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Article

Does the Use of Adjuvants Alter Surface Tension and Contact Angle of Herbicide Spray Droplets on Leaves of *Sida* spp.?

*O Uso de Adjuvantes Altera a Tensão Superficial e o Ângulo de Contato da Gota da Calda Herbicida em Folhas de **Sida** spp.?*

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ABSTRACT - Droplet spreading on plant surfaces may indicate greater efficiency in herbicide application. The aim of this study was to evaluate surface tension and contact angle of the aminopyralid + fluroxypir herbicide droplets associated with adjuvants on the leaf surface of three species of the genus *Sida*. The experiment was carried out in a completely randomized design, in a 4x2+1 factorial arrangement, with four replications. Four treatments containing two rates of the herbicide (0.04 + 0.08 kg a.i. ha^{-1} and 0.08+0.16 kg a.i. ha^{-1}) were evaluated, associated or not with the adjuvants vegetable oil, mineral oil and lecthin; and water was used as a control. Surface tension and contact angle of the syringes were measured with a tensiometer. Surface tension was evaluated at 5, 15 and 25 seconds after droplet formation. Contact angle was measured at 5, 15 and 25 seconds after droplet deposition on the adaxial and abaxial surfaces of *Sida rhombifolia*, *S. glaziovii* and *S. cordifolia*. The results were submitted to analysis of variance by the F-test and the means of the treatments were compared by Tukey's test (p>0.05). There was no interaction between the factors for surface tension. The contact angles of *S. cordifolia* and *S. glaziovii* were lower after addition of lecthin on the adaxial face. The addition of the adjuvants to the spray solution provided lower contact angles at the rate of 0.04 + 0.08 kg a.i. ha^{-1}, except for *S. rhombifolia*, whose contact angle was lower with the spray solution without adjuvant.

Keywods: aminopiralide + fluroxipir, spreading, *Sida cordifolia, Sida glaziovii, Sida rhombifolia*.

*RESUMO - O espalhamento das gotas sobre superfícies vegetais pode indicar melhor eficiência numa aplicação de herbicidas. Com este trabalho, objetivou-se avaliar a tensão superficial e o ângulo de contato de gotas do herbicida aminopiralide + fluroxipir associado a adjuvantes sobre a superfície foliar de três espécies do gênero **Sida**. O experimento foi realizado em delineamento inteiramente ao acaso, disposto em arranjo fatorial 4x2+1, com quatro repetições. Foram utilizadas oito caldas contendo duas dosagens do herbicida (0,04 + 0,08 kg i.a. ha^{-1} e 0,08+0,16 kg i.a. ha^{-1}), associado ou não aos adjuvantes óleo vegetal, óleo mineral e lecitina, e água como testemunha. Foram feitas medições da tensão superficial e de ângulo de contato das caldas com tensiômetro. A tensão superficial foi quantificada aos 5, 15 e 25 segundos após a formação da gota. O ângulo de contato foi medido nos tempos de 5, 15 e 25 segundos, após depósito das gotas sobre as superfícies adaxial e abaxial de folhas de **Sida rhombifolia**, **S. glaziovii** e **S. cordifolia**. Os resultados foram submetidos à análise de variância, pelo teste F, e as médias dos tratamentos, comparadas pelo teste de Tukey (p>0,05). Não houve interação entre os fatores para tensão superficial. Os ângulos de contato de*

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S. cordifolia *e* ***S. glaziovii*** *foram menores após a adição da lecitina na face adaxial. A adição dos adjuvantes na calda proporcionou menores ângulos de contato na dosagem de 0,04 + 0,08 kg i.a. ha*$^{-1}$*, exceto para* ***S. rhombifolia****, cujo ângulo de contato foi menor com a calda sem adjuvante.*

Palavras-chave: aminopiralide + fluroxipir, espalhamento, *Sida cordifolia*, *Sida glaziovii*, *Sida rhombifolia*.

