

RESEARCH PAPER

Increased foliar activity of clodinafop-propargyl and/or tribenuron-methyl by surfactants and their synergistic action on wild oat (*Avena ludoviciana*) and wild mustard (*Sinapis arvensis*)

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Surfactants can improve postemergence herbicide efficacy and reduce the amount of herbicide required to obtain weed control. The effect of surfactants on the efficacy of herbicides is complicated and depends on the interaction among the plant, surfactant, and herbicide. The effects of surfactants on the efficacy of clodinafop-propargyl and/or tribenuron-methyl on wild oat (*Avena ludoviciana*) and wild mustard (*Sinapis arvensis*) under greenhouse conditions were investigated. In addition, the surface tension of aqueous solutions of the surfactants and surfactants + herbicides was determined. Significantly lower surface tension values were obtained with the aqueous solutions of citofrigate (Citogate plus Frigate) alone and with the herbicides used in this study. The citofrigate surfactant led to the greatest enhancement of clodinafop-propargyl and/or tribenuron-methyl efficacy and the effect was species-dependent. The efficacy of clodinafop-propargyl and/or tribenuron-methyl in the presence of surfactants in controlling wild oat was higher than for wild mustard. The foliar activity of the tested herbicides rose with increasing surfactant concentrations. The tank mixture of clodinafop-propargyl and tribenuron-methyl showed a synergistic effect in controlling wild oat and wild mustard. The synergistic effect in controlling wild mustard was greater than for wild oat.

Keywords: herbicide activity, surface tension, surfactant, synergistic, tank mixture.

Clodinafop-propargyl and tribenuron-methyl are post-emergence herbicides that are used for the selective control of grasses and broad-leaved weeds in wheat fields (Baghestani *et al.* 2008). Clodinafop-propargyl is an acetyl coenzyme A carboxylase (ACCase) inhibitor that is considered to be a key enzyme in lipid biosynthesis. Tribenuron-methyl belongs to the sulfonyleurea herbicide group, which exerts its lethal activity by inhibiting acetolactate synthase (ALS), the key enzyme in the biosynthesis of branched-chain amino acids (Dollinger

2005). Tank mixtures of two herbicides can have increased efficacy as a result of the herbicides' combination, compared with a single herbicide application. These combinations are referred to as "synergistic" (Scott *et al.* 1998). Farmers usually mix grass and broad-leaved herbicides in order to reduce the number of machinery passes across the field, increasing efficacy, preventing weed resistance to herbicides, and saving time and money (Baghestani *et al.* 2007). Montazeri (1995) also reported that mixing clodinafop-propargyl and tribenuron-methyl herbicides had a synergistic effect in controlling wild oat (*Avena ludoviciana* Durieu.) and wild mustard (*Sinapis arvensis* L.).

Similar to other foliar-applied herbicides, clodinafop-propargyl and/or tribenuron-methyl need to be associated with a surfactant for more effective control (Bunting

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et al. 2004). Surfactants lead to the decreased surface tension of the herbicide droplets (Jinxia 1996; Zabkiewicz 2000). The decrease in the droplet's surface tension by surfactants results in a decrease of the contact angle (Sharma & Singh 2000) and an increase in the leaf surface deposition (Jinxia 1996). This process can lead to more cuticular penetration and stomatal infiltration, increasing the amount of herbicide translocation (Penner 2000); more herbicide absorption and translocation imply a greater achievement of control (Jinxia 1996).

In the current situation, where chemical control is dominant, the farmer should try to decrease the amount of herbicide that is used and/or reduce the herbicide usage per unit area (Kudsk 1997). Surfactants can be used with herbicides very effectively (Robin *et al.* 2003); consequently, environmental health and herbicide usage also would be improved (Bunting *et al.* 2004).

