



Article

Effects of Different Spray Adjuvants on the Permeation of Dinotefuran in Rice Leaves

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Abstract: This study investigated the efficacy of three spray adjuvants (Coerce, Wetcit, and Silwet408) in enhancing dinotefuran permeation in rice leaves. Different concentrations of these adjuvants were tested using an external standard method. The rice leaf surface was analyzed by using the van Oss–Chaudhury–Good method to establish a link between surface free energy (SFE) and dinotefuran permeation. All of the adjuvants effectively increased dinotefuran permeation in rice leaves, with the highest permeation of 8.496 mg/kg achieved using Wetcit at 1000 mg/L. The SFE of the rice leaf surface was determined to be 29.28 mJ/m². A notable correlation was observed between the energy difference (the SFE of the pesticide liquid versus the SFE of the rice leaf surface) and permeation. Various fitting methods, including linear, exponential, logarithmic, polynomial, and power methods, were applied. Polynomial fitting demonstrated the highest coefficient of determination ($R^2 > 0.9000$). The relationship between the permeation (y) and energy difference ($\Delta\gamma$) conformed to the polynomial equation $y = a\Delta\gamma^2 + b\Delta\gamma + c$, where a , b , and c are constants. This model provides a predictive tool for the optimal dosage of spray adjuvants according to target plant characteristics, enhancing the understanding of the interaction between pests and pesticides.

Keywords: spray adjuvant; permeation; surface free energy; rice leaf surface



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1. Introduction

Foliar spray application remains a vital method of pest and disease control. Pesticide formulations are diluted and applied by spraying equipment, targeting initial hosts (typically plants, the primary subjects of protection or the habitats of pests) before they reach the final targets (the pests). In most cases, less than 1% of the pesticide effectively reaches the final target to exert its insecticidal effect [1,2]. The inefficiency of the entire pesticide delivery process primarily stems from the diverse and complex factors involved in the spraying procedure [3,4]. The efficacy of pesticide dose delivery hinges on various factors, such as the affinity between the spray solution and the leaves of the initial target plant, the physicochemical properties of the solution, the type of spray nozzle, and climatic conditions [5–7]. Controlling agricultural pests ultimately depends on two factors: the level of toxicity and the amount of active ingredient in the pesticide [8,9]. Dinotefuran, classified by the IRAC as a neonicotinoid pesticide, is widely applied in the control of rice planthoppers and rice borers in paddy fields [10]. Some insects, including *Nilaparvata lugens* and *Bemisia tabaci*, have developed resistance to dinotefuran [11,12]. To delay pest resistance, it is recommended to use spray adjuvants or synergists in a rational manner [13]. Spray adjuvants are a class of highly active substances employed to modulate the physical and chemical attributes of liquids. They effectively reduce the surface tension at the interface between the liquid and solid phases, enhance interfacial activation to promote compatibility, and subsequently regulate the permeation of pesticide solutions onto the leaves of target plants [14]. In the domain of pest control in China, silicone and vegetable

oils are the prevailing choices for spray adjuvants [15,16]. In comparison, vegetable oil adjuvants, such as green orange oil (Coerce) and orange peel oil (Wetcit), enjoy wider usage and demonstrate superior affinity [17,18]. These vegetable oil adjuvants contribute significantly to herbicidal efficacy postgermination. Primarily, they enhance the permeation of [^{14}C]-labeled quizalofop-ethyl ($\log K_{ow}$ 4.5) and fenoxaprop-ethyl ($\log K_{ow}$ 4.58) into the target epidermis, which is contingent upon the ability of the oil to promote the distribution of these pesticides within the epidermis. Additionally, vegetable oils can dissolve epidermal wax, disrupting the barrier pathway of the target plant and facilitating pesticide permeation [18,19]. Furthermore, vegetable oils activate the contact surface of the target plant and droplets, leading to a reduction in the surface energy of the droplets. This alteration enables the droplets to spread more effectively across the target foliage while reducing the contact angle. The incorporation of orange peel oil adjuvants at concentrations ranging from 0.01% to 1.00% can reduce the surface tension of the pesticide solution by 48.17% to 55.73%. This increase in surface tension improves the wettability of pesticide solution droplets on *pittosporum tobira* leaf surfaces, ensuring effective control of *Edentatipsylla shanghaiensis* Li et Chen and reducing the requisite pesticide quantities [20]. Therefore, it is important to consider the appropriate amount of spray adjuvants when using the product.

