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Sulfentrazone Adsorbed on Micelle−Montmorillonite Complexes for Slow Release in Soil

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Interactions of the herbicide sulfentrazone with the cationic surfactants octadecyltrimethylammonium (ODTMA), hexadecyltrimethylammonium (HDTMA), and benzyldimethylhexadecylammonium (BDMHDA) have been studied for the design of slow-release formulations based on sulfentrazone adsorbed on a micelle−montmorillonite complex. Adsorbed amounts of sulfentrazone on ODTMA− and BDMHDA−montmorillonite complexes were 99.2−99.8% of that added, and desorption of herbicide in water during 24 h was low. After 10 washings in funnels with soil, only 2.6% of herbicide was released from ODTMA−montmorillonite formulations versus 100% release from the commercial formulation. The strong binding of sulfentrazone to micelles was confirmed by pH and spectroscopic measurements and was explained by the formation of ionic pairs between cationic surfactant and anionic herbicide. The ODTMA−clay and commercial formulations of sulfentrazone yield almost complete and 40% growth inhibition of green foxtail, respectively, at 700 g of active ingredient/ha. Hence, the slow release from micelle−clay formulations of sulfentrazone promotes its biological activity and reduces environmental contamination.

KEYWORDS: Surfactant; micelle; montmorillonite; sulfentrazone; adsorption; slow release

INTRODUCTION

Sulfentrazone [*N*-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1*H*-1,2,4-triazol-1-yl]phenyl]methanesulfonamide] is a triazolinone herbicide (*1*) registered for weed control in soybeans [*Glycine max* (L.) Merr.] and applied to control broadleaf and grass weed species (*2*). Sulfentrazone inhibits protoporphyrinogen oxidase, an enzyme in the chlorophyll biosynthetic pathway (*3*, *4*). The herbicide is a weak acid with $pK_a = 6.56$ (*5*). Adsorption and mobility of sulfentrazone in soil are significantly affected by pH; adsorption decreased with pH increase, especially above the pK_a of the herbicide (*6*). When sulfentrazone is adsorbed on soil at pH values below the pK_a, desorption of the molecules can occur by simply raising the pH above the pK_a (*7*). The herbicide is negatively charged at basic pH, which is common in the Mediterranean zone (*8*), and the severe problem of leaching and mobility of sulfentrazone persists in this region. Herbicide leaching contaminates the ground water and reduces the efficacy of herbicide applied.

The application of slow-release formulations can help reduce leaching of herbicides in soils. Our aim was to design formulations based on sulfentrazone adsorbed on micelle−montmorillonite complexes. This approach is based on the incorporation of the herbicide into the quaternary ammonium cation micelles and adsorption of these micelles on the negatively charged montmorillonite (*9*). The micelle−montmorillonite complex was found to be very efficient for the slow release of sulfonylurea herbicides (*10*). The current work presents a study of interactions of sulfentrazone with the cationic surfactants octadecyltrimethylammonium (ODTMA), hexadecyltrimethylammonium (HDTMA), and benzyldimethylhexadecylammonium (BDMHDA). We will show that the new formulations based on micelle−clay complexes yield slow release and consequently enable reduction of sulfentrazone leaching and promotion of herbicide activity.

MATERIALS AND METHODS

Materials. The clay used was Wyoming sodium montmorillonite SWy-2 obtained from the Source Clays Repository (Clay Minerals Society, Columbia, MO). ODTMA and HDTMA were purchased from Sigma-Aldrich (Sigma Chemical Co., St. Louis, MO). BDMHDA was purchased from Fluka Chemie (Buchs, Switzerland). Sulfentrazone technical (purity = 91.3%) was obtained from FMC (Princeton, NJ); commercial formulation of sulfentrazone [Boral 75% active ingredient (ai); water dispersible granular] was obtained from FMC (Philadelphia, PA). The structural formulas of sulfentrazone and cations of surfactants are presented in **Figure 1**.

