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Surfactant Effects on the Affinity of Plant Cuticles with Organic Pollutants

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To precisely predict organics accumulation and crop safety, the affinity of fruit cuticles for naphthalene and 1-naphthol was investigated with the presence of three surfactants below and above the critical micelle concentration (CMC), including anionic sodium dodecylbenzene sulfonate (SDBS), cationic cetyltrimethylammonium bromide (CTMAB), and nonionic polyoxyethylene (20) sorbitan monolaurate (Tween 20). Tomato and apple cuticles with distinct compositions were selected. With increasing SDBS concentrations, apparent sorption coefficients (K_d*) of 1-naphthol by both cuticles first increased a bit and then decreased slightly. The K_d* of naphthalene by tomato cuticle is sensitive to SDBS concentration with a sharp increase and then decrease, whereas SDBS has little effect on naphthalene K_d* by apple cuticle. For CTMAB with lower CMC, the naphthalene K_d* decreased more quickly. Tween 20 seems to be ineffective on naphthalene sorption by both cuticles. Nevertheless, the intrinsic sorption coefficients (K_d) were almost promoted by the coexisting surfactants, resulting from the cuticle-sorbed surfactant's plasticizing effect.

KEYWORDS: Plant cuticle; surfactant; sorption; organic pollutant; plasticizing effect; enhancement solubilization

INTRODUCTION

Plant cuticle is not only an important route for the uptake of airborne pollutants into plants but also acts as a good reservoir for persistent organic pollutants (*1*−*5*). Several studies have demonstrated that plant cuticles exhibit high sorption capabilities for hydrophobic organic contaminants (HOCs) (*6*−*14*). Plant cuticle is a heterogeneous membrane, consisting of extractable lipids (waxes), polymeric lipids (cutin and cutan), and polysaccharides (*10*, *11*). However, cutin and cutan biopolymers are identified as the dominant sorbents for HOCs due to their hydrophobic nature and the presence of polar sites in their condensed domains (*1*, *9*, *10*, *13*, *14*). Their high sorption capability may be seriously suppressed and even inhibited by the cuticular waxes deposited within and on the surface of the polyester matrix because of their partially crystalline nature (*9*−*11*). Removal of waxes from bulk plant cuticles promotes their sorption capability (*6*, *9*−*11*) and leads to an increase in the permeability by several orders of magnitude (*15*, *16*).

As a determinant penetration barrier of plant cuticles, wax plays a crucial role in preventing the plant's water loss and environmental pollution. Moreover, the transporting-limiting barrier restricts the performance of foliar-applied agrochemicals molecules such as pesticides, fruit chemical thinning, and growth regulators (*3*, *15*, *17*). To enhance the efficacy of foliar-applied agrochemicals, surfactants are widely used in spray solution to increase active ingredient solubility, to improve wetting of the plant cuticle, and to increase cuticular penetration (*17*). Around 230,000 tonnes of surfactants is used annually in agrochemical products, with a formulation typically containing 1−10% of one or more surfactants (*18*). Surfactant, as a plasticizer, softens the crystalline waxes in cuticle and thus increases the mobility of the agrochemicals across the cuticular membrane (*3*, *16*, *19*). As reported, nonionic surfactant (Triton X-100) effectively enhances the penetration performance of benzyladenine (BA) and 2-(1-naphthyl)acetic acid (NAA) in isolated tomato cuticle, but has little effect on the sorption behavior until above the critical micelle concentration (CMC) of surfactant (*17*, *20*). However, the effect of surfactant on the affinity of plant cuticle with HOCs, which is prevailing in the environment, has not been well understood.

With the presence of surfactant, the sorption behavior of plant cuticle becomes very complex. Derived from similar studies (*21*−*23*), surfactant demonstrates two opposite effects on the cuticle sorption behavior: (i) surfactant solutions decrease the distribution of organic contaminant onto the cuticle by increasing the solute aqueous solubility, that is, a negative effect; (ii) surfactants increase the sorption capability by softening of cuticular wax (i.e., plasticizing effect) or by forming a new partition phase for the cuticle-sorbed surfactant, that is, a positive effect. The apparent effects of surfactants on sorption depend on the balance of the two opposite effects, which are dominated by the compositional characteristics of plant cuticles, surfactant type and concentration, and the solute's properties (*3*, *23*, *24*).

The main objective of this study is to evaluate the surfactant effects on the sorption of organic contaminants by plant cuticle for precise prediction of HOC accumulation and crop

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safety. Apple and tomato cuticles were used for their distinct compositions. Naphthalene and 1-naphthol were selected as a pair of nonpolar and polar sorbates with similar structures and distinct properties. Sodium dodecylbenzene sulfonate (SDBS), cetyltrimethylammonium bromide (CTMAB), and polyoxyethylene (20) sorbitan monolaurate (Tween 20) were chosen, respectively, as representative anionic, cationic, and nonionic surfactants.