In practice, most pesticide formulations used in pest control contain surfactants. Unfortunately, surfactants often prioritize the stability of pesticide formulations, disregarding the surface tension of the liquid, the concentration of the surfactant in the liquid, and the characteristics of the application target. Consequently, recommended dosages fail to ensure proper adhesion of the liquid to the target plant surface, leading to substantial environmental pollution [21,22]. Leaf surface free energy and its components are intrinsic properties of the leaf surface. They can guide the design of pesticide foliar application and specific pesticide formulations. The main methods for measuring surface free energy are the Owens–Wendt–Rabel–Kaelble (OWRK) method and the van Oss–Chaudhury–Good method (OCG) [23–25]. Detection liquids typically used for the OCG method are water, glycerol, and diiodomethane [24]. These liquids offer good reproducibility and yield a large amount of characterization [26]. The OCG method can be used to determine the surface free energy of leaves, as confirmed through mathematical methods. Measuring contact angles of liquids with varying degrees of polarity and apolarity is a common method for characterizing surface free energy in recent studies. The physicochemical properties of *Eucalyptus sideroxylon* leaves were analyzed using the OCG method to predict polar, nonpolar, and intermolecular hydrogen bond interactions [24]. Rice leaves exhibit high hydrophobicity [21] and their physicochemical characteristics are closely related to foliar permeation of pesticides. Due to the lack of data on the surface properties of plants targeted for spraying, the internal relationship between liquid surface tension and pesticide leaf permeation is often ignored during the spraying process, which affects the efficacy to a certain extent.

Considering this, we conducted the permeation of dinotefuran in rice leaves using varying amounts of vegetable oil and silicone adjuvants. Additionally, we aimed to establish the intrinsic correlation between the physicochemical properties of the liquid and rice leaf permeation. To simplify the experiment and reduce influencing factors, we chose the dipping method instead of the more complex foliar spray application process. This would enable us to quickly determine the optimal dosage of spray adjuvants for production based on the correlation. These efforts provide a scientific foundation for the utilization of pesticide adjuvants in the management of rice insects and diseases.

2. Materials and Methods

2.1. Experimental Materials

The rice variety subjected to testing was Nanjing 9108, which was cultivated in pots and maintained until the rupturing stage. The reagents employed in this experiment included deionized water, acetonitrile of chromatographic grade, and carbinol (provided by Tedia Company Inc., Fairfield, CT, USA). Additionally, 99% glycerol and 98%

diiodomethane were obtained from Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China. Furthermore, we used 20% dinotefuran soluble granules (produced by Mitsui Chemical Co., Ltd., Tokyo, Japan), dinotefuran standard (provided by Tan-Mo Technology Co., Ltd., Changzhou, China), Coerce (provided by Axeb biotech S.L., Lleida, Spain), Wetcit (provided by American Oro Agri Agricultural Chemicals Company, Fresno, CA, USA), and Silwet408 (provided by Momentive performance materials Co., Ltd., Wilton, CT, USA).

2.2. Instruments and Software

The following instruments and equipment were used in this study: a contact angle meter (JC2000C1B) manufactured by Shanghai Powereach Digital Technology Equipment Co., Ltd., Shanghai, China; a microsyringe (0–50 μ L) designated MS50 produced by Shanghai Gauge Industry and Trade Co., Ltd., Shanghai, China; a surface tension meter (DCAT11EC) sourced from Germany Dataphysics Instruments Company, Filderstadt, Germany; and a hyper-pure water system established by the Plant Protection Institute of Jiangsu Academy of Agricultural Sciences, Nanjing, China. A high-performance liquid chromatography (HPLC) instrument (2695) equipped with a diode array detector (Waters Corporation, Milford, CT, USA) was used for analysis. An electronic balance (JY20002) was obtained from Shanghai Shunyu Hengping Scientific Instrument Co., Ltd., Shanghai, China, and a water bath nitrogen blower (HSC-24B) was obtained from Tianjin Hengao Technology Development Co., Ltd., Tianjin, China.

2.3. Treatment

The experiment was designed with nine treatments involving the use of adjuvants (Coerce, Wetcit, and Silwet408), and each treatment was repeated three times for robustness. Various quantities of adjuvants (1.000 g, 0.500 g, 0.250 g, 0.125 g, 0.063 g, 0.031 g, and 0.016 g) were dissolved in 1 L of deionized water, which included 0.655 g of 20% soluble dinotefuran granules. Simultaneously, a reagent blank (comprising 1 L of deionized water with 0.655 g of 20% soluble dinotefuran granules) and a blank control (consisting of 1 L of deionized water) were also prepared for reference.

2.4. Sample Preparation

The rice leaves cultivated in plastic pots were immersed in the prepared solutions for a duration of 30 s in a glass beaker. Subsequently, the leaves were removed from the solutions. After an interval of one hour, the dipped leaves were collected for further experimentation. All of the rice leaf samples were finely pulverized, and four grams of each sample was accurately weighed into a centrifuge tube. To ensure complete saturation, 24 mL of acetonitrile and 3 g of NaCl were added to the powder, followed by one minute of vigorous shaking. Next, the samples underwent 15 min of ultrasonic extraction and were subsequently filtered into conical bottles. From this, 12 mL of the supernatant was extracted and reduced to a volume of less than 4 mL through nitrogen blowing. Additional acetonitrile was added to reach a final volume of 4 mL. Following this step, 4 mL of the supernatant was transferred from the centrifuge tube to another centrifuge tube containing 200 mg of PSA (ethylenediamine-N-propyl), 200 mg of C₁₈, and 150 mg of anhydrous MgSO₄ as sorbents. The extract was then vortexed for 2 min and centrifuged at 5000 revolutions per minute for 5 min. Subsequently, a 2 mL portion of the supernatant was dried using N₂. This dried residue was dissolved in 0.1 mL of methanol, after which 0.9 mL of deionized water was added and thoroughly mixed. The concentrated samples were subjected to HPLC [27].