INTRODUCTION

The species *S. rhombifolia*, *S. glaziovii* and *S. cordifolia*, which belong to the family Malvaceae, known popularly as mallows, infest several agricultural crops, such as sugar cane, coffee, soybean and pastures, causing considerable damage to production. Poor management of these species in areas destined for livestock, in Brazil, reduces forage yield and, consequently, availability of food for animals (Noronha et al., 2010; Inoue et al., 2013; Lorenzi, 2014).

In Brazil, these species have been basically controlled through herbicide application (Ferreira et al., 2014). The herbicide aminopyralid + fluroxypyr, whose mechanism of action is to mimic auxin, interferes in the apical meristem of plants, thus affecting the division of tissues; it has been used in Brazil to control these weeds in pasture areas. Plants treated with this herbicide have symptoms such as wilting and curling of leaf edges, with subsequent chlorosis and necrosis, which also occur in stems (Santos et al., 2013).

To improve deposition of the spray applied, adjuvants are added to the spray tank; they are substances that alter the chemical and physical properties of sprays. Adjuvants have the function of mitigating the risk of drift and improving penetration and absorption of products by reducing surface tension and contact angle of droplets on the surface (Cunha et al., 2010).

Droplet spreading is dependent on the dynamics of surface tension, spray properties, contact angle, nature of spray formulation and application volume (Taylor, 2011; Barbosa et al., 2013).

Surface tension is the result of unbalanced molecular forces, and it varies from liquid to liquid and is dependent on solutes. In the case of water, tension tends to form spherical droplets; in general, the lower the surface tension, the more easily a liquid will spread. Contact angle depends on the characteristics of the surface on which the droplet was deposited. If a surface is hydrophobic, there will be little contact and the droplet will remain spherical. If a surface is more hydrophilic, a water droplet will spread, and it may form a uniform film. In plants, leaf wettability depends on leaf anatomy (Kissmann, 1998).

However, it should be noted that using adjuvants will not always establish a favorable condition to the spray tank on a given target, especially when one does not take into account droplet size effects and different anatomical compositions and epicuticular waxes of weeds (Maciel et al., 2010).

Although the species *S. rhombifolia*, *S. glaziovii* and *S. cordifolia* belong to the same genus, they have different characteristics on the leaf surface; if there are differences between the adaxial and abaxial faces in the same species, sprayed droplets may spread differently. According to Albert & Victoria Filho (2002), the leaf surface influences absorption, and there is an inverse relationship between absorption and quantity of cuticular wax; this characteristic interferes in the susceptibility of species to weed control with herbicides.

In Brazil, there are few studies on the physicochemical characteristics of mixtures between adjuvants and herbicides. Further research can provide additional information to corroborate the results of efficacy and selectivity (Maciel et al., 2010; Melo et al., 2015), especially in pastures. Therefore, the objective of the present study was to evaluate surface tension and contact angle of spray droplets of the herbicide aminopyralid + fluroxypyr associated with adjuvants on the leaf surface of three weed species of the genus *Sida*.

MATERIAL AND METHODS

The experiment was carried out in 2016. The experimental design was completely randomized with four replications, in a 4x2+1 factorial arrangement. The interaction factors were spray containing the herbicide without addition of adjuvants and herbicides associated with adjuvants (vegetable oil, mineral oil and lecithin), two application rates and water as control (Table 1).

Table 1 - Description of the products used in the experiment

Product	Trade name	Active Ingredient	Company	Type of product
Aminopyralid + fluroxypyr	Dominum®	0.04 + 0.08 kg ha^{-1}	Dow AgroSciences	Herbicide
Esters of fatty acids with glycerol.	Veget'oil®	930 g	Oxiquímica Agrociência	Adjuvant*
Aliphatic hydrocarbons	Argenfrut®	845.575 g	Agrovant Comércio de Produtos Agrícolas	Adjuvant*
Mixture of phosphatidylcholine (lecithin) and propionic acid	LI-700®	712.88 g	DE SANGOSSE Agroquímica	Adjuvant*

* Adjuvants have been added to the droplet in the proportion of 0.3% v v^{-1}.

