☘Surface Tension and Contact Angle of Herbicide Solutions Affected by Surfactants[1]

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ABSTRACT

Contact angle and surface tension were measured for distilled and hard water solutions of adjuvants, Ortho X-77, Span-20, Sterox-NJ. Surfactant-WK, Triton B-1956, Triton X-114, Tween-20, and Sun Oil 11E. The same parameters were measured for suspensions of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine] and ametryne [2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine] with and without each adjuvant. All adjuvants reduced surface tension and contact angle of distilled water; Surfactant-WK was most effective and Tween-20 was least effective. Increasing concentration of surfactants from 0 to 0.1% (v/v) gave progressive reduction in surface tension and contact angle while higher concentrations, 0.1 to 2.0% (v/v), had no further effect. Surfactant-WK at 0.1% (v/v) in distilled water reduced the surfact tension from 72.8 dynes/cm to 27 dynes/cm and contact angle from 110° to 41°. An additional increase in Surfactant-WK concentration from 0.1% (v/v) to 2% (v/v) did not further reduce surface tension and contact angle. Sun Oil 11E was identical in behavior except that it was less effective than the surfactants. Water hardness up to 1,000 ppm as Ca ions did not affect surface tension and contact angle in surfactant solutions. An aqueous solution of atrazine had a higher surface tension and contact angle than ametryne in the absence of surfactants. However, these differences were not observed when surfactants were added to either herbicide.

INTRODUCTION

In recent years, the use of additives with herbicides has drawn the attention of research workers. Surfactants increase wetting ability as they reduce the surface tension and contact angle of the spray on the plant surface (1, 2, 3, 15). They also may reduce the rate of evaporation, allowing a longer retention of spray as a liquid on a plant surface and permit greater adsorption (5). Surfactants and other additives modify the phytotoxicity of herbicides (4, 7–9, 11, 13, 17). Adjuvants are used to reduce surface tension (7) and enhance cuticular penetration (6, 10, 18).

Surfactants have been evaluated with herbicides to determine their effect on efficacy while very little work has been done on the quantitative determination of surface tension and contact angle. In the present study, we have determined the surface tension and contact angle for 7 surfactants at various concentrations. These data could be helpful in judging surfactant suitability for application in combination with herbicides. The information could also be used to correlate the effect of these surfactants on the phytotoxicity of herbicides and their surface tension and contact angle.

EXPERIMENTAL PROCEDURES

The parameters studied in the laboratory were surface tension and contact angle for various combinations of water, surfactants, and herbicides. The adjuvants were: Ortho X-77, Span-20, Sterox-NJ, Surfactant-WK, Triton B-1956, Triton X-114, Tween-20, and Sun Oil 11E (Table I). All surfactants were nonionic. The herbicides were commercial 80% wettable powder formulations of atrazine and ametryne. All observations were recorded at a room temperature (25 C).

Preparation of Solutions

Solutions were prepared separately for each series of measurements. All adjuvants were tested in distilled water (DW), tap water (TW) and synthetic hard water of 250, 500, 750, and 1,000 ppm Ca ions. The tap water hardness was 100 ppm of Ca. Artificial water hardness was developed by adding calcium chloride ($CaCl_2$) to distilled water. Stock solutions containing 2% surfactant or Sun Oil 11E were prepared and then diluted to 1, 0.5, 0.25, 0.125, 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5}% by volume (v/v). Each sample was used to measure both surface tension and contact angle. Each measurement was repeated until 3 consistent values were obtained.

In a second series of experiments, atrazine and ametryne

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TABLE I

Technical Information About the Surfactants Used in the Studies

Trade name	Chemical description	Conc. (%)	Form	HLB	Ionic form	Source
Ortho X-77	Alkylaryl polyoxyethylene glycol	90	liquid	13.5	Nonionic	Chevron Chemical Co. Richmond, CA
Span-20	Sorbitan monolaurate	100	liquid	8.6	Nonionic	ICI America, Inc. Wilmington, DE
Sterox-NJ	Nonylphenyl hydroxypoly oxyethylene	100	liquid	13.0	Nonionic	Monsanto, Co. St. Louis, MO
Surfactant-WK	Trimethyl nonylpolyethoxy ethanol	90	liquid	11.7	Nonionic	E. I. Du Pont Co. Wilmington, DE
Triton X-114	Octylphenoxy polyethoxy ethanol	100	liquid	12.4	Nonionic	Rhom and Haas Co. Philadelphia, PA
Triton B-1956	Modified phthalic glycerol alkyl resin	77	liquid	N.A.	Nonionic	Rohm and Haas Co. Philadelphia, PA
Tween-20	POE (20) Sorbitan monolaurate	100	liquid	16.7	Nonionic	ICI America, Inc. Wilmington, DE

suspensions were prepared using 2.67, 5.34, and 10.68 g/L of distilled water to simulate the application rates of 1, 2, and 4 kg/ha at 400 L/ha of water. The adjuvants were added at concentrations of 0, 0.5, 1, and 2% (v/v). The same sample was used to measure surface tension and contact angle. Measurements were repeated until 3 consistent values were obtained.