MATERIALS AND METHODS

Plant Cuticle Isolation. Apple and tomato cuticle sheets were manually peeled from the freshly ripe fruits and boiled in water for 1 h, and then the pulp was removed manually as much as possible. After that, the bulk cuticle sheets were treated with a solution of oxalic acid (4 g/L) and ammonium oxalate (16 g/L) at 90 °C for 24 h and washed with deionized distilled water to remove any residual fruit pulp materials and the used chemicals. This procedure yielded the bulk cuticle fractions, that is, apple cuticle (AC) and tomato cuticle (TC). Isolated fractions were dried, ground, and sieved (< 0.18 mm) before analysis and sorption experiments. Apple cuticle consists of 44.7% waxes, 34.6% cutin, 13.2% polysaccharide, and 7.5% cutan, whereas tomato cuticle contains 6.5% waxes, 69.5% cutin, and 24% polysaccharide (*10*).

Solubility Enhancement Experiment. Surfactants and organic compounds of analytical grade were all purchased from Shanghai Chemical Co. and used without further treatment. Selected properties of all compounds are listed in **Table 1**. Batch experiments were performed in duplicate to determine the solubility enhancement of naphthalene and 1-naphthol by surfactants. Surfactant solutions below and above the CMC were placed in 8 mL vials sealed with aluminum foil-lined Teflon screw caps, and the solutes were subsequently added to the vials in amounts more than required to saturate the solution. The samples (surfactant solution with solutes) and controls (surfactant solution without solutes) were placed on a rotating shaker and agitated in the dark for 3 days at 25 ± 0.5 °C to reach apparent solubilization equilibrium and then centrifuged at 4000 rpm for 15 min. An aliquot amount of the supernatant was removed and diluted with deionized distilled water for analysis. The determined supernatant concentrations were the apparent solubility (S_w*) of organic pollutant in the surfactant solutions. Aqueous naphthalene and 1-naphthol concentrations were quantified by a UV-2550 spectrophotometer (Shimadzu) at wavelengths of 284, and 332 nm, respectively. To further enhance detection sensitivity, the analyzed solution was basified to pH 12 with 0.1 M NaOH solution to ensure 1-naphthol present in dissociation state [pK_a = 9.34 (*9*)]. The selected surfactants, that is, SDBS, CTMAB, and Tween 20, have little absorbance at the detection wavelength to ensure the analysis results. Solubility enhancement experiments of 1-naphthol by CTMAB and Tween 20 were not conducted because of the chemical reaction (i.e., forming precipitates) between the solute and these two surfactants. Sorption experiments of 1-naphthol in CTMAB and Tween 20 solutions were also excluded for the same reason.

Sorption Experiment. Sorption isotherms of the isolated apple cuticle (AC) and tomato cuticle (TC) with or without the presence of surfactants were obtained using a batch equilibration technique. In brief, initial concentrations ranged from 0.28 to 28 mg/L for naphthalene and from 10 to 600 mg/L for 1-naphthol. The background solution included 0.005 mol/L NaCl to maintain a constant ionic strength with a given surfactant solution. The initial concentrations of surfactants (X_0) in the background solution were from 0 to 2061 mg/L for SDBS, from 0 to 500 mg/L for CTMAB, and from 0 to 200 mg/L for Tween 20, ranging from below the CMC to 2−3 times the CMC. The solid-to-solution ratios were adjusted to achieve 20−80% sorption of organic compounds at apparent equilibrium. Each isotherm consisted of 8−10 concentration points; each point, including the blank, was run in duplicate. The 8 mL vials were sealed with aluminum foil-lined Teflon screw caps and then placed on a rotating shaker and agitated in the dark for 3 days at 25 ± 0.5 °C. The solution was separated from the remaining solids by centrifugation at 4000 rpm for 15 min. An aliquot amount of the supernatant was removed and diluted with deionized distilled water for further determination. Because of minimal sorption by the vials and no biodegradation, the amount sorbed by the cuticle sorbents was calculated by mass difference of a sorbate (i.e., naphthalene or 1-naphthol) in aqueous concentration between nominal aqueous concentration without sorbent and with sorbent.

Sorption behavior of SDBS on apple and tomato cuticles was investigated by the same batch equilibration technique, such as background solution of 0.005 mol/L NaCl, initial concentration of SDBS ranging from 0 to 2000 mg/L, and equilibration time of 3 days. Aqueous SDBS concentration was determined by a UV-2550 spectrophotometer (Shimadzu) at the wavelength of 224 nm. The amount sorbed by cuticle sorbents was calculated by mass difference of SDBS in the solution. However, sorption experiments of CTMAB and Tween 20 onto both cuticles were excluded from this study for their detected limits by UV-2550 spectrophotometer.

Data Analysis. The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e{*}^N$, where Q is the amount sorbed per unit weight of sorbent, mg/kg; C_e* is the apparent equilibrium concentration of sorbate in the surfactant solution, mg/L, which is obtained by experimental determination; K_f is the Freundlich capacity coefficient, (mg/kg)/(mg/L)^N; and N (dimensionless) describes the isotherm curvature. The solute apparent sorption coefficients ($K_d{*} = Q/C_e{*}$) were calculated from the slope of the linear isotherms of naphthalene and 1-naphthol in the presence of surfactants. The intrinsic sorption coefficient was defined as $K_d = Q/C_e$, where C_e is the equilibrium concentration of sorbate in the water.

RESULTS AND DISCUSSION

Solubility Enhancement of Organic Contaminants by Surfactant Solutions. On the basis of the solubility enhancement curves (selected curve shown in **Figure 1**), the monomer−water partition coefficient (K_{