With respect to ionizing ability, surfactants are divided into ionic and non-ionic groups. Ionic surfactants can be divided further into cationic and anionic groups (Penner 2000). Non-ionic surfactants are effective in the improvement of foliar activity in several ACCase-inhibitor herbicides, including tralkoxydim (Devilliers *et al.* 2001), fluazifop-P-ethyl (Scott *et al.* 1998), and clethodim (Nandula *et al.* 2007), and several ALS-inhibitor herbicides such as primisulfuron (Sanyal *et al.* 2006) and foramsulfuron (Bunting *et al.* 2004). The cationic surfactant, Frigate, is effective in the improvement of foliar activity in some herbicides such as glyphosate (Collins & Helling 2002) and quinclorac (Zawierucha & Penner 2001).

A physico-chemical characteristic of surfactants, such as surface tension and critical micelle concentration (CMC), depends on surfactant chemistry (Sharma & Singh 2000). Thus, the nature of surfactant activity on herbicide absorption is complicated and depends on the interactions among the herbicide, surfactant, and leaf surface (Molin & Hirase 2005). However, it is believed that no surfactant is able to increase the absorption rate of a specific herbicide unless it has been proven experimentally. Also, applying the right concentration and type of surfactant is not an easy task for the user (Kudsk & Mathiassen 2007).

The subject of this article is to compare the efficacy of clodinafop-propargyl and/or tribenuron-methyl with surfactants for weed control. Two weeds, wild mustard (representing broad-leaved species) and wild oat (representing grass species), which differ greatly in their wetability properties, were used in this study.

MATERIALS AND METHODS

Surface tension studies

The surface tension of a range of concentrations (0.01, 0.05, 0.1, 0.15, 0.2, 0.25, and 0.3% v/v) of aqueous surfactant solution alone and formulated with clodinafop-propargyl and/or tribenuron-methyl was determined. The surface tension was determined by using the capillary tube technique with four replications for each value. The surface tension, γ , of the solution was computed and expressed in N m^{-1} , as follows (Vanhanen *et al.* 2008):

$$\gamma = \frac{1}{2} \rho \cdot g \cdot r \left(h + \frac{r}{3} \right) \quad (1)$$

where ρ is the liquid density (kg m^{-3}), g is the acceleration due to gravity (9.8 m s^{-2}), r is the radius of the capillary (m), and h is the capillary rise (m). The temperature of the laboratory during the measurements was $25 \pm 1^\circ\text{C}$ and, for measurement, a capillary tube with a 1 mm section diameter was selected. Then, the data were changed to mN m^{-1} .

Plant growth

Wild oat seeds were collected from plants in the field near the research greenhouse at Ferdowsi University of Mashhad, Iran. They were dehulled and placed in 11 cm-diameter Petri dishes on top of a single layer of filter paper (Whatman International, Maidstone, UK). Then, 10 mL of 0.2% KNO_3 solution were added to each Petri dish and the seeds were incubated for 48 h at $4\text{--}5^\circ\text{C}$ in the dark. The seeds then were germinated under temperature and relative humidity control conditions in the dark (16 h at 20°C and 8 h at 10°C , with 45% and 65% relative humidity, respectively) (Andersen 1968). By this method, 92–98.5% of the seeds were germinated. Ten germinated seedlings were planted in each 1.5 L plastic pot (1 cm depth) that was filled with a mixture of sand, clay loam soil, and peat (1:1:1; v/v/v), provided by the Department of Horticulture, Ferdowsi University of Mashhad, Iran. The pots were subirrigated every 3 days. The seedlings were thinned to four per pot at the one-leaf stage and 40 mL of a water-soluble N:P:K (20:20:20) fertilizer, at a concentration of 3 g of fertilizer per liter of tap water, were supplied to each pot. The greenhouse temperature varied from $22\text{--}31^\circ\text{C}$ during the day and $16\text{--}20^\circ\text{C}$ at night. The wild mustard seeds were obtained from the Plant Protection Research Institute in Tehran, Iran. They were treated in the same manner as the wild oat seeds, except that for the germination of the wild mustard seeds, they were incubated for 7 days at $4\text{--}5^\circ\text{C}$.

in the dark (Paolini *et al.* 2001) and the seedlings were planted at a depth of 0.5 cm. In this way, a homogeneous population of experimental units was obtained on the day of treatment.