The herbicide rates were 0.04 + 0.08 kg a.i. ha^{-1} and 0.08+0.16 kg a.i. ha^{-1}. They were chosen for control in accordance with the manufacturer's instructions for the herbicide, aiming at evaluating the minimum and maximum rates. The concentration used as a basis was equivalent to the volume of 150 L ha^{-1}, which is usual in Brazilian pastures.

Surface tension and contact angle were determined with a Contact Angle System OCA 15-Plus (Dataphysics®) tensiometer, fitted with a digital camera with high temporal resolution and definition, and the software SCA20® was used for automation and processing of images. For determination of the variables, the droplets were formed in a Hamilton® precision syringe (500 µL), and droplet release rate was 3 µL s^{-1} in all treatments.

Surface tension was determined by the pendant droplet method. The image of the droplet formed at the tip of the syringe was captured by a high temporal resolution CCD camera (30 frames per second) and sent for processing. Droplet size was analyzed through axis asymmetry. Calculation of surface tension was based on the equation of Yang-Laplace, on the basis of deformation of droplets produced in each sampling (Ferreira et al., 2013).

Static tension was measured for 60 seconds after droplet formation. All comparisons were made at 5, 15 and 25 seconds, and time was determined by analysis of the reduction curve of the contact angle of droplets. For contact angle of droplets, evaluations were performed in three species: *S. rhombifolia*, *S. glaziovii* and *S. cordifolia*, on the adaxial and abaxial surfaces (Table 2). Contact angle is regularly used to characterize the droplets of aqueous sprays deposited on the solid surface, while considering the interaction factors of liquid spreading on the surface and the area covered as a result of spraying. When the contact angle is wider than 90°, the surface is called hydrophilic, otherwise, it is called hydrophobic. When it is wider than 160°, the surface is considered to be super-hydrophobic (Tang et al., 2008).

For collection of leaves, the three species were grown in a greenhouse for 45 days, and the plants were in phenological stage V2 (Cunha et al., 2013). The pots were filled with substrate

Table 2 - Leaf surface characterization for the three weeds species

Species	Surface	Stomata	Trichomes	Waxes
Sida cordifolia(2)	Adaxial	Anomocytic stomata.	A smaller number of trichomes.	Flat and smooth epicuticular wax.
	Abaxial	Anomocytic stomata.	A large amount of stellar trichomes.	Epicuticular waxes and smooth surface
Sida glaziovi(2, 3)	Adaxial	Anomocytic stomata, low stomatal density.	A large amount of glandular and stellar trichomes.	Hardly visible epicuticular striate wax.
	Abaxial	Anomocytic stomata, deposited at the same level or in depressions.	A large amount of glandular and stellar trichomes.	Hardly visible epicuticular striate wax.
Sida rhombifolia(1, 2)	Adaxial	Randomly scattered stomata.	A smaller number of stellar and simple trichomes.	Randomly orientated epicuticular striate wax.
	Abaxial	Randomly scattered stomata.	A large number of glandular and stellar trichomes.	Randomly orientated epicuticular striate wax.

Source: (1) Cunha et al. (2013); (2) Albert and Victória Filho (2002); (3) Procópio et al. (2003).

composed of sand, cattle manure and soil, at a ratio of 3:1:3. After collection, the leaves were sectioned in longitudinal rectangles measuring 5 x 1 cm, approximately. These sections were arranged horizontally on stretchers to reduce curls that could compromise the leaf structure and the capture of images for readings of contact angle. The images were evaluated every second for 60 seconds after the deposition of each droplet on the leaf surface; three times were considered for the purpose of evaluation: 5, 15 and 25 seconds after the droplet was deposited on the surface. The mean values for temperature and relative humidity during the readings were 24.3 °C and 56%, respectively.

The results for surface tension and contact angle were submitted to analysis of variance by the F-test; when they were significant, the means of the treatments were compared by Tukey's test (p>0.05) (Barbosa and Maldonado Júnior, 2013).