2.5. Quantification of Dinotefuran Concentrations

The quantification of dinotefuran in rice leaves was conducted using HPLC with a Waters 2695 model instrument equipped with a DAD set at a wavelength of 270 nm. A symmetric C18 column (4.6 mm $\times$ 250 mm, 5 μ m) was used for separation. The mobile

phase comprised HPLC grade carbinol and water at a ratio of 20:80 (*v/v*) and was delivered at a flow rate of 1 mL/min. Each injection consisted of 30 µL of the sample. With these operational parameters, the retention time of dinotefuran was determined to be 5.7 min. The identification of dinotefuran was validated by comparing its retention time with that of an authentic standard. To prepare the dinotefuran standard stock solution (10 mg/L), HPLC grade acetonitrile was used. Calibration curve standard solutions for dinotefuran (at concentrations of 0.02 mg/L, 0.05 mg/L, 0.1 mg/L, 0.2 mg/L, and 0.5 mg/L) were generated from the stock solution through sequential dilutions using HPLC grade acetonitrile. These standard solutions were essential for the quantification of dinotefuran in rice leaves. Prior to utilization, the solutions for the permeation experiments were thoroughly prepared via serial dilutions and stored at -4°C in a refrigerator.

2.6. Permeation of Dinotefuran

The determination of dinotefuran permeation in rice leaves followed the external standard method [28] and was calculated using the following formula: $\omega = (\rho \times v \times f) / m$. In this formula, ω represents the amount of dinotefuran permeation in rice leaves to be measured (mg/kg), ρ denotes the quantity of dinotefuran to be measured in the sample solution (mg/L), m represents the weighed sample amount (g), v represents the constant volume (mL), and f signifies the dilution ratio.

2.7. SFE of Rice Leaf Surfaces and Surface Tension

Determination of the static contact angle of three different detection liquids (deionized water, glycerol, and diiodomethane) on the rice leaf surface was conducted at a temperature of $20 \pm 3^{\circ}\text{C}$ and a relative humidity of $65 \pm 5\%$. Subsequently, the surface free energy of the leaf surface was calculated utilizing the van Oss–Chaudhury–Good (OCG) method. The surface free energy (SFE, γ) of the rice leaf surface can be expressed as the sum of two components: the Lifshitz–van der Waals component (γ^{LW}), representing nonpolar interactions of SFE, and the acid–base interaction component (γ^{AB}), representing polar interactions of SFE. Within γ^{AB} , there exists a Lewis acid component γ^{+} and a Lewis base component (γ^{-}). Surface polarity calculations were performed considering the SFE components of deionized water ($\gamma = 72.80 \text{ mJ/m}^2$, $\gamma^{\text{LW}} = 21.80 \text{ mJ/m}^2$, and $\gamma^{+} = \gamma^{-} = 25.50 \text{ mJ/m}^2$), glycerol ($\gamma = 63.70 \text{ mJ/m}^2$, $\gamma^{\text{LW}} = 33.60 \text{ mJ/m}^2$, $\gamma^{+} = 8.41 \text{ mJ/m}^2$, and $\gamma^{-} = 31.16 \text{ mJ/m}^2$), and diiodomethane ($\gamma = 50.80 \text{ mJ/m}^2$, $\gamma^{\text{LW}} = 50.80 \text{ mJ/m}^2$, $\gamma^{+} = 0.56 \text{ mJ/m}^2$, and $\gamma^{-} = 0 \text{ mJ/m}^2$) [23–25].

The software program SACT31, integrated with a surface tension meter, was used to determine the surface tension (γ) of the fully stirred pesticide solution, which was prepared with three different spray adjuvants at various concentrations (1000 mg/L, 500 mg/L, 250 mg/L, 125 mg/L, 63 mg/L, 31 mg/L, and 16 mg/L). It is important to note that the surface tension of the pesticide solution, measured at room temperature and under atmospheric pressure, is correlated with the surface free energy.

2.8. Statistical Analysis

All of the data analyses were performed using Excel 365 software V16.0 (Microsoft, Redmond, WA, USA). To assess significant differences, one-way ANOVA followed by Duncan's new multiple range test was conducted, and the data were processed using DPS 17.10 software (Hangzhou Ruifeng Information Technology Co., Ltd., Hangzhou, China). Furthermore, regression analyses, including linear, exponential, logarithmic, polynomial, and power fitting between the energy difference and the permeation, were executed using Excel 365 software V16.0 (Microsoft, Redmond, WA, USA) and Origin 8 software V 8.0725 (OriginLab Corporation, Northampton, MA, USA).