Treatments

Clodinafop-propargyl at 0, 8, 16, 32, 48, and 64 g ai ha⁻¹ (Tapik 80 EC, 80 g ai L⁻¹ clodinafop-propargyl, EC; Syngenta, Basel, Switzerland) was used on wild oat and tribenuron-methyl at 0, 1.85, 3.75, 7.5, 11.25, and 15 g ai ha⁻¹ (Granestar 750 DF, 750 g ai kg⁻¹ tribenuron-methyl, DF; DuPont, De Nemours, France) was used on wild mustard for experiments 1 and 3, respectively. In experiments 2 and 4, clodinafop-propargyl and tribenuron-methyl, respectively, were mixed at 0:15, 8:11.25, 16:7.5, 32:3.75, 48:1.85, and 64:0 g ai ha⁻¹ separately for both wild oat and wild mustard. There were four replicates for both the treated and control plants. Three surfactants were evaluated for bioefficacy assays: (i) the cationic Frigate, a mixture of ethoxylated long-chain fatty amines at 0.1% and 0.2% (v/v) (ISK Biosciences Crop, Mentor, UK); (ii) the non-ionic Citogate, alkyl aryl polyglycol ether at 0.1% and 0.2% (v/v) (Zarnegaran Pars Company, Karaj, Iran); and (iii) an equivalent mixture of Citogate and Frigate (citofrigate) at 0.1% and 0.2% (v/v). The plants were treated at the four-leaf stage by using an overhead trolley sprayer that was equipped with a flat-fan nozzle (8002 Tee-jet; Spraying Systems Company, Wheaton, IL, USA), delivering 200 L ha⁻¹ at 200 kPa. The conditions of the treatment days were almost the same in all experiments; that is, 25 ± 3°C and 44 ± 6% relative humidity. The control and treated plants were harvested 4 weeks after treatment. The fresh and dry weights of the shoots of wild oat and wild mustard were determined.

Statistical analyses

The response of the wild oat and wild mustard dry matter, U , to the herbicide dose, z , was analyzed with a non-linear regression technique, as described previously by Streibig *et al.* (1993):

$$U_{ij} = \frac{D - C}{1 + \exp[b_i(\log(z_{ij}) - \log(ED_{50(i)}))]} + C, \quad (2)$$

where U_{ij} is the percentage efficacy of the herbicide, z_{ij} is the dose of the herbicide, and parameter b_i is proportional to the slopes of the curves around $ED_{50(i)}$. The $ED_{50(i)}$ denotes the required dose of herbicide, i , to reduce the dry matter by half between the upper and lower limits, D and C . By reparameterizing equation (2),

the ED_{50} parameter can be replaced by any ED level (e.g. ED_{90}) that is of more relevance than the ED_{50} parameter when comparing herbicide preparations (Kudsk & Mathiassen 2007). The ED_{90} denotes the required dose of herbicide, i , to reduce the dry matter by 90% between the upper and lower limits, D and C . The logistic dose-response model was directly fitted to the experimental data by SlideWrite software (Advanced Graphics Software, Carlsbad, CA, USA). Previous studies have shown that the dose-response curves of a herbicide applied with and without surfactant is considered to be parallel (Kudsk *et al.* 1987; Hsiao *et al.* 1996; Devilliers *et al.* 2001); that is, the D , C , and b parameters are similar and equation (2) can be reduced to:

$$U_{ij} = \frac{D - C}{1 + \exp[b_i(\log(R_i z_{ij}) - \log(ED_{50(i)}))]} + C, \quad (3)$$

where the relative potency parameter, R , is the horizontal displacement between two curves. When R was not significantly different from 1.00, the addition of a surfactant would not have an effect on the responses of clodinafop-propargyl and/or tribenuron-methyl. If R was significantly bigger or smaller than 1.00, the mixture of the herbicides and surfactants would be more or less potent than the herbicides used in this study applied alone.

