surfaces of negatively charged particles by the electrostatic action of ammonium ions. The lipophilic segment extends into the medium and disperses the whole system by steric hindrance. However, they exist as ions, and thus, their stability is poor, making them easily affected by strong electrolytes, acids, and alkalis.[32,33] Compared with other types of surfactants, the two non-ionic surfactants not only have larger hydrophilic groups but also have hydroxyl groups. The presence of hydroxyl groups allows for the formation of intermolecular hydrogen bonds, causing surfactant molecules to be more closely arranged on the surface of the plant leaves and increasing the adsorption amount. Thus, the wetting ability of non-ionic surfactants on the surface of plant leaves is significantly enhanced compared with those of anionic and cationic surfactants. The results showed that polyether non-ionic surfactants had the best wetting ability on jujube tree leaves. Zhang (2017) tested the wetting and adhesion behavior of Triton X-100, DTAB, and SDS on the surface of wheat leaves and Triton X-100 on the surface of rice leaves and found that the contact angles of surfactants began to decrease with increasing surfactant concentration.[34] When the concentration of Triton X-100 reached 5×10^{-4} mol/L, the contact angle decreased significantly. At a given concentration, the contact angles of Triton X-100 droplets were smaller than those of SDS and DTAB droplets. The results obtained in this experiment are consistent with those obtained by Zhang. Both experiments prove that the molecular structure of a surfactant has a significant influence on its wetting behavior. Zdziennicka et al. studied the wetting and adhesion behavior of a series of non-ionic, anionic, and cationic surfactants on a polymethyl methacrylate surface and found that, regardless of the type of surfactant used, its adhesive tension and surface tension exhibited a linear relationship across the tested concentration range. Due to the difference in molecular structures of the surfactants, their linear slopes differed.[35,36] In this experiment, comparing the fit slopes corresponding to the linear relationships between the surface tension and adhesive tension of different solutions shows that the slopes of different surfactants on jujube tree leaves were all more positive than −1. This indicates that a fully wetted state was not reached and that the surfactants could not overcome the pinning effect on the three-dimensional leaf surface to replace the air layer inside, showing that the solutions could not easily wet the jujube tree leaves. However, in previous experiments conducted by Gao et al., it was found that the slopes of different surfactants on the adaxial surface of apple tree leaves were all greater than −1 at the first stage and that the slopes of $C_{12}E_5$ and Triton X-100 were less than −1 at the second stage,[37] which indicates that they had very good wetting abilities on the surface of apple tree leaves. In tests conducted by Zhang on wheat leaves, the slopes of Triton X-100, DTAB, and SDS were close to −1 at the first stage and less than −1 in the second stage, finally indicating a fully wetted state.[9] This indicated that there are significant differences in the behavior of surfactant molecules on the surfaces of different plant leaves. On the basis of this information, we can find that if the surface free energy of the leaves of different fruit tree species is similar to that of crisp jujube tree leaves, polyether surfactants with molecular structures similar to those of $C_{12}E_5$ and Triton X-100 are also suitable for their leaf surfaces and will have good wetting effects.

Due to the existence of a precursor water film in the droplets, surfactant molecules on the interface continuously move to the water film on the surface of jujube tree leaves, thus causing interactions between the droplets and the leaves. Furthermore, the micro-mechanisms in jujube tree leaves, such as wax coats in the three-dimensional structure, enhance the force acting between the droplets and leaves. An understanding of these mechanisms is important for guiding research on pesticide synergies for jujube trees in the future. A field efficacy test of this experiment was performed to prove that two kinds of surfactants have a synergistic effect. Since the concentration of only one kind of surfactant was varied in the test, whether there is a clear quantitative relationship between the wetting ability of surfactants and their field control effect is still unknown. Gao et al. measured the effects of adding different types of surfactants on the wetting properties of fungicides and found that surfactants changed the solution crystal structure of the agents, thus enhancing the control effect of the agents in the field.[25] By using structural equation modeling and IBM SPSS Amos software, they proved that different parameters were related to the field control effect to some extent. With the rapid economic development of the market and continuous improvement in living and consumption standards, the jujube industry will face more challenges. The relevant theoretical results of the research in this paper will provide theoretical guidance for the future improvement of pesticide wetting and adhesion on jujube tree leaves, thus achieving the goals of reducing their application and increasing their efficacy. A fundamental understanding of these wetting phenomena and mechanisms of action is also of great significance for the study of new pesticide additives and formulations to be applied to jujube trees in the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c02317.

Information on the five surfactants used in the experiment; and laboratory instruments and manufacturers (PDF)

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Notes

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