Rehovot soil was collected from the top 30 cm of a sandy loam soil at the Faculty's Experimental Farm in Rehovot, Israel, air-dried, and

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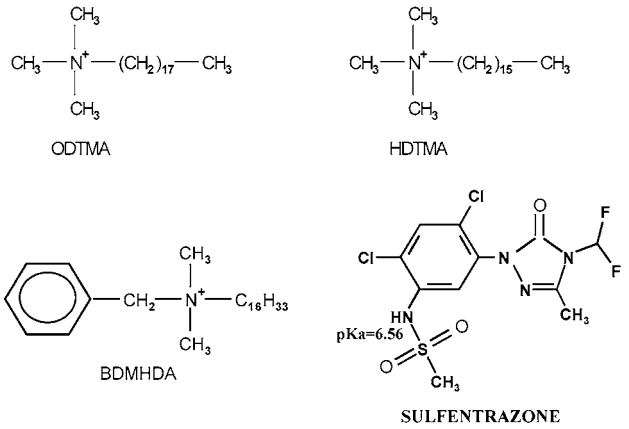

Figure 1. Structural formulas of the surfactants and sulfentrazone molecules.

Table 1. Experimental Conditions in Measurements of Sulfentrazone Adsorption

surfactant added, mM	clay concn, g L^{-1}	sulfentrazone added, mmol kg^{-1}
ODTMA, 2.5	2	21.5
ODTMA, 2.5	2	34.4
ODTMA, 2.5	2	43
ODTMA, 2.5	2	68.9
ODTMA, 5	2	43
ODTMA, 10	2	43
ODTMA, 2.5	5	43
ODTMA, 2.5	10	43
BDMHDA, 2.5	2	21.5
BDMHDA, 2.5	2	43
montmorillonite	2	43

sieved through a 2 mm screen. The pH of the soil is 7.5, organic matter content 0.2%, sand 95.5%, silt 3.3%, and clay 1.2% (*11*). Green foxtail (*Setaria viridis* L. cv. Beauvios) (Hazera-Quality Seeds) was used as a test plant.

Adsorption. Experimental conditions in adsorption measurements of sulfentrazone are presented in the **Table 1**; ODTMA and BDMHDA were added to the solutions of sulfentrazone (80, 50, and 25 mg L^{-1}). The sulfentrazone−micelle complexes were kept stirring for 24 h, which was sufficient for reaching the adsorption equilibrium for sulfentrazone. Ten milliliters of micelle−sulfentrazone complexes was mixed in a polypropylene copolymer centrifuge tube with 5 mL of a water suspension of montmorillonite. Preliminary experiments showed no adsorption of sulfentrazone on the tubes. Tubes were kept at 25 ± 1 °C under continuous agitation for 24 h. Then the tubes were centrifuged for 20 min at 15000*g*, and concentrations of sulfentrazone in supernatants and pH values were measured. The pH values were also monitored in sulfentrazone, micelle−sulfentrazone, and micelle−water solutions. The same experiment was performed for pure montmorillonite.

Absorption spectra of solutions containing organic cations in concentrations below and above the critical micelle concentration (CMC), sulfentrazone solutions at pH below and above the pK_a of the herbicide (6.56), and herbicide−micelle solutions were obtained by HP8452A diode array UV−vis spectrophotometer (Hewlett-Packard Co., Palo Alto, CA).

Desorption. Two experiments of desorption were performed. In the first experiment desorption was studied for wet samples by using distilled water. Amounts of 0.03 g of sulfentrazone−micelle−clay complexes (obtained in adsorption experiments at 2.5 mM ODTMA, 2 g L^{-1} clay, and 43 mmol kg^{-1} sulfentrazone added) after removal of the supernatants were mixed in centrifuge tubes with 15 mL of distilled water; the final complex concentrations were 2 g L^{-1}. Tubes were kept at 25 ± 1 °C under continuous agitation for 24 h. Then the tubes were centrifuged for 20 min at 15000*g*, and concentrations of sulfentrazone in supernatants were measured. In the second experiment the kinetics of desorption was studied from the lyophilized complexes using tap water: 15 mL of tap water was added to the tubes containing 0.03 g of lyophilized complexes (obtained in adsorption experiments at the same micelle and clay concentrations as in the first experiment and at 68.9, 43, and 34.4 mmol kg^{-1} sulfentrazone added). The suspensions were centrifuged following 10 min and 2, 8, and 24 h of desorption, and the concentrations of sulfentrazone were measured.