RESULTS AND DISCUSSION

Surface tension studies

Citogate, Frigate, and citofrigate decreased the surface tension of water significantly ($P < 0.01$). The surface tension of Citogate and citofrigate decreased significantly with an increasing concentration of surfactants of up to 0.15% (v/v). Also, the surface tension of water decreased significantly with an increasing Frigate concentration of up to 0.1% (v/v), and followed a steady state thereafter (Table 1). These concentration points are considered to be the CMC. The CMC is the primary point at which the least concentration of a surfactant leads to depletion of the surface tension (Lownds *et al.* 1987). Increasing the surfactant concentration leads to a decrease in the surface tension of water more when its concentration increases more than the CMC, but these differences were not found to be significant (Sharma & Singh 2000). Surface tension values were in a steady state in concentrations of >0.15% (v/v) for Citogate and >0.1% (v/v) for citofrigate and Frigate. The CMC of Frigate was lower than those of Citogate and citofrigate, whereas the surface tension value of Frigate (42.36 mN m⁻¹) was higher than those of Citogate

Table 1. Influence of surfactant concentrations on water surface tension

Concentration (% v/v)	Surface tension (mN m ⁻¹) \pm SD		
	Citogate	Frigate	Citofrigate†
No surfactant		72.24 \pm 0.32	
0.01	61.10 \pm 0.22	57.79 \pm 0.47	59.13 \pm 0.58
0.05	40.38 \pm 0.34	47.69 \pm 0.35	37.00 \pm 0.36
0.10	35.58 \pm 0.29	42.36 \pm 0.16	34.42 \pm 0.12
0.15	34.36 \pm 0.35	40.17 \pm 0.18	33.11 \pm 0.12
0.20	33.86 \pm 0.20	39.79 \pm 0.21	32.94 \pm 0.17
0.25	33.65 \pm 0.19	39.69 \pm 0.11	32.91 \pm 0.19
0.30	33.64 \pm 0.23	39.53 \pm 0.26	32.35 \pm 0.22
LSD _{0.01}		0.809	

† Citofrigate is an equivalent mixture of Citogate and Frigate. The temperature of the laboratory during the measurements was 25 \pm 1°C.

(34.36 mN m⁻¹) and citofrigate (33.11 mN m⁻¹) at the CMC point (Table 1). The results revealed that the mixture of two surfactants, compared with other surfactants separately, lead to a larger decrease in the surface tension of distilled water, but that Citogate had no significant difference compared with citofrigate. The surface tension value of Frigate was higher than those of the other surfactants used in this study when it was added to clodinafop-propargyl and/or tribenuron-methyl (Table 2).

Adding citofrigate to clodinafop-propargyl and/or clodinafop-propargyl plus tribenuron-methyl lead to a greater decrease of surface tension, but the surface tension of Citogate and citofrigate was not significantly different from the applied herbicide solutions ($P < 0.01$). The surface tension of the herbicide solutions decreased with an increasing concentration of the above surfactants. The benefit of decreasing the surface tension at a higher CMC was observed formerly (Anderson *et al.* 1987; Zabkiewicz 2000).

Bioefficacy studies

Experiment 1 showed the influence of Frigate, Citogate, and citofrigate at 0.1% and 0.2% (v/v) on the response of wild oat treated with clodinafop-propargyl (Table 3). All of the surfactants decreased the ED_{50} and ED_{90} values, indicating an increase in the foliar activity of clodinafop-propargyl. The foliar activity (relative potency) of clodinafop-propargyl in the presence of Frigate and citofrigate, compared with that of clodinafop-propargyl alone, lead to the lowest (31% and 47%, respectively) and the highest (64% and 86%, respectively) efficacy, both at 0.1% and 0.2% (v/v), respectively. The efficacy of

clodinafop-propargyl was increased by increasing the surfactants' concentration. The surfactants alone had no visible effect on wild oat. Increasing the concentration of citofrigate had more of an effect on the efficacy of clodinafop-propargyl than increasing the concentration of the other surfactants, whereas Frigate had less of an effect on the efficacy of clodinafop-propargyl than did the other surfactants (Table 3).