RESULTS AND DISCUSSION

Overall, droplet spreading on the leaf surface resulted from the surface tension of the liquid deposited and the interaction between the fluid and the surface, which, in turn, resulted from the morphological characteristics and the composition of the leaf surface.

Surface tension

There was no difference between the rates used for surface tension and for interaction between the factors adjuvant and rate at the three evaluated times (Table 3). However, there was a difference among the three adjuvants at 15 and 25 seconds. At 15 and 25 seconds, the adjuvant lecithin showed the lowest surface tension value compared to the others.

The control (water) showed the highest surface tension value in comparison to the treatments adopted (p>0.01). In general, the addition of plant protection products in water has the ability to reduce surface tension and increase the affinity of the liquid with the surface (Melo et al., 2015; Cunha et al., 2017).

The surface tension values of the sprays were lower than that of water, enabling greater droplet spreading when they were deposited on the leaf surfaces. Surface tension stems from an imbalance between the forces that act on the molecules on the surface of a liquid in comparison to those that are on the inside. Thus, the lower the surface tension, the more easily a liquid may spread (Behring et al., 2004).

As for surface tension, in a general, there was no statistically significant interaction between the factors adjuvant and rate.

The contact angle of the three species (Table 4) resulted in statistically significant differences, showing that the addition of adjuvant to the herbicide provides greater spreading and, consequently, increased coverage of the surface.

Table 3 - Mean surface tension values (mNm^{-1}) at 5, 15 and 25 seconds after droplet formation

	5s	15 s	25 s
Sprays			
Without adjuvants	32.87a	32.63a	32.46a
Vegetable oil	32.57a	32.45a	32.36a
Mineral Oil	32.78a	32.61a	32.42a
Lecithin	32.13a	31.55b	31.34b
LSD (5%)	0.77	0.77	0.74
Rate			
0.04 + 0.08 kg a.i. ha^{-1} of herbicide	32.59a	32.24a	32.09a
0.08+0.16 kg a.i. ha^{-1} of herbicide	32.58a	32.38a	32.20a
Control			
Water	72.24	72.14	71.84
LSD (5%)	0.40	0.41	0.39
F Sprays	2.71^{NS}	6.53**	7.80**
F Rate	0.00^{NS}	0.46^{NS}	0.30^{NS}
F Sprays vs Rate	2.56^{NS}	2.72^{NS}	2.45^{NS}
F Factorial vs Control	17544.28**	17617.16**	18912.38**
CV (%)	1.52	1.54	1.48

Means followed by the same letter do not differ by Tukey's test (p>0.05). ^{NS} non-significant; * significant at 5% probability; ** significant at 1% probability. LSD: least significant difference. F-test values and CV (coefficient of variation).

Contact angle

In general, there was a significant interaction between sprays and rates used for the contact angle on the surfaces (Table 4). The control (water) showed significant differences (p>0.01) in

Table 4 - Mean contact angle (è) values at 5, 15 and 25 seconds after droplet formation, for the adaxial and abaxial surfaces of *Sida cordifolia*, relative to the offshoot of the degrees of freedom of the interaction between sprays and rates

	Adaxial					
	5 s		15 s		25 s	
	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}
Without adjuvant	68.67Aa	59.22Ab	54.42Aa	50.05Aa	43.05Aa	45.87Aa
Vegetable oil	49.11Ba	56.29Aa	45.26ABa	45.51Aa	36.04ABa	41.17Aa
Mineral Oil	48.80Ba	56.20Aa	41.30BCa	47.78Aa	32.62Ba	38.42Aa
Lecithin	43.44Ba	49.47Aa	31.65Cb	40.93Aa	26.31Ba	37.36Aa
LSD Column	12.20		10.99		9.79	
LSD Row	9.15		8.24		7.34	
CV (%)	10.54		11.05		11.39	
	Abaxial					
	5 s		15 s		25 s	
Without adjuvant	64.95Aa	64.33Aa	46.03Aa	55.47Aa	38.74Ab	51.87Aa
Vegetable oil	64.76Aa	59.62Aba	48.82Aa	46.66ABa	40.91Aa	39.97Ba
Mineral Oil	55.14Aa	46.16Ba	41.83Aa	36.13Ba	37.37Aa	33.69Ba
Lecithin	60.00Aa	50.93Aba	48.55Aa	37.32Bb	39.54Aa	33.38Ba
LSD Column	15.54		13.01		10.49	
LSD Row	11.65		9.75		7.86	
CV (%)	12.54		13.01		11.63	