Preparation of Formulations. ODTMA was stirred for 24 h with 200 mL of sulfentrazone solutions of 33, 50, and 80 mg L^{-1} in 250 mL centrifuge tubes; the final concentration of ODTMA was 2.5 mM. Then sulfentrazone−micelle solutions were combined with 0.4 g of montmorillonite. Tubes were kept at 25 ± 1 °C under continuous agitation for 24 h. Then the tubes were centrifuged for 20 min at 15000*g*, and concentrations of sulfentrazone in supernatants were measured. The supernatants were removed, and sulfentrazone−micelle−montmorillonite formulations were lyophilized.

Release of Sulfentrazone from Formulations to Soil. The release of sulfentrazone from organoclay and commercial formulations was measured in Rehovot sandy soil. Fifty grams of soil was placed in a funnel, the bottom of which was covered by Whatman no. 41 filters. The formulations were prepared from ODTMA−montmorillonite complexes (ODTMA, 2.5 mM; clay, 2 g L^{-1}; and 43 mmol kg^{-1} sulfentrazone added) and contained 1.6% of ai. The formulations were mixed with water, and the suspensions were transferred to the soil by using a syringe; then soil samples were covered by the Whatman no. 41 filters. The formulations contained 10 mg of ai per funnel. Soils were washed by tap water 10 times with 10 min intervals; the volume of one washing was 35 mL. Effluents of each washing were collected, and the concentrations of sulfentrazone were measured.

Sulfentrazone Analysis. For analysis, supernatants were passed through Teflon filters (ISI) of 0.2 μm pore diameter. Sulfentrazone was analyzed by HPLC (Merck Hitachi 6200) equipped with a diode array detector set at 220 nm. The column was a LiChrospher 100 RP-18 (5 μM), and the mobile phase was a water/acetonitrile mixture (1:1) with 0.65 mM trifluoroacetic acid at a flow rate of 1.0 mL min^{-1}.

Plant Bioassay. Tin columns, with an upper exposed surface of 100 cm^2 and 20 cm long, were filled with a sandy loam Rehovot soil. The column surfaces were sprayed with the sulfentrazone micelle−clay formulations or the commercial formulation at a rate of 700 g of ai/ha or with water (control). The micelle−clay formulations contained 1.6, 2.48, and 4% of ai. The columns were carefully irrigated with 500 m^3 of water/ha (a total of 500 mL per column); 50 mL was added every 10 min. This irrigation level (which was equivalent to 50 mm of rain) was selected to ensure water movement up to a 20 cm depth. Four columns of each treatment were sown with the test plant green foxtail (*S. viridis* L. cv. Beauvios). The plants were irrigated by minisprinklers with 30 m^3 of water/ha per day. After 25 days, the plants were harvested and weighed.

The percent of plant growth inhibition was calculated by comparing the fresh weight of plants in each column to the average fresh weight of the plants from the control columns.

Data Analysis. Statistical analysis was conducted by JMPIN Program (JMPIN, v. 4.0.4, SAS Institute Inc., Cary, NC) using multiple-range means comparison by the Tukey−Kramer HSD test ($\alpha = 0.05$).

RESULTS AND DISCUSSION

Sulfentrazone Adsorption—Desorption. Adsorption of sulfentrazone on ODTMA and BDMHDA micelle−clay complexes was very high: 99.2−99.8% was adsorbed for the concentrations of sulfetrazone added at 2.5 mM micelles and 2 g L^{-1} clay concentrations (**Table 1**); pH values of the supernatants were 8.2 ± 0.09. In contrast, adsorption of sulfentrazone on pure montmorillonite was insignificant—0.014% of the herbicide was adsorbed when added at 43 mmol kg^{-1}; pH values of the supernatants were 8.8 ± 0.07.