Surface Tension Measurements

A sample of 100 mL was drawn from the solution for surface tension measurement by Wilhelmy's detachment method, using a torsion balance (12). The instrument was calibrated using double-distilled water with a surface tension of 72.8 dynes/cm at 20 C and was confirmed by using absolute ethyl alcohol with a surface tension of 22.0 dynes/cm. All observations were converted to dynes/cm.

Contact Angle Measurement

A drop of solution was used to measure the contact angle with a contact angle goniometer on a clean and dry Teflon (tetrafluoroethylene) surface. The contact angle goniometer was calibrated with distilled water, which has a contact angle of 108° on a Teflon surface. The uniformity in the size of a drop was maintained by using a microsyringe. The drop of a solution was placed gently on the Teflon plate. The horizontal and vertical axes were adjusted according to the shape of the drop, and the contact angle was read directly on the circular graduated dial. Contact angles were read from opposite sides of the drop, and the average of both readings was recorded.

RESULTS AND DISCUSSION

Surface Tension

Surface tension was measured for Ortho X-77, Span-20, Sterox-NJ, Surfactant-WK, Triton B-1956, TritonX-114, Tween-20, Span-20 + Tween-20 (50:50 v/v), and Sun Oil 11E in DW, TW, artificial hard water of 250, 500, 750, and 1,000 ppm as Ca ions and at adjuvant concentrations of 0, 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}. 0.125, 0.25, 0.5, 1, and 2% (Table II).

All adjuvants reduced surface tension. However, the lower concentrations had greater effects than higher concentrations. Surfactant concentrations ranging from 10^{-5} – 10^{-2}% were most effective in reducing surface tension. The reduction in surface tension from 10^{-2} to 2% was slight or none (Fig. 1). A marked decrease in surface tension at lower surfactant concentrations and modest reduction at higher surfactant concentrations is noted

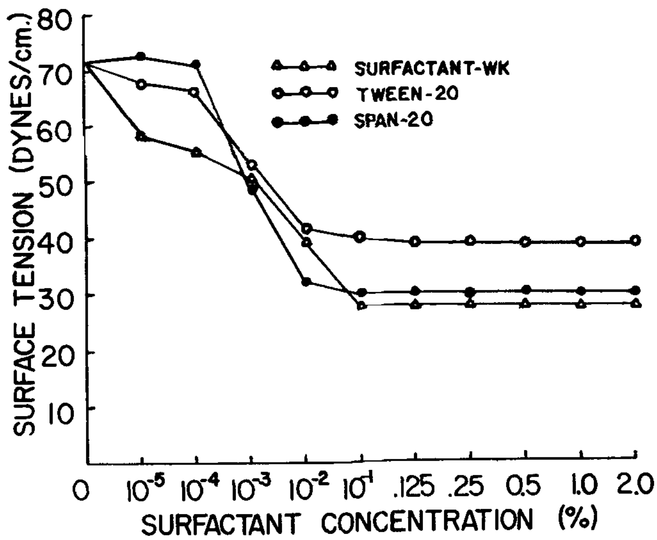

FIG. 1. Effect of surfactant concentration on surface tension in aqueous solutions.

because surfactant molecules align themselves randomly on the liquid surface with the polar end (head) up and the nonpolar end (tail) down when small amounts of surfactants are added to a surfactant-free surface. The presence of surfactant molecules on the surface resuces surface tension. Reduction in surface tension continues with an increase in surfactant molecules until the whole surface is saturated with a monolayer of surfactant molecules, and further reduction in surface tension does not occur with additional surfactant. This surfactant saturation concentration is named critical micelle concentration (CMC) (12). Excess surfactant causes micelle formation in liquid.