Experiment 2 showed the efficacy of a tank mixture of clodinafop-propargyl and tribenuron-methyl on wild oat, compared with that of clodinafop-propargyl alone. The value of the relative potency ($R = 1.19$) was different from 1, indicating an increase in clodinafop-propargyl efficacy when tribenuron-methyl was added to the spray solution (Table 3). The efficacy of 1 kg ha⁻¹ of clodinafop-propargyl, in the presence of tribenuron-methyl, equals the efficacy of 1.19 kg ha⁻¹ of clodinafop-propargyl alone in wild oat control. In a previous study, it was shown that a tank mixture of clodinafop-propargyl and tribenuron-methyl had a synergistic effect in controlling wild oat and wild mustard (Montazeri 1995). Also, it has been reported that applying a tank mixture of these herbicides has lead to higher performance in wheat, compared with a single-herbicide application (Baghestani *et al.* 2007, 2008). The results of this study confirmed not only the previous results but also showed that the application of clodinafop-propargyl plus tribenuron-methyl in the presence of Citogate, Frigate, and citofrigate leads to more efficacy in controlling wild oat. Moreover, the foliar activity of clodinafop-propargyl was the highest in the presence of tribenuron-methyl plus citofrigate, so that the application of this combination lead to a doubled relative potency, both at 0.1% ($R = 2.00$) and 0.2% (v/v) ($R = 2.01$) (Table 3). Increasing

Table 2. Influence of surfactant concentrations on the surface tension of different herbicides

Concentration (% v/v)	Surface tension (mN m ⁻¹) ± SD							
	Clodinafop-propargyl†				Tribenuron-methyl‡			
	Citogate	Frigate	Citofrigate¶		Citogate	Frigate	Citofrigate	
No surfactant		57.39 ± 0.37				69.10 ± 0.52		
0.01	49.35 ± 0.45	52.55 ± 0.44	48.66 ± 0.28	53.59 ± 0.29	56.03 ± 0.60	51.79 ± 0.94	47.01 ± 0.44	54.67 ± 0.56
0.05	36.97 ± 0.30	42.54 ± 0.28	36.29 ± 0.47	37.43 ± 0.71	43.43 ± 0.11	35.47 ± 0.41	36.13 ± 0.43	51.12 ± 0.59
0.10	33.90 ± 0.88	39.25 ± 0.49	33.83 ± 0.42	34.27 ± 0.29	40.02 ± 0.89	33.42 ± 0.38	33.16 ± 0.24	40.97 ± 0.58
0.15	32.66 ± 0.43	38.76 ± 0.27	32.66 ± 0.33	33.34 ± 0.25	39.78 ± 0.47	32.51 ± 0.29	32.11 ± 0.38	38.55 ± 0.95
0.20	32.56 ± 0.38	38.10 ± 0.47	32.27 ± 0.26	32.88 ± 0.31	39.23 ± 0.28	31.94 ± 0.30	31.58 ± 0.66	37.99 ± 0.37
0.25	32.08 ± 0.29	38.01 ± 0.38	31.43 ± 0.53	32.55 ± 0.21	38.33 ± 0.43	31.41 ± 0.31	31.26 ± 0.23	37.53 ± 0.47
0.30	31.89 ± 0.24	37.90 ± 0.34	31.42 ± 0.25	32.48 ± 0.26	38.10 ± 0.26	31.33 ± 0.15	31.15 ± 0.13	37.37 ± 0.24
LSD _{0.01}		1.037				1.107		1.130

† 64 g ai clodinafop-propargyl per 200 L of distilled water; ‡ 15 g ai tribenuron-methyl per 200 L of distilled water; § 64 g ai clodinafop-propargyl plus 15 g ai tribenuron-methyl per 200 L of distilled water; ¶ citofrigate is an equivalent mixture of Citogate and Frigate. The temperature of the laboratory during the measurements was 25 ± 1°C.

the surfactant concentrations lead to an increase in the efficacy of clodinafop-propargyl plus tribenuron-methyl. Unlike Experiment 1, increasing the concentration of Frigate had more of an effect on the efficacy of clodinafop-propargyl plus tribenuron-methyl than increasing the concentration of the other surfactants, whereas citofrigate had less of an effect on the efficacy of clodinafop-propargyl plus tribenuron-methyl than did the other surfactants (Table 3).