The adsorption of sulfentrazone depended on the micelles and clay concentrations during the preparation of the complex. The maximal adsorption of the herbicide and the minimal

Table 2. Adsorption of Sulfentrazone (SF) on ODTMA–Montmorillonite Complexes (SF Added at 43 mmol kg^{-1})

complex	SF adsorbed, mmol kg^{-1}	SF adsorbed, % from added	SF desorbed, mmol kg^{-1}	SF desorbed, % from adsorbed
ODTMA, 2.5 mM; clay, 2 g/L	42.7 ± 3.0	99.3	0.13 ± 0.01	0.3
ODTMA, 5 mM; clay, 2 g/L	33.8 ± 2.0	78.6	11.2 ± 0.67	33.1
ODTMA, 10 mM; clay, 2 g/L	30.2 ± 1.8	70.2	11.9 ± 0.78	39.4
ODTMA, 2.5 mM; clay, 5 g/L	34.9 ± 2.4	81.2	nd	nd
ODTMA, 2.5 mM; clay, 10 g/L	26.7 ± 1.34	62.1	nd	nd

[a] Not determined.

Table 3. Kinetics of Sulfentrazone (SF) Desorption from ODTMA–Montmorillonite–Herbicide Formulations in Tap Water

time of desorption	SF added, mmol kg^{-1}	SF adsorbed, mmol kg^{-1}	SF desorbed, mmol kg^{-1}	SF desorbed, % from adsorbed
10 min	34.4	34.3 ± 2.7	0.20 ± 0.01	0.58
2 h	34.4	34.3 ± 2.7	0.14 ± 0.01	0.41
8 h	34.4	34.3 ± 2.7	0.12 ± 0.01	0.35
24 h	34.4	34.3 ± 2.7	0.1 ± 0.002	0.29
10 min	43	42.7 ± 3.0	0.29 ± 0.02	0.68
2 h	43	42.7 ± 3.0	0.22 ± 0.02	0.52
8 h	43	42.7 ± 3.0	0.2 ± 0.01	0.47
24 h	43	42.7 ± 3.0	0.16 ± 0.01	0.38
10 min	68.9	68.7 ± 4.2	2.0 ± 0.11	2.9
2 h	68.9	68.7 ± 4.2	1.96 ± 0.12	2.9
8 h	68.9	68.7 ± 4.2	1.58 ± 0.13	2.3
24 h	68.9	68.7 ± 4.2	0.73 ± 0.06	1.1

desorption was obtained for 2.5 mM ODTMA (mostly micelles) and 2 g L^{-1} clay (**Table 2**). When the concentrations of surfactant increased at the same clay concentration, adsorption of sulfentrazone decreased and desorption increased. In this case sulfentrazone remained in the supernatant solution with non-adsorbed surfactant. When the surfactant was adsorbed on the clay in excessive amount, it also desorbed easily and carried the herbicide away from the surface to the solution. When the clay concentration increased at the same concentration of surfactant, the adsorption of sulfentrazone decreased. In this case ODTMA monomer adsorption on excess clay resulted in the decomposition of micelles to monomers; consequently, the adsorption of sulfentrazone on the monomer−clay complexes was lower than on the micelle−clay complexes as was previously found for sulfometuron (*9*).

Desorption of sulfentrazone in distilled water from a wet ODTMA−montmorillonite complex after 24 h was 0.3% for 42.7 mmol kg^{-1} adsorbed, when the concentration of the organoclay complex was 2 g L^{-1}. The study of the kinetics of sulfentrazone desorption from lyophilized complexes by tap water demonstrated that a maximal amount of less tightly bound herbicide desorbed during the first 10 min; then the desorbed amounts gradually decreased (**Table 3**). This effect can probably be explained by the changes in the surface of complexes under lyophilization and the gradual return to the initial state under rewetting, because the amounts of sulfentrazone desorbed from lyophilized and wet complexes were similar. The effect of tap water was similar to that of distilled water.