CMC varies from surfactant to surfactant, depending upon chemical composition, structure, and physicochemical conditions. CMC for Ortho X-77, Span-20, Sterox-NJ, Triton B-1956, Tween-20, and Span-20 + Tween-20 was at ca. 10^{-2}%, and for Surfactant-WK, Triton X-114, and Sun Oil 11E, it was at 10^{-1}% (Table II). Maximum and minimum reductions in surface tension (ca. 26.5 and ca. 35.4 dynes/cm) were recorded at 0.125% or higher concentrations of Surfactant-WK and 0.25% or higher

TABLE II

Effect of Various Surfactants and Their Concentrations on Surface Tension

Surfactant concentration (% v/v)	Ortho X-77	Sterox-NJ	Triton B-1956	Triton X-114	Span-20 + Tween-20	Sun Oil 11E
	(dynes/cm)					
0	72.8	72.8	72.8	72.8	72.8	72.8
10^{-5}	69.5	68.4	71.8	67.4	71.4	57.5
10^{-4}	58.5	64.6	72.2	62.9	65.7	52.2
10^{-3}	37.7	39.6	45.1	48.2	51.5	47.4
10^{-2}	32.2	32.2	31.0	32.4	32.6	36.6
10^{-1}	32.0	32.4	30.3	30.3	30.4	33.0
0.125	31.6	32.4	30.1	30.1	30.1	32.4
0.25	31.4	32.6	29.7	29.5	29.8	32.6
0.50	31.6	32.4	29.9	29.7	30.0	32.4
1.0	31.6	32.2	29.7	29.7	28.9	32.6
2.0	31.2	32.2	29.9	29.1	29.8	32.4

TABLE III

Effect of Various Surfactants on Surface Tension of Herbicide Solutions

Herbicide	Rate kg/ha	No Surfactant	Ortho X-77	Span-20	Sterox-NJ	Surfactant-WK	Triton B-1956	Triton X-114	Tween-20	Span-20 + Tween-20	Sun Oil 11E
		(dynes/cm)									
Atrazine	1.0	57.0	31.9	29.0	32.1	28.6	33.0	30.4	39.3	34.8	34.0
Atrazine	2.0	51.2	31.7	29.4	32.0	28.7	33.1	30.8	39.5	34.7	36.9
Atrazine	4.0	41.7	31.9	30.6	32.1	28.7	33.1	30.6	39.2	34.0	37.6
Ametryne	1.0	35.5	32.2	30.4	31.9	28.7	32.6	30.6	38.4	35.2	34.6
Ametryne	2.0	33.3	31.9	31.0	31.9	28.9	32.6	30.7	38.4	34.4	34.7
Ametryne	4.0	33.5	32.1	31.3	31.8	28.8	32.7	30.8	38.3	35.2	34.4

concentrations of Tween-20. Water hardness ranging from 250 to 1,000 ppm as Ca ions did not affect surface tension appreciably. Since the water hardness did not have a significant effect on surface tension, the data in Table I are presented only for distilled water. Water hardness should not affect results of herbicide solutions, when surfactants are added to these solutions, up to the limits tested.

A mixture of Span-20 and Tween-20 was intermediate in terms of surface tension reduction at lower concentrations (10^{-5}–10^{-2}%) but was much closer to Span-20 at concentrations of 10^{-1}% or higher (Table II). Tween-20 was more effective at 10^{-4} and 10^{-5}% compared with Span-20; however, the trend reversed at higher concentrations. Surfactants can be arranged in the following order on the basis of their effect on surface tension reductions: Surfactant-WK > Triton X-114 > Span-20 > Span-20 + Tween-20 > Triton B-1956 > Ortho X-77 > Sterox-NJ > Sun Oil 11E > Tween-20.

Surface tension was measured also for the above surfactants at 0.5, 1, and 2% (v/v) concentraions in suspensions of commercial formulations of atrazine and ametryne to simulate application rates of 1, 2, and 4 kg/ha in 400 L/ha (Table III). Atrazine solutions at 1.0, 2.0, and 4.0 kg/ha had substantially higher surface tension than similar rates of ametryne in the absence of surfactant. An increase in rate of atrazine from 1 kg to 4 kg/ha reduced the surface tension from 57 to 41.7 dynes/cm while ametryne rate increases did not affect surfact tension. Lower and constant surface tension of ametryne solutions indicates that ametryne probably had sufficient surfactant in the formulatin to provide a monolayer of surfactant molecules on the solution surface. Atrazine at 1 kg/ha did not have enough surfactant molecules present to form a surface monolayer of molecules; additional molecules supplied by the higher rates of atrazine lowered the surface tension.