3. Results

3.1. Method Validation

A linear correlation analysis was conducted with mass concentration (c) as the horizontal coordinate and peak area (S) as the vertical coordinate (Figure 1), yielding the linear equation $S = 121560c - 187.31$ ($R^2 = 1.0000$) for dinotefuran.

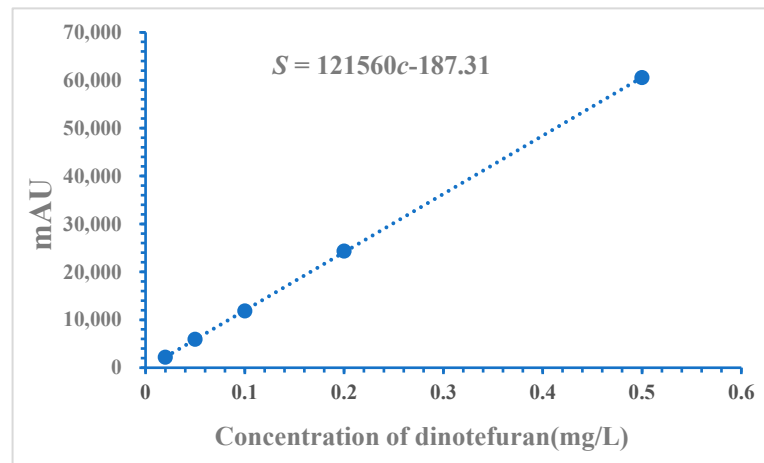


Figure 1. Standard curve of dinotefuran.

To confirm the accuracy and precision of the detection method, a standard solution of dinotefuran (0.1 mg/kg) was added to the test sample, and the analysis was performed in triplicate. The results indicated recoveries ranging from 72.5% to 78.5%, with a relative standard deviation (RSD) of 4.3%, when utilizing the solvent standard curve method at 0.1 mg/kg. Calibration using the matrix matching standard curve method yielded recoveries between 81.6% and 88.4%, with an associated RSD of 4.4%. A representative chromatogram is shown in Figure 2.

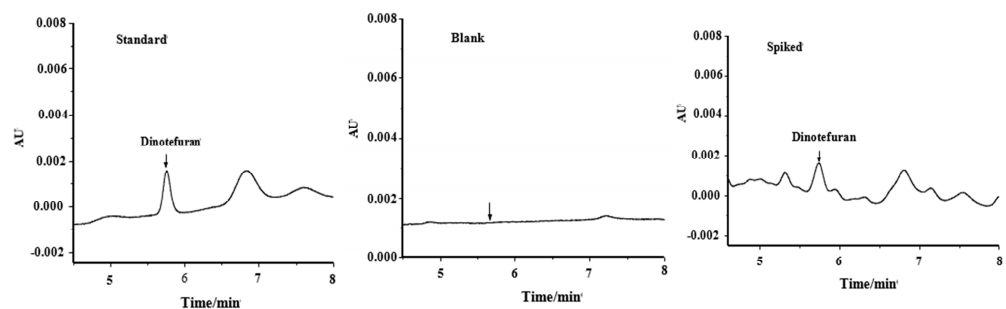


Figure 2. HPLC chromatogram calibration of dinotefuran.

3.2. Permeation of Rice Leaves with Dinotefuran

Dinotefuran was not detected in the rice leaves immersed in deionized water. However, in the pesticide solution, the permeation of dinotefuran in rice leaves was 3.381 ± 0.081 mg/kg. The effects of different spray adjuvants on the permeation of dinotefuran in rice leaves are summarized in Table 1. In general, the permeation of dinotefuran in rice leaves exhibited an upward trend with increasing adjuvant concentration, particularly in the case of Coerce and Wetcit. Notably, the recorded permeation of dinotefuran in rice leaves with Coerce and Wetcit reached 8.149 ± 0.190 mg/kg and 8.496 ± 0.124 mg/kg, respectively, representing significantly greater permeation than that of the other adjuvants ($p < 0.05$). Compared to the 16 mg/L, 31 mg/L, 63 mg/L, and 125 mg/L treatments, the permeation of dinotefuran solutions with spray adjuvants at 250 mg/L and 500 mg/L showed a significant increase ($p < 0.05$). In contrast to Coerce and Wetcit, permeation in

rice leaves with Silwet 408 first increased and then decreased with increasing concentration. Specifically, at a concentration of 63 mg/L, the maximum permeation of dinotefuran in rice leaves was 8.177 ± 0.363 mg/kg. Compared to the 16 mg/L, 500 mg/L, and 1000 mg/L treatments, the permeation of dinotefuran solutions with spray adjuvants at 31 mg/L, 63 mg/L, 125 mg/L, and 250 mg/L showed a significant increase ($p < 0.05$). Figure 3 provides a comparative illustration of the maximum values achieved with each spray adjuvant at the three different concentrations. With Coerce, dinotefuran permeation in rice leaves was greater at 1000 mg/L, with Wetcit at 250 mg/L and 1000 mg/L, and with Silwet408 at 63 mg/L and 125 mg/L. Notably, no significant differences were observed among the treatments ($p > 0.05$).