Release of Sulfentrazone from Organoclay Formulations in Soil. Release of sulfentrazone from ODTMA−montmorillonite formulations in funnels with a thin layer of soil was also small (**Figure 2**): after the first washing, 0.41% of the added sulfentrazone was released; after 10 washings, 2.6% of herbicide was released. For commercial formulations 85.4% of the added herbicide was released after the first washing,

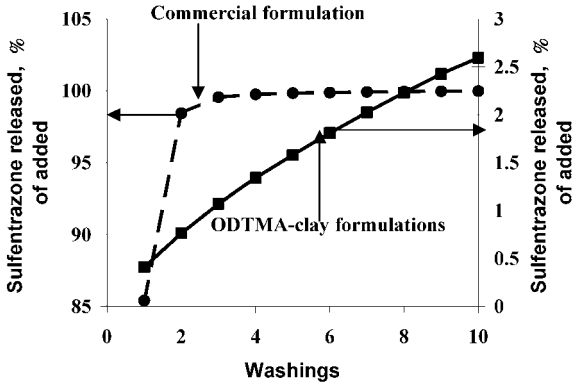

Figure 2. Percent release of sulfentrazone from commercial formulations (left ordinate) and from ODTMA–montmorillonite formulations (right ordinate).

Table 4. Changes in pH in Sulfentrazone–Surfactant Systems

system	pH
sulfentrazone, 50 mg L^{-1}	5.59 ± 0.06
ODTMA, 3.75 mM	5.48 ± 0.07
sulfentrazone, 50 mg L^{-1}, + ODTMA, 3.75 mM	4.39 ± 0.05
ODTMA, 0.1 mM	5.62 ± 0.06
sulfentrazone, 50 mg L^{-1}, + ODTMA, 0.1 mM	5.0 ± 0.07
BDMHDA, 3.75 mM	6.59 ± 0.07
sulfentrazone, 50 mg L^{-1}, + BDMHDA, 3.75 mM	4.27 ± 0.06
BDMHDA, 0.2 mM	6.24 ± 0.08
sulfentrazone, 50 mg L^{-1}, + BDMHDA, 0.2 mM	5.1 ± 0.07
HDTMA, 3.75 mM	6.53 ± 0.06
sulfentrazone, 50 mg L^{-1}, + HDTMA, 3.75 mM	4.30 ±0.05
HDTMA, 0.2 mM	6.49 ± 0.07
sulfentrazone, 50 mg L^{-1}, + HDTMA, 0.2 mM	5.55 ± 0.06

99.9% was released after 6 washings, and 100% was released after 10 washings.

Interactions of Sulfentrazone with the Organic Cations ODTMA, HDTMA, and BDMHDA: pH and Spectrum Measurements. For all three micelles the pH of 50 mg L^{-1} sulfentrazone solutions, containing 3.75 mM of organic cation in micelles, was much lower than the pH of 3.75 mM of the cation alone or that of a water solution containing 50 mg L^{-1} herbicide (**Table 4**). Hence, the interaction of sulfentrazone with the micelles resulted in deprotonation of the herbicide molecules. The calculated value of apparent pK_a of the herbicide−micelle solution was 4.7, that is, 2 units lower than the pK_a of sulfentrazone, which is 6.56.

The spectrum of a sulfentrazone solution in water, which was adjusted to pH 8.45 by 0.01 M NaOH, characterizes the anionic form of the molecules (**Figure 3**). This spectrum differs from the spectrum at pH 6.29 by the appearance of a peak at 262 nm. The molecules of sulfentrazone were transformed into anionic form due to interactions with micelles; this transformation was confirmed by the changes in the spectrum of sulfentrazone (**Figure 3**). A solution of sulfentrazone with 0.5 mM

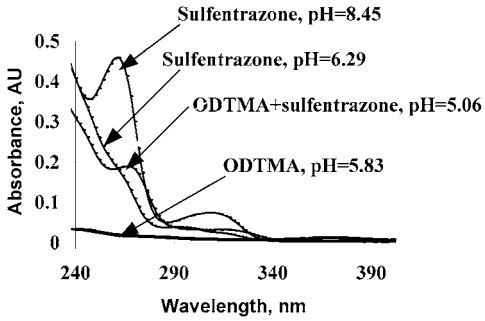

Figure 3. Spectra of sulfentrazone solutions (12.5 mg L^{-1}) at different pH values 0.5 mM ODTMA alone, and 0.5 mM ODTMA + sulfentrazone.