Means followed by the same lowercase letters for each time on the same row and uppercase letters in the same column for each surface do not differ by Tukey's test ($p<0.05$). LSD: least significant difference, CV: coefficient of variation.

the three study species and, on the adaxial and abaxial surfaces, it had the highest mean values for contact angle. Therefore, the use of adjuvants provided greater spreading on the surface.

Sida cordifolia

For *S. cordifolia*, there was an interaction between rates and contact angles (Table 4). The control showed the highest mean values on the adaxial surface at 5, 15 and 25 seconds (107.32°105.1° and 98.97°, respectively); thus, it differed from the other treatments.

On the adaxial surface of the leaf and at the rate of 0.04 + 0.08 kg a.i. ha^{-1}, it was found that, five seconds after droplet deposition ($p>0.03$), only the treatment without adjuvant differed from the others, as it presented the highest contact angle (Table 4). At 15 and 25 seconds, there was a reduction of the contact angle of the droplet that contained mineral oil and lecithin, leading to greater droplet spreading, owing to a reduction of the contact angle. At the rate of 0.08+0,16 kg a.i. ha^{-1}, there was no difference among droplets at all times assessed.

Thus, the smallest contact angles were possibly due to the interaction of the droplet with the surface, since superficial tension did not result in significant differences between sprays (Hess and Falk, 1990).

In the analysis of rates at different times, there was no significant difference at the time of 5 seconds at the rate of 0.08+0.16 kg a.i. ha^{-1} (Table 4). In the adjuvants vegetable oil and mineral oil, there were no differences between rates at the evaluated times. However, for lecithin, there was a difference only at 15 seconds, and the smallest contact angle was found at the rate of 0.04 + 0.08 kg a.i. ha^{-1}.

Among the sprays in use, vegetable oil was expected to promote greater spreading, given its affinity with the surface (Kirkwood, 1993). However, the smallest contact angles of this species and surface occurred for the spray with the adjuvant lecithin.

S. cordifolia can be classified as hydrophilic, as well as the glass surface. According to Iost and Raetano (2010), the behavior of the spray composed of lecithin is different on the leaf surface, because on the glass, the spray with lecithin does not differ from water, showing the interaction of lecithin with the leaf surface.

For the abaxial surface, the control showed the highest means at 5, 15 and 25 seconds (110.8°, 104.32 and 103.90°, respectively), hence it was different from the treatments. There were no significant differences between treatments in any of the times assessed at the herbicide rate of 0.04 + 0.08 kg a.i. ha^{-1} (Table 4). At the rate of 0.08+0,16 kg a.i. ha^{-1}, at five seconds, there was a significant decrease in the contact angle of the spray without adjuvant and the mixture of the herbicide with the mineral oil. At 15 seconds, there was a significant decrease in the contact angle of the droplet with mineral oil and lecithin. At 25 seconds, the spray with addition of adjuvants resulted in a significant decrease in the contact angle.

In the evaluation of rates within times, in the spray without adjuvant, there was a difference at 25 seconds: the contact angle at the rate of 0.04 + 0.08 kg a.i. ha^{-1} was smaller than at the rate of 2 L ha^{-1}. In the vegetable and mineral oils, there were no significant differences between the rates at the evaluated times. For lecithin, there was a difference at 15 seconds: the rate of 0.08+0.16 kg a.i. ha^{-1} had the lowest contact angle (Table 4).