Table 1. Effects of adjuvants with different concentrations on the permeation of dinotefuran in rice leaves.

Concentrations (mg/L)	Permeation (mg/kg)		
	Coerce	Wetcit	Silwet408
16	3.840 ± 0.161 d	4.011 ± 0.208 e	6.406 ± 0.222 c
31	3.297 ± 0.147 d	3.853 ± 0.084 ef	7.340 ± 0.197 b
63	3.812 ± 0.127 d	4.925 ± 0.259 d	8.177 ± 0.363 a
125	5.343 ± 0.073 c	5.625 ± 0.197 c	7.718 ± 0.152 ab
250	7.264 ± 0.116 b	7.884 ± 0.067 b	7.191 ± 0.296 b
500	7.181 ± 0.445 b	7.628 ± 0.237 b	6.510 ± 0.005 c
1000	8.149 ± 0.190 a	8.496 ± 0.124 a	6.488 ± 0.022 c
0	3.381 ± 0.081 d	3.381 ± 0.081 f	3.381 ± 0.081 d

Note: the data in the table are mean $\pm$ standard deviation ($n = 3$). Different letters in the same column indicate a significant difference at the level of $p < 0.05$ according to Duncan's new multiple range test.

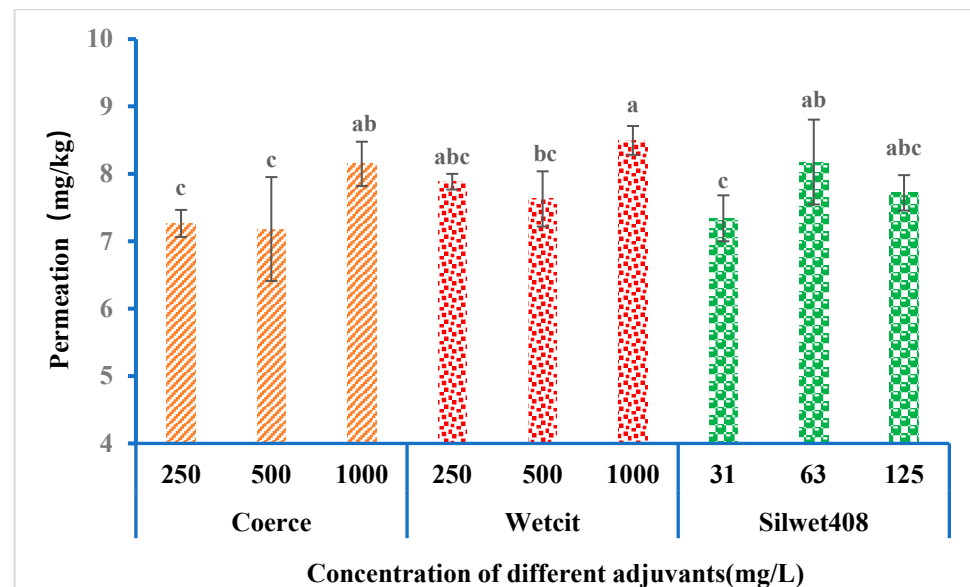


Figure 3. Comparison of the maximum permeation of dinotefuran in rice leaves treated with different adjuvants. Different letters indicate a significant difference at the level of $p < 0.05$ according to Duncan's new multiple range test.

3.3. Surface Free Energy of Rice Leaf Surfaces

The characterization of rice leaf surfaces by measuring contact angles of three liquids with different disperse and non-disperse contributions (W, G, and DM) is presented in Table 2. The data revealed that rice leaf surfaces led to very high static contact angles ($>100^\circ$) with polar liquids (W and G), with a notable difference observed between the adaxial and abaxial surfaces of the rice leaves. In contrast, the static contact angles of the apolar liquid (DM) were less than 90° , and no significant difference was detected between the adaxial and abaxial surfaces. After calculation by using the OCG method, the SFE

values for the adaxial and abaxial leaf surfaces were determined to be 28.56 mJ/m² and 30.00 mJ/m², respectively. These values indicate that the number of Lifshitz–van der Waals components (γ^{LW}) were greater than the number of acid–base components (γ^{AB}), suggesting that nonpolar interactions predominate over polar interactions. Additionally, the mean SFE for the leaf surface was less than 100 mJ/m², indicating that the rice leaf surface possessed low energy.

3.4. Energy Difference ($\Delta\gamma$)

Table 3 shows the effects of three adjuvants at different concentrations on the surface free energy of dinotefuran solutions. The surface tension of the pesticide solution was initially measured to be 36.80 mN/m. With the addition of various concentrations of spray adjuvants (Coerce and Wetcit), the surface tension of the solution generally decreased, except for that with Coerce at a concentration of 16 mg/L, which exhibited a slight increase. In particular, the surface tension of the solution containing Silwet408 decreased rapidly and became stable. A maximum reduction of 16.40 mN/m was achieved with Silwet408. Coerce and Wetcit have a similar ability to reduce surface tension, with a maximum reduction of 6.27 mN/m and 6.90 mN/m, respectively.