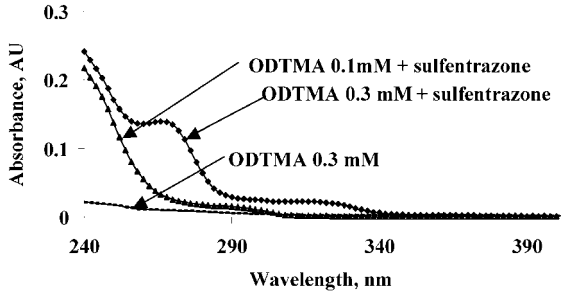

Figure 4. Effect of ODTMA micelles on the spectrum of sulfentrazone. Sulfentrazone concentration was 10 mg L^{-1}.

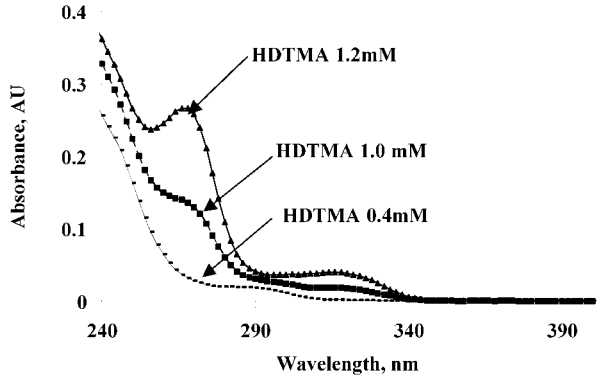

Figure 5. Effect of HDTMA micelles on sulfentrazone spectra. Sulfentrazone concentration was 12.5 mg L^{-1}.

ODTMA at pH 5.06, which is below the pK_a of the herbicide, exhibited a spectrum with a peak at 266 nm. The CMC of ODTMA is 0.3 mM; hence, ODTMA was largely present in solution in the form of micelles. The similarity of this spectrum to the spectrum of a sulfentrazone solution in water at pH 8.45 confirms the hypothesis about deprotonation of the molecules of sulfentrazone and stabilization of anions of the herbicide as a result of interactions of positively charged ODTMA micelle with sulfentrazone.

The reduction in the pH of the sulfentrazone−surfactant systems was lower when the cation concentration was below the CMC of the surfactants (**Table 4**): the CMC values of ODTMA, BDMHDA, and HDTMA are 0.3, 0.6, and 1 mM, respectively. The pH values of a sulfentrazone solution (12.5 mg L^{-1}) decreased gradually from 6.32 ± 0.06 to 5.0 ± 0.05 when HDTMA was added from 0.2 to 1.2 mM, indicating the growing intensity of sulfentrazone−surfactant interactions as the HDTMA concentration approached the CMC. Changes in sulfentrazone spectra at different concentrations of ODTMA and HDTMA are presented in **Figures 4** and **5**. For both cases the spectra of sulfentrazone exhibited peaks (266 nm for ODTMA and 268 nm for HDTMA) characterizing the anionic form of

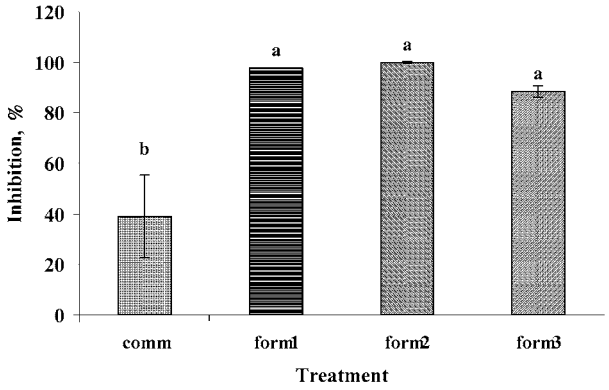

Figure 6. Growth inhibition of green foxtail in soil columns sprayed by commercial (comm.) and ODTMA–montmorillonite sulfentrazone formulations: form1, form2, and form3 contained 1.6, 2.48, and 4% of active ingredient, respectively. Letters identify statistically different results based on the Tukey–Kramer HSD test.

the herbicide when the concentration of surfactant equaled or exceeded the CMC.