Experiment 3 presented the influence of Frigate, Citogate, and citofrigate on the response of wild mustard plants treated with tribenuron-methyl (Table 3). On the whole, the foliar activity of tribenuron-methyl increased in the presence of the tested surfactants and with an increase in their concentration. The surfactants alone had no visible effect on wild mustard. The efficacy of tribenuron-methyl increased more with an increased Citogate concentration than with an increased Frigate or citofrigate concentration (Table 3).

Comparing the results of Experiment 1 and Experiment 3 revealed that the application of Frigate at 0.1% (v/v) lead to the increased foliar activity of tribenuron-methyl, which was higher than that of clodinafop-propargyl, but that the application of Frigate at 0.2% (v/v) increased the foliar activity of clodinafop-propargyl more than that of tribenuron-methyl. However, these differences were not remarkable. Furthermore, most of the surfactants indicated that clodinafop-propargyl was more effective in the control of wild oat than was tribenuron-methyl in the control of wild mustard. This result might be related to differences in cuticle composition and/or the spray retention of small droplets that were generated by the surfactants on the vertical leaves of wild oat. Scott *et al.* (1998) and Zhiqian (2004) stated that surfactants increased the efficacy and foliar uptake of herbicides in controlling grasses more than broad-leaved weeds. The branching habit of a plant is very critical for foliar-applied herbicides. Most broad-leaved weeds have an open or horizontal branching habit with expanded leaves and exposed growing regions. This facilitates the retention of spray droplets and easy surface coverage. Grass species, in contrast, have minutely ridged surfaces on the leaves. They are often vertically arranged and the growing regions are enclosed by sheaths that serve as a protective cover (Rao 2000). Thus, spray retention critically depends on the leaf angle; that of grass species is more than that of broad-leaved weeds (Jinxia 1996). Moreover, in the absence of surfactants, the contact angle of water and the leaf surface of wild oat ($\theta = 161$) was more than that of the leaf surface of wild mustard ($\theta = 64$), but in the presence of surfactants, that of *Avena* sp.

Table 3. Estimated ED_{50} and ED_{90} doses and the relative potency of clodinafop-propargyl alone and/or tribenuron-methyl alone or in the presence of surfactants