Table 2. Surface free energy of rice leaf surface.

Rice Leaf	Static Contact Angle (°)			γ^{LW} (mJ/m ²)	γ^{AB} (mJ/m ²)	SFE γ_s (mJ/m ²)	Mean (mJ/m ²)
	Water (W)	Glycerol (G)	Diiodomethane (DM)				
Adaxial Leaf	137.8 ± 2.4 a	108.4 ± 2.2 a	88.9 ± 1.6 a	16.08	12.48	28.56	29.28
Abaxial Leaf	132.5 ± 1.9 b	104.5 ± 1.8 b	89.7 ± 1.3 a	15.55	14.45	30.00	

Note: the data in the table are mean ± standard deviation ($n = 10$). Different letters in the same column indicate a significant difference at the level of $p < 0.05$ according to Duncan's new multiple range test.

Table 3. Effects of three adjuvants at different concentrations on the surface free energy of dinotefuran solutions.

Concentrations (mg/L)	Coerce			Wetcit			Silwet408		
	γ (mN/m)	γ^s liquid (mJ/m ²)	$\Delta\gamma$	γ (mN/m)	γ^s liquid (mJ/m ²)	$\Delta\gamma$	γ (mN/m)	γ^s liquid (mJ/m ²)	$\Delta\gamma$
16	37.17	37.17	7.89	36.31	36.31	7.03	33.07	33.07	3.79
31	36.75	36.75	7.47	35.29	35.29	6.01	28.32	28.32	−0.96
63	35.39	35.39	6.11	34.53	34.53	5.25	23.57	23.57	−5.71
125	34.31	34.31	5.03	32.78	32.78	3.5	20.67	20.67	−8.61
250	32.66	32.66	3.38	30.46	30.46	1.18	20.69	20.69	−8.59
500	31.25	31.25	1.97	30.41	30.41	1.13	20.46	20.46	−8.82
1000	30.53	30.53	1.25	29.90	29.90	0.62	20.40	20.40	−8.88
0	36.80	36.80	7.52	36.80	36.80	7.52	36.80	36.80	7.52

Note: $\Delta\gamma = \gamma^s_{\text{liquid}} - \gamma^s_{\text{rice}}$; $\gamma^s_{\text{rice}} = 29.28$ mN/m.

Directly related to foliar permeation, the SFE of a material is an essential property that determines its surface and interfacial properties in processes such as wetting and adhesion. Under standard temperature and pressure conditions, the surface tension and surface energy of a liquid are equivalent, despite being measured in different units. The mean SFE for the rice leaf surface was determined to be 29.28 mJ/m² (Table 2). When the solution was supplemented with Coerce, its SFE surpassed that of the rice leaves, resulting in an energy difference ($\Delta\gamma$) ranging from 1.25 to 7.89. Similarly, the SFE of the solution supplemented with Wetcit exceeded that of the rice leaves. However, when the concentration reached 1000 mg/L, the SFE of the solution became lower than that of the rice leaves, with an energy difference ranging from 0.62 to 7.03. In contrast, the SFE of the solution supplemented with Silwet408 was lower than that of the rice leaves, except for at 16 mg/L, where the SFE exceeded the SFE of the rice leaves, resulting in an energy difference ranging from −8.88 to 3.79.

3.5. Correlation Analysis between Permeation and Energy Difference ($\Delta\gamma$)

A scatterplot depicting the differences in permeation and energy can be found in Figure 4, and the correlation analysis results of the difference in energy and the permeation of dinotefuran in rice leaves (y) are presented in Table 4. Various curve fitting methods were applied to Coerce, Wetcit, and Silwet408, including linear, exponential, logarithmic, polynomial, and power functions. These were then aggregated for analysis. Linear and polynomial fitting were applied to Coerce and Wetcit, revealing a robust correlation with R^2 (coefficient of determination) values exceeding 0.8000. The correlation analysis between the functions of Coerce and Wetcit revealed a high degree of similarity. Given the negative energy difference between the surface energy of the pesticide liquid and the surface free energy of the rice leaf, only linear and polynomial fittings could be performed for Silwet408. Consequently, only linear and polynomial functions with satisfactory polynomial fitting ($R^2 > 0.9000$) were considered. Both the linear and exponential functions yielded R^2 values less than 0.5000. In general, the energy difference provided the most suitable polynomial ($y = -0.04512\Delta\gamma^2 - 0.27985\Delta\gamma + 7.9777$) fit for permeation ($R^2 = 0.9167$, $F = 1054.70187$, $DF = 3$, $p < 0.0001$).