In this way, there was a greater expression of the effects at a rate of 0.04 + 0.08 kg a.i. ha^{-1} of the sprays, possibly because of the lower concentrations of the herbicide. Because the rate of 0.08+0.16 kg a.i. ha^{-1} has the highest herbicide concentration, adjuvants that compose the formulation of the herbicide may have interacted with the leaf surface, reducing the effect of adjuvants added to the spray, as 84.89% of the product corresponds to inert substances, which are composed of emulsifiers.

For the abaxial surface, the pattern was similar to that of the adaxial face in droplet spreading for the spray with adjuvants. However, the same pattern was not found for the concentrations of the herbicide, possibly because of differences in morphology between the faces and the composition of both products for their own surfaces, since the contact angle is dependent on the characteristics of the surface (Queiroz et al., 2008).

Thus, the characteristics of the species *S. cordifolia* - smooth and flat cuticle, amorphous wax - have to be taken into account, because leaf anatomy interferes in droplet spreading on leaves, with an effect on the susceptibility to the control of the species (Albert and Victoria Filho, 2002). Thus, a reduction of the contact angle of the droplet on the leaf surface may be important in deciding on the best adjuvant to be used during spraying (Decaro Júnior et al., 2015), considering the ultimate goal of the application of the product, which may depend on spreading and absorption of the ingredients deposited on surfaces.

Sida glaziovii

For *S. glaziovii*, there was an interaction between rates and contact angles. The control showed the highest means on the adaxial surface at 5, 15 and 25 seconds (101.41°, 96.23° and 93.98°, respectively), which was a different result from that of the treatments.

For the adaxial face, at the rate of 0.04 + 0.08 kg a.i. ha^{-1}, it was found that the spray with lecithin presented the smallest contact angle at 5 and 15 seconds, which differed only from the mineral oil (Table 5). At 25 seconds, lecithin presented the smallest contact angle, unlike the other treatments. At 0.08+0.16 kg a.i. ha^{-1}, there was no difference in any of the treatments at the evaluated times, similarly to the results found for *S. cordifolia*.

After an evaluation of the contact angles values between the rates at different times for each treatment, there were differences in those without adjuvant and vegetable oil at 15 and 25 seconds, and the rate of 0.08+0.16 kg a.i. ha^{-1} had the smallest angles. For mineral oil and lecithin, there no differences between rates (Table 5).

On the abaxial surface of *M. glaziovii*, the control showed the highest contact angle means at 5, 15 and 25 seconds (86.30°, 83.21° and 81.85°, respectively), unlike the rest of the treatments. There were no differences among the treatments at the two rates at 5, 15 and 25 seconds (($p>0.2490$, $p>0.1945$ and $p>0.0366$, respectively) (Table 5). When comparing the contact angles among times for each spray, the sprays without adjuvant and with addition of lecithin showed no differences, while the spray with vegetable oil showed a difference between the two rates, and the rate of 0.04 + 0.08 kg a.i. ha^{-1} resulted in the smallest contact angle. In the spray with mineral oil, there was a difference only at 5 seconds, with the rate of 0.08+0.16 kg a.i. ha^{-1} with the smallest contact angle.

Table 5 - Mean contact angle (è) values at 5, 15 and 30 seconds after droplet formation, for the adaxial and abaxial surfaces of *Aids glaziovii*, referring to the offshoot of the degrees of freedom of the interaction between sprays and the rates