Experimental treatment	$ED_{50} \pm SD$ (g ai ha ⁻¹)	$ED_{90} \pm SD$ (g ai ha ⁻¹)	Relative potency	
			Surfactants + herbicides alone	Surfactants + tank mixture of herbicides
1. Clodinafop alone	19.97 ± 1.62	38.45 ± 1.59	1.00	—
Clodinafop + Frigate (0.1%)	15.21 ± 1.58	28.61 ± 1.55	1.31 ± 0.21	—
Clodinafop + Frigate (0.2%)	13.56 ± 1.36	24.22 ± 1.34	1.47 ± 0.14	—
Clodinafop + Citogate (0.1%)	12.96 ± 0.40	22.88 ± 0.41	1.54 ± 0.20	—
Clodinafop + Citogate (0.2%)	11.31 ± 0.69	21.17 ± 0.68	1.76 ± 0.18	—
Clodinafop + citofrigate (0.1%)	12.24 ± 0.58	22.11 ± 0.59	1.63 ± 0.19	—
Clodinafop + citofrigate (0.2%)	10.71 ± 0.84	19.64 ± 0.82	1.86 ± 0.24	—
2. Clodinafop alone	18.77 ± 1.45	38.25 ± 0.43	1.00	—
Clodinafop + tribenuron alone	15.99 ± 1.06	32.56 ± 1.03	1.19 ± 0.26	1.00
Clodinafop + tribenuron + Frigate (0.1%)	13.14 ± 1.81	28.17 ± 1.77	1.43 ± 0.42	1.18 ± 0.25
Clodinafop + tribenuron + Frigate (0.2%)	11.57 ± 1.38	24.04 ± 1.35	1.62 ± 0.30	1.39 ± 0.19
Clodinafop + tribenuron + Citogate (0.1%)	10.11 ± 1.46	19.16 ± 1.43	1.87 ± 0.34	1.53 ± 0.25
Clodinafop + tribenuron + Citogate (0.2%)	9.46 ± 2.50	19.31 ± 2.45	1.98 ± 0.74	1.64 ± 0.49
Clodinafop + tribenuron + citofrigate (0.1%)	9.36 ± 1.46	18.65 ± 1.42	2.00 ± 0.22	1.65 ± 0.23
Clodinafop + tribenuron + citofrigate (0.2%)	9.34 ± 2.64	17.27 ± 2.59	2.01 ± 0.68	1.66 ± 0.48
3. Tribenuron alone	4.54 ± 1.22	7.66 ± 1.17	1.00	—
Tribenuron + Frigate (0.1%)	3.37 ± 0.37	6.78 ± 0.35	1.34 ± 0.18	—
Tribenuron + Frigate (0.2%)	3.21 ± 0.13	6.34 ± 0.12	1.41 ± 0.10	—
Tribenuron + Citogate (0.1%)	3.04 ± 0.18	5.98 ± 0.21	1.49 ± 0.17	—
Tribenuron + Citogate (0.2%)	2.83 ± 0.23	5.36 ± 0.22	1.60 ± 0.11	—
Tribenuron + citofrigate (0.1%)	2.91 ± 0.36	5.38 ± 0.37	1.56 ± 0.15	—
Tribenuron + citofrigate (0.2%)	2.80 ± 0.09	5.12 ± 0.19	1.61 ± 0.14	—
4. Tribenuron alone	4.36 ± 1.49	7.98 ± 0.91	1.00	—
Tribenuron + clodinafop alone	3.24 ± 0.69	6.25 ± 0.66	1.34 ± 0.18	1.00
Tribenuron + clodinafop + Frigate (0.1%)	2.87 ± 0.58	5.57 ± 0.56	1.52 ± 0.13	1.09 ± 0.11
Tribenuron + clodinafop + Frigate (0.2%)	2.78 ± 0.76	5.18 ± 0.73	1.57 ± 0.17	1.13 ± 0.11
Tribenuron + clodinafop + Citogate (0.1%)	2.95 ± 0.66	5.00 ± 0.63	1.48 ± 0.20	1.06 ± 0.15
Tribenuron + clodinafop + Citogate (0.2%)	2.27 ± 0.84	4.09 ± 0.80	1.92 ± 0.10	1.38 ± 0.09
Tribenuron + clodinafop + citofrigate (0.1%)	2.51 ± 0.58	4.47 ± 0.56	1.74 ± 0.12	1.25 ± 0.12
Tribenuron + clodinafop + citofrigate (0.2%)	2.26 ± 0.83	4.11 ± 0.80	1.92 ± 0.12	1.39 ± 0.21

Clodinafop-propargyl and tribenuron-methyl are shortened to clodinafop and tribenuron, respectively. Citofrigate is an equivalent mixture of Citogate and Frigate. Experiments 1 and 2 were conducted on wild oat. Experiments 3 and 4 were conducted on wild mustard.

was affected severely. The wettability will be hard if the contact angle exceeds 90° (Kudsk 1997). The application of surfactants in a spray solution generates smaller droplets (Jinxia 1996). Thus, the use of surfactants resulted in more retention and wettability of the spray solution, especially with grass species (Rao 2000).