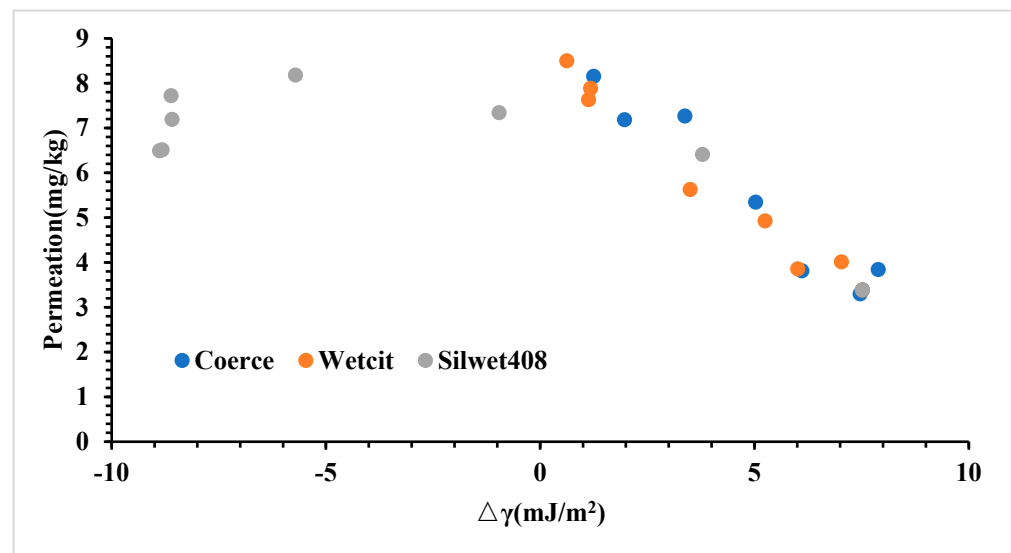


Figure 4. Scatterplots of the permeation vs. the energy difference ($\Delta\gamma$).

Table 4. Curve fitting of the permeation (y) vs. the energy difference ($\Delta\gamma$).

Spray Adjuvant	Curve Fitting	Function	Coefficient of Determination (R^2)
Coerce	Linear	$y = -0.7357\Delta\gamma + 9.0189$	0.9401
	Exponential	$y = 10.012e^{-0.138\Delta\gamma}$	0.9306
	Logarithmic	$y = -2.718\ln(\Delta\gamma) + 9.2369$	0.8919
	Polynomial	$y = 0.0104\Delta\gamma^2 - 0.8331\Delta\gamma + 9.182$	0.9406
	Power	$y = 10.309\Delta\gamma^{-0.502}$	0.8304
Wetcit	Linear	$y = -0.71\Delta\gamma + 8.5868$	0.9718
	Exponential	$y = 9.0115e^{-0.126\Delta\gamma}$	0.9854
	Logarithmic	$y = -2.036\ln(\Delta\gamma) + 7.8845$	0.9715
	Polynomial	$y = 0.0528\Delta\gamma^2 - 1.1277\Delta\gamma + 9.0493$	0.9854
	Power	$y = 7.8818\Delta\gamma^{-0.354}$	0.9389
Silwet408	Linear	$y = -0.1562\Delta\gamma + 6.0604$	0.4782
	Exponential	$y = 5.7649e^{-0.03\Delta\gamma}$	0.4255
	Polynomial	$y = -0.0381\Delta\gamma^2 - 0.2621\Delta\gamma + 7.6066$	0.9113
Aggregate analysis	Polynomial	$y = -0.04512\Delta\gamma^2 - 0.27985\Delta\gamma + 7.9777$	0.9167

4. Discussion

In general, the rate of material accumulation on surfaces that are difficult to wet is comparatively slower than that on easily wettable surfaces. Rice leaves, characterized by high hydrophobicity, exhibit a surface free energy of 29.28 mJ/m^2 . In the SFE of the rice leaf surface, the proportion of γ^{LW} is higher than that of γ^{AB} , suggesting that nonpolar interactions predominate over polar interactions. It is the same as the SFE of the adaxial leaf of blue gum eucalypt and the adaxial leaf of rubber tree, but different from the adaxial leaf of red iron bark, the abaxial leaf of holm oak, and the adaxial and abaxial leaves of maize [24,29]. Therefore, rice leaves are extremely hydrophobic with high static contact angles of water ($>130^\circ$). This hydrophobicity predominantly stems from the distinctive morphology of the plants, which consists of ‘micronano papillae + hydrophobic waxes’ that are naturally present on rice leaves [30]. The inherent hydrophobic nature of rice leaves directly leads to inadequate retention of conventional pesticide spray droplets on their surface, resulting in pesticide solution loss. Furthermore, the permeation of pesticide solution into the leaves remains relatively limited [31]. Specifically, the permeation of simple soluble dinotefuran granules in rice leaves reached 3.381 mg/kg . Despite the presence of some wetting agents, the primary emphasis lies in the stability of the formulation, particularly in the context of the extreme hydrophobicity of rice leaves. Hence, the incorporation of adjuvants becomes crucial for enhancing liquid wettability.