	Adaxial					
	5 s		15 s		25 s	
	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}
Without adjuvant	67.82ABa	66.80Aa	64.84ABa	57.63Ab	63.05Aa	55.70Ab
Vegetable oil	68.47ABa	65.63Aa	65.13ABa	56.86Ab	63.56Aa	52.07Ab
Mineral Oil	70.92Aa	71.03Aa	68.09Aa	63.46Aa	66.23Aa	61.01Aa
Lecithin	61.41Ba	64.25Aa	58.61Ba	59.72Aa	53.27Ba	57.71Aa
LSD Column	7.13		7.88		9.14	
LSD Row	5.35		5.91		6.85	
CV (%)	5.2		6.21		7.5	
	Abaxial					
	5 s		15 s		25 s	
Without adjuvant	65.06Aa	65.01Aa	57.34Aa	56.40Aa	54.55Aa	45.88Aa
Vegetable oil	70.75Aa	62.47Ab	63.40Aa	51.38Ab	57.92Aa	44.41Ab
Mineral Oil	67.71Aa	58.86Ab	58.43Aa	52.67Aa	54.53Aa	50.55Aa
Lecithin	65.27Aa	63.01Aa	57.74Aa	55.77Aa	49.12Aa	47.26Aa
LSD Column	9.93		10.58		13.07	
LSD Row	7.44		7.93		9.80	
CV (%)	7.64		9.17		12.51	

Means followed by the same lowercase letters for each time on the same row and uppercase letters in the same column for each surface do not differ by Tukey's test ($p<0.05$). LSD: least significant difference.

The species *S. glaziovii* has a greater quantity of surface waxes and trichomes on the adaxial surface, as well as low stomatal density, which is one of the main barriers to herbicide penetration (Albert and Victoria Filho, 2002; Procópio et al., 2003). Although it has similar morphological characteristics to those of the species *S. rhombifolia*, droplet behavior was different. Therefore, the difference may have been due to the chemical composition of the wax.

The affinity of the surface with the sprays did not allow the expression of the adjuvants; moreover, there may have been the formation of micelles based on a minimum concentration (Iost and Raetano, 2010). This explains the non-occurrence of differences between the adjuvants at the two rates, on the abaxial surface.

Sida rhombifolia

For *S. rhombifolia*, there was an interaction between rates and contact angles. The control showed the highest means on the adaxial surface at 5, 15 and 25 seconds (71.46°, 68.47° and 66.46°, respectively), which was a different result from that of the treatments. On the adaxial surface and at the herbicide rate of 0.04 + 0.08 kg a.i. ha^{-1}, there was a significant reduction of the contact angles in the sprays without adjuvant at 5 seconds (Table 6). At 15 seconds, the mineral oil and the spray without adjuvant presented smaller contact angles. At 25 seconds, the spray without adjuvant resulted in a smaller contact angle.

At the rate of 0.08+0.16 kg a.i. ha^{-1} of the herbicide, it was found that at 5, 15 and 25 seconds, the spray containing mineral oil and lecithin had smaller contact angles (Table 6).

When comparing the rate within the times, the treatment without adjuvant showed difference only at 15 and 25 seconds, in which the herbicide rate of 0.04 + 0.08 kg a.i. ha^{-1} resulted in a smaller contact angle. For the vegetable oil, there was a difference only at 25 seconds, when the herbicide rate of 0.08+0.16 kg a.i. ha^{-1} presented the smallest angle. For mineral oil and lecithin, all contact angles differed at the evaluated times, and the herbicide rate of 0.08+0.16 kg a.i. ha^{-1} presented lower values (Table 6).

Therefore, there was a different behavior of the contact angles when it was compared with that of the two previous species. This is probably due to the characteristics of the composition of the leaf surface in the vegetative stage, which presents a smaller amount of stomata on the

Table 6 - Mean contact angle values (è) to 5, 15 and 25 seconds after droplet formation, for the adaxial and abaxial surfaces of *Sida rhombifolia*, relative to the offshoot of the degrees of freedom of the interaction between sprays and rates