Experiment 4 showed that the combination of the tribenuron-methyl and clodinafop-propargyl herbicides also had a synergistic effect in wild mustard control (Table 3). The value of the relative potency ($R = 1.34$) was >1 , indicating a significant increase of foliar activity on wild mustard by tribenuron-methyl when clodinafop-propargyl was added to the spray solution. The efficacy of 1 kg ha^{-1} of tribenuron-methyl, in the presence of clodinafop-propargyl, equals the efficacy of 1.34 kg ha^{-1} of tribenuron-methyl alone in wild mustard control. The synergistic effect of this combination in wild mustard control ($R = 1.34$) was more effective than in wild oat control ($R = 1.19$). It is possible that adding clodinafop-propargyl to the solution of tribenuron-methyl decreases the surface tension of tribenuron-methyl ($>14 \text{ mN m}^{-1}$), resulting in greater penetration of tribenuron-methyl in wild mustard tissues (Table 2). This could be attributed to the inactive ingredient of the herbicide formulation (8% EC clodinafop-propargyl). Adding tribenuron-methyl to the clodinafop-propargyl solution could reduce the surface tension of the clodinafop-propargyl solution by $\leq 3 \text{ mN m}^{-1}$ (Table 2). In contrast, the efficacy of clodinafop-propargyl plus tribenuron-methyl in controlling wild oat, in the presence of the above surfactants, was higher than that for wild mustard (except Frigate at 0.1% [v/v]). This might be related to the spray retention of small droplets on the vertical leaves of wild oat. Anderson and Van-Haaren (1989) stated that the surface tension in herbicide solution droplets correlated positively to the droplet retention on the leaf surface. Penner (2000) reported that the decrease of surface tension leads to the production of smaller droplets and, because of low energy in smaller droplets, more of the droplet retention would be on the leaf surface. The greater the retention of the impacting droplets, the greater the effectiveness of the herbicide formulation.

The results of experiments 1, 2, and 3 showed that the application of Citogate at 0.1% (v/v) was more effective than the application of Frigate at 0.2% (v/v) in herbicidal efficacy (Table 3). This could be attributed to the lower surface tension of Citogate at 0.1% (v/v) than Frigate at 0.2% (v/v) (Tables 1,2). But, the result of Experiment 4 showed that Frigate at 0.2% (v/v) was more effective than Citogate at 0.1% (v/v) in the

combination of clodinafop-propargyl and tribenuron-methyl (Table 3).

The data obtained in these experiments indicated that the efficacy of clodinafop-propargyl and/or tribenuron-methyl depends on the kind of surfactants used and their potential in the reduction of surface tension. Citogate decreased the surface tension more than did Frigate and resulted in greater effectiveness of the herbicides. The application of two surfactants, compared with a single surfactant application, brought about a greater decrease in surface tension and increased the efficacy of the herbicides remarkably. The results revealed that the non-ionic surfactant, Citogate, and the cationic surfactant, Frigate, had synergistic effects on clodinafop-propargyl and/or tribenuron-methyl. However, Collins and Helling (2002) reported that the cationic surfactant, Frigate, had an antagonistic effect with ionic surfactants on glyphosate's effectiveness.

The results of current research showed that the efficacy of the tested herbicides increased with an increase in surfactant concentration higher than the CMC and explained that an increase in biological activity of the herbicide molecule depended on other factors, with the exception of decreasing surface tension. Hazen (2000) stated that spreading and solubilization are affected favorably by a surfactant concentration above the CMC. Nonetheless, regarding cuticular waxes that were treated with an extra amount of non-ionic surfactants, no effects were found that related to the softening or disruption of the cuticular waxes (Kudsk 1997). Penner (2000) believed that, although surfactants are not directly effective in herbicide penetration, they indirectly facilitate the process of herbicide penetration through the waxy cuticle of the leaf surface. However, there is a strong relationship between the absorption of a herbicide and the surfactant's concentration and chemistry (Zabkiewicz 2000). Previous studies also have reported that an increase of surfactant concentration is an important factor in the retention of a herbicide on the leaf surface (Scott *et al.* 1998; Sharma & Singh 2000). Collins and Helling (2002) concluded that an increase in the concentration of Frigate and an anionic surfactant resulted in the greater effectiveness of glyphosate. Generally, increasing the concentration of surfactants will increase herbicide absorption (Jinxia 1996) but, in some cases, such as glyphosate, despite an increase in the surfactant concentration leading to a decrease in the surface tension and contact angle on the leaf surface, the increase of surfactant concentration might result in a decrease of the herbicide rate per unit area and reduce the uptake of glyphosate (Zabkiewicz 2000; Zhiqian 2004).

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