The wettability and permeability of the pesticide solution on the target exhibit a positive correlation to some extent. After spraying chlorantraniliprole and difenoconazole with the vegetable oil adjuvant, the cuticular wax of the rice leaf was destroyed, which reduced the hydrophobicity of the rice leaf and facilitated the wetting and penetration of pesticides onto the rice leaf. The amount of chlorantraniliprole and difenoconazole in rice leaves was increased by the vegetable oil adjuvant in the first 2 h [32]. In this study, lime peel oil and orange peel oil are vegetable oil adjuvants [33]. The impact of these two factors on dinotefuran permeation in rice leaves was remarkably similar. With increasing concentration, the surface free energy of the pharmaceutical solution progressively approached that of the rice leaves, resulting in enhanced dinotefuran permeation. On the other hand, a remarkable ability to reduce the surface tension of the pesticide solution was demonstrated by organosilicon adjuvants. Silwet L77 and silicon-modified adjuvants have a lower surface energy and contact angle at the low-energy interface [34,35]. Silwet408 also has the same function. This brings the pesticide solution surface free energy closer to or below the rice leaf surface free energy, improving overall dinotefuran permeation. Following the addition of adjuvants, the surface tension of the dinotefuran solution decreased, consequently decreasing the surface energy of the dinotefuran solution. This reduction in surface energy facilitated increased liquid adsorption on the rice leaf surface, activating their surface properties. The heightened compatibility arising from the increased surface energy of the contact surface guided dinotefuran within the liquid, facilitated by nonpolar groups, to enter the surface wax and permeate downwards. As liquid infiltration continued, the adjuvant coating facilitated the entry of dinotefuran into the surface wax and its subsequent downward penetration [36]. As the liquid gradually permeated, the protective effect of the adjuvants gradually diminished. Upon entering the aqueous system, dinotefuran exhibited greater compatibility due to its inherent strong polarity. Further investigations have revealed that the liquid surface tension and the surface characteristics of the target play pivotal roles in influencing pesticide wetting and permeation [37,38]. Hence, achieving optimal pesticide efficacy necessitates the harmonization of liquid properties with the surface properties of the target. However, it is essential to consider the presence of wax, stomata, or other surface attachments on organisms, which can potentially hinder pesticide permeation. Further research is therefore needed to investigate this complex relationship.

In agricultural pest control, achieving precise delivery of an effective dose to the target pest plays a pivotal role in ensuring efficacy. The objective of pest control typically involves killing, stunning, or sterilizing pests through contact or ingestion. Rice plants, due to their inherent characteristics, such as a substantial inclination angle and pronounced

hydrophobicity, present challenges during the spraying process. Droplets find it difficult to adhere to leaf surfaces, resulting in low pesticide permeation into leaves. This, in turn, diminishes the likelihood of contact with the pests [39]. To enhance the effectiveness of pest control products, spray adjuvants are employed. The purpose of these methods is to increase the likelihood of contact between the active ingredients within the product and the target pests, thereby improving product efficacy. Given the complex nature of real-world application scenarios, the surface energy of the liquid and the surface energy of the target are pivotal factors influencing the interaction between pests and the active ingredient [40]. Using the dipping method rather than the more complex foliar spraying process reduces the impact of spray pressure, spray pattern and other factors. Therefore, an established relationship between the energy difference ($\Delta\gamma$) and the permeation quantity is highly important. A polynomial fit was determined to be the most suitable mathematical model for describing the interplay between these two factors, serving as a predictive tool for assessing the effect of adjuvants on pesticide permeation. In the present study, the adaxial and abaxial surfaces of rice leaves showed hydrophobic properties, whereas the leaves of *Gossypium hirsutum* (cotton) and *Phaseolus vulgaris* (bean) showed hydrophilic properties. Moreover, the leaves of *Ruellia devosiana* demonstrated amphiphilic properties [41–43]. We can still calculate the leaf surface energy by the OCG method and perform a fit check of the model. These will be the focus of research in the future.

5. Conclusions

At appropriate concentrations, all three adjuvants significantly enhanced the permeation of dinotefuran on rice leaves. Over the experimental range, the permeation of dinotefuran into rice leaves gradually increased upon the addition of Coerce and Wetcit to a certain extent. However, Silwet 408 exhibited a trend of initial increase and subsequent decrease with increasing additive amount. Specifically, the permeation of dinotefuran within the liquid solution on rice leaves exhibited a noteworthy increase when the Coerce concentration ranged from 250 mg/L to 1000 mg/L, the Wetcit concentration ranged from 250 mg/L to 1000 mg/L, and the Silwet 408 concentration ranged from 31 mg/L to 250 mg/L.

The polynomial model that best described the relationship between the energy difference (the SFE of the liquid and the SFE of the rice leaf surface) and pesticide permeation in rice leaves was represented by the equation $y = a\Delta\gamma^2 + b\Delta\gamma + c$ (where a , b , and c are constants). According to this model, it becomes possible to estimate pesticide permeation within the target plant leaf based on these variables.

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