	Adaxial					
	5 s		15 s		25 s	
	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}	0.04+0.08 kg a.i. ha^{-1}	0.08+0.16 kg a.i. ha^{-1}
Without adjuvant	52.71Ba	58.52Aba	43.35Bb	54.10Aa	39.65Cb	51.19Aa
Vegetable oil	66.20Aa	64.56Aa	61.18Aa	57.84Aa	58.37Aa	52.94Ab
Mineral Oil	57.29ABa	47.19Cb	51.13Ba	38.62Bb	41.91Ba	36.08Bb
Lecithin	65.19Aa	50.10BCb	60.49Aa	39.09Bb	56.54Aa	34.08Bb
LSD Column	9.66		7.91		6.97	
LSD Row	7.24		5.93		5.23	
CV (%)	8.42		7.75		7.31	
	Abaxial					
	5 s		15 s		25 s	
Without adjuvant	69.18Aa	49 Ab	62.18Aa	42.18Ab	62.18Aa	36.16Ab
Vegetable oil	66.48ABa	59.07Aa	61.88Aa	47.16Ab	61.88Aa	43.86Ab
Mineral Oil	54.49BCa	45.7Aa	48.28Ba	42.06Aa	48.28Ba	39.56Aa
Lecithin	47.69Ca	47.53Aa	35.72Ba	38.74Aa	35.72Ba	35.48Aa
LSD Column	14.34		13.17		14.59	
LSD Row	10.75		9.87		10.94	
CV (%)	12.75		13.24		15.77	

Means followed by the same lowercase letters for each time on the same row and uppercase letters in the same column for each surface do not differ by Tukey's test ($p<0.05$). LSD: least significant difference.

adaxial face and higher content of randomly orientated epicuticular striate wax (Albert and Victoria Filho, 2002; Cunha et al., 2013). It should be noted that the leaves were in the vegetative stage when they were collected for analysis. The number of stomata may have interfered in droplet spreading on the surface, resulting in the differences found between the species on the adaxial face (Hess and Falk, 1990).

In the spray without adjuvant, there were smaller contact angles at the rate of 0.04 + 0.08 kg a.i. ha^{-1} (Table 6), because of the formulation of the herbicide, which has emulsifiers that interact with the leaf surface and reduce the contact angle.

On the abaxial surface, the control presented the highest means for contact angle at 5, 15 and 25 seconds (86.68°, 84.14° and 83.18°, respectively), differing from the treatments. At the herbicide rate of 0.04 + 0.08 kg a.i. ha^{-1}, the spray with mineral oil and lecithin presented the smallest contact angle at 5 and 15 seconds. At 25 seconds, lecithin presented the smallest angle, unlike the other adjuvants. At the herbicide rate of 0.08+0,16 kg a.i. ha^{-1}, there was no statistical difference in any of the times assessed (Table 6).

When the differences in rates on the abaxial surface were compared within the times, the spray without adjuvant at the herbicide rate of 0.08+0.16 kg a.i. ha^{-1} presented the lowest values for contact angle. For vegetable oil, differences were found at 15 and 25 seconds, and the rate of 0.08+0.16 kg a.i. ha^{-1} presented the smallest angle. For the adjuvants mineral oil and lecithin, there were no differences between the times evaluated at the two rates (Table 6).

The rate of 0.08+0.16 kg a.i. ha^{-1} did not result in differences between adjuvants (Table 6), possibly as a result of micelle formation, because after saturation of the surface, addition of new molecules has little effect on contact angle, where molecular aggregates of colloidal dimensions form spontaneously. Critical micelle concentration (CMC) depends on surfactant structure and on experimental conditions. Therefore, there is a limit on the addition of adjuvants to the spray to reduce the contact angle (Behring et al., 2004; Mendonça et al., 2007).

In general, the adaxial surface showed bigger differences between the adjuvants than the abaxial surface. The rate of 0.04 + 0.08 kg a.i. ha^{-1} resulted in increased expression of differences between the sprays for droplet spreading on the leaf surface.

Addition of adjuvants does not affect superficial tension. Lecithin added to the herbicide aminopyralid+ fluroxypyr reduces the contact angle of droplets on the adaxial and abaxial surfaces of *Sida cordifolia* and *Sida glaziovii*. For *Sida rhombifolia*, addition of adjuvants to the herbicide does not favor the reduction of the contact angle. The vegetable oil, associated with the herbicide aminopyralid + fluroxypyr, is not recommended for the species *Sida rhombifolia, Sida cordifolia* and *Sida glaziovii*.

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