Addition of surfactants of atrazine solutions reduced surface tension whereas the addition of surfactants in ametryne solutions did not affect surface tension except for a reduction of about 5 dynes/cm observed for Surfactant-WK compared with no surfactant. This confirmed the earlier assumption that the ametryne formulation contained surfactant levels that developed concentrations close to the CMC and additional surfactant did not further reduce surface tension. With the atrazine formulation, CMC was reached with an additional amount of surfactant, and surface tension values were reduced. The surfactant concentrations ranging from 0.5 to 2% did not change surface tension, therefore, the mean values for 0.5, 1, and 2% have been reported in Table III. The addition of Tween-20 to ametryne solutions increased surface tension, which could be caused by an interaction between Tween-20 and the unknown surfactant(s) already present in the ametryne formulation. In the atrazine solutions, Tween-20 reduced surface tension to about 39 dynes/cm whereas the other surfactants reduced surface tension to about 30 dynes/cm, again suggesting that Tween-20 is a poor surface tension reducer with wettable powder formulations.

Contact Angle

Contact angle was determined for all herbicide and water hardness combinations described in the previous section. The addition of surfactant reduced the contact angle compared with no surfactant (Table IV). The increase in surfactant concentration from 10^{-5} to 10^{-1} or 10^{-2}% decreased the contact angle sharply (Fig. 2). After the CMC was reached, the decrease was either small or none. Contact angle is predominantly a function of surface tension. Higher values of the contact angle were recorded from solutions having higher surface tension, and vice-versa. Maximum and minimum reductions in contact angle (38° and 67°) were obtained at 0.25% or higher concentration of Surfactant-WK and 0.125% or higher concentration

TABLE IV

Effect of Various Surfactants and Their Concentrations on Contact Angle

Surfactant concentration (% v/v)	Ortho X-77	Sterox-NJ	Triton B-1956	Triton X-114	Span-20 + Tween-20	Sun Oil 11E
	(degree)					
0	110	110	110	110	110	110
10^{-5}	90	96	97	96	102	75
10^{-4}	78	91	99	91	94	73
10^{-3}	67	70	72	78	79	71
10^{-2}	63	48	61	57	72	53
10^{-1}	61	48	60	54	65	51
0.125	60	48	58	53	64	50
0.25	58	49	56	52	58	49
0.50	51	48	57	51	55	47
1.0	51	47	56	50	54	48
2.0	50	46	55	49	52	48

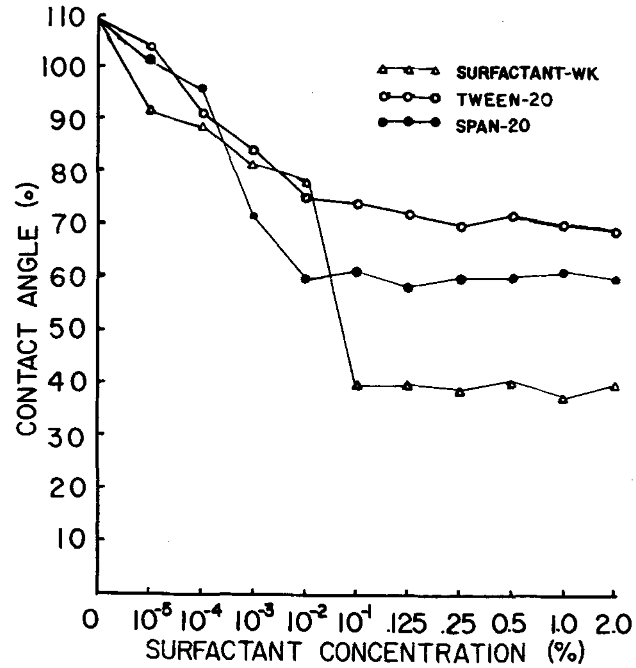

FIG. 2. Effect of surfactant concentration on contact angle in aqueous solution.