We suggest that the strong binding between sulfentrazone and micelles is due to interactions of sulfentrazone, which is a weak acid, with micelles of cationic surfactant. The solutes localized in the micellar pseudophase are exposed to a microenvironment, which is dramatically different from water, because of a combination of a hydrophobic core and charged exterior. Combined electrostatic and hydrophobic effects induce the perturbation of the physicochemical properties of solutes (*13*−*15*). This is reflected by micelle-induced enhanced dissociation of sulfentrazone in the presence of micelles, stabilization of the anion of sulfentrazone, and formation of ionic pairs between the positively charged cations forming the micelle and the anionic herbicide:

$$SH + [M^+] \Leftrightarrow [S^- M^+] + H^+$$

SH is the neutral form of sulfentrazone molecule, M^+ is the positively charged cation of the ODTMA micelle, $[S^- M^+]$ is an ionic pair between the anion of sulfentrazone and the positively charged ODTMA in a micelle.

The surfactant micelles shift the acid−base equilibria of solutes; the magnitude of shifts in pK_a values is a function of the dielectric constant of micelles and their surface potential (*14*−*18*).

Our results indicate that the interaction of sulfentrazone molecules with micelles is stronger than with surfactant monomers. Higher hydrophobicity of the core of micelles than that of monomers leads to lower hydration of the micelle in comparison with that of monomers; hence, the interaction of the herbicide with a micelle and formation of ionic pairs is facilitated.

The micelles of cationic surfactants with incorporated anionic herbicide adsorbed on the clay. Adsorption of ODTMA on the clay can exceed the cation exchange capacity of montmorillonite, resulting in charge reversal of the clay (*19*, *20*), which was also modeled (*9*, *21*). The structural arrangement of ODTMA on the clay surface was suggested on the basis of XRD measurements: ODTMA formed pseudotrimolecular layers between the silicate layers and, in addition, micelles adsorbed on the external surfaces of montmorillonite (*9*).

Reduced Leaching from a Micelle—Clay Formulation: Bioassay Test. The results of soil column experiments are presented in **Figure 6**. The ODTMA−clay formulations of

sulfentrazone yielded almost complete inhibition of the growth of green foxtail, whereas only 40% growth inhibition was achieved by applying the commercial formulation (all formulations were applied at 700 g of ai/ha). The organoclay formulations retained the herbicide activity significantly better than the commercial formulation, due to low leaching of sulfentrazone from the formulations under conditions of irrigation common in the field. The bioassay test with the soil column, containing formulation 2 (2.48% ai), was repeated after 4 weeks. Still the formulation inhibited the growth of green foxtail by 90%. The results of soil column experiments are in agreement with the results of the experiment of sulfentrazone release from soil performed in funnels (**Figure 2**). Low release and low leaching of sulfentrazone were achieved by the strong ionic binding between sulfentrazone and micelles, which was confirmed by the pH and spectra measurements. Hence, the better herbicide activity of sulfentrazone when applied in micelle−clay formulations is a consequence of the design, which slowed the release of the herbicide from the formulations. High and strong adsorption and slow release of sulfentrazone from micelle−montmorillonite complexes enables the use of the micelle−clay system for herbicide formulations, which may reduce significantly herbicide leaching and maintain high herbicide activity. At the same time, a significant reduction in leaching amounts to a significant reduction in the contamination of ground water.

ABBREVIATIONS USED

ODTMA, octadecyltrimethylammonium; BDMHDA, benzyldimethylhexadecylammonium; HDTMA, hexadecyltrimethylammonium; CMC, critical micelle concentration.

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