of Tween-20. The measured contact angle of distilled water on the Teflon surface was 110°. The contact angle of 1,000 ppm hard water as Ca ions was slightly lower than distilled water, but water hardness of 250, 500, 750, and 1,000 ppm did not seem to affect the contact angle. Therefore, the data in Table IV pertain only to distilled water. Water hardness from 0 to 1,000 ppm as Ca ions did not seem to affect the contact angle, in presence of surfactants, except at lower concentrations (10^{-5} to 10^{-3}) of Span-20, Sapn-20 + Tween-20, and Triton B-1956, where a slight decreasing trend with increasing hardness was recorded. Reduction in surface tension lowers the pulling force of the surface of the drop; the drop tends to flatten, reducing the contact angle and providing greater plant surface wetting by a given drop of liquid (14). In the absence of surfactant, atrazine solutions had greater contact angles than ametryne solutions at the 2 highest rates (Table V). The contact angle increased with increased rates of application (1-4 kg/ha) of atrazine and ametryne, and the increases were greater with atrazine than with ametryne (Table V). The addition of surfactant to both atrazine and ametryne solutions reduced the contact angle considerably. Rates of surfactants ranging from 0.5 to 2% did not have any effect on the contact angle except with Triton B-1956, where lower contact-angle values were recorded at 2% compared with 0.5 and 1%. In the presence of surfactants, no difference was found between the contact angles of atrazine and ametryne solutions at any rate. Minimum contact-angle values were recorded with Surfactant-WK and maximum with Tween-20.

The effect of Sun Oil 11E on the contact angle was comparable to that of surfactants, especially Ortho X-77 and Triton X-114. The effect of herbicide surfactant combinations on surface tension and contace angle could not be determined more precisely as technical material about atrazine and ametryne was not evaluated and commercial formulations contain unspecified additives. Surfactant-WK, Span-20, and Tween-20 were classified as strong, intermediate, and weak surfactants, respectively, on the basis of surface tension and contact-angle reduction ability. The effect of these 3 surfactants on herbicide efficacy was studied further (16).

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TABLE V

Effect of Various Surfactants on Contact Angle of Herbicide Solutions

Herbicide	Rate kg/ha	No Surfactant	Ortho X-77	Span-20	Sterox-NJ	Surfactant-WK	Triton B-1956	Triton X-114	Tween-20	Span-20 + Tween-20	Sun Oil 11E
		(degree)									
Atrazine	1.0	59	54	65	59	35	36	47	76	69	46
Atrazine	2.0	83	53	64	59	35	36	50	75	68	48
Atrazine	4.0	93	55	64	59	35	38	50	76	69	51
Ametryne	1.0	58	56	62	59	36	35	50	75	65	53
Ametryne	2.0	62	55	62	60	36	37	51	77	66	53
Ametryne	4.0	65	55	63	58	35	36	50	74	66	53

ERRATUM

In the article "Primary Alkane Sulfonates," by J. R.Wechsler and A. M. Koberda (*JAOCS* 60:2012-2014, 1983), the tables were inadvertently omitted. The following are the tables from that paper.

TABLE I

Solubility, % in Saturated Aqueous Solution

$R\text{-}SO_3^-$ Chain length	Na^+ 25 C	Na^+ 45 C	K^+ 25 C	K^+ 45 C	NH_4^+ 25 C
R = 12	0.18	18.7	3.0	34.6	36.5
R = 14	0.09	0.38	0.40	9.8	27.9
R = 14-16	0.31	0.71	–	–	–
R = 16	0.03	0.14	0.08	0.58	27.9
R = 18	0.005	–	0.08	0.17	26.9

TABLE II

Krafft Points (for Clarity of 1.0% Solutions) (temperature [C])

Chain length	RSO_3Na	RSO_3K	RCO_2Na
R = 12	38	10	24
R = 14	48	38.5	43
R = 14-16	47	39	–
R = 16	57	50	57
R = 18	70	57	–

TABLE III

Surfactancy of Sodium Salts, 0.10% Active Solutions, Measured at 45 ± 1 C (above Krafft Point)

Anion	Chain length	Wetting draves (sec)	Foam height Ross-Miles (cm)	Surface tension (dyne/cm)
AOS	14-16	10.7	16.0/15.0	36.5
PAS	12	30.7	4.5/0	42.3
PAS	14	8.5	15.5/12.5	41.0
PAS	14-16	10.6	16.0/14.0	43.5
PAS	16	19.0	14.5/14.0	38.0

TABLE IV

Detergency (as Percentage of Standard)

RSO_3Na	US testing swatch (%)	Test fabrics swatch (%)
$R = C_{12}$	89.2	88.1
$R = C_{14}$	97.3	89.3
$R = C_{16}$	98.8	98.3
$R = C_{18}$	100	98.3
$R = C_{20}$	103.3	100
$R = C_{22}$	95.8	87.9
$R = C_{11}\text{-}C_{14}$	89.5	85.7
$R = C_{15}\text{-}C_{18}$	98.5	98.6
$R = C_{15}\text{-}C_{20}$	101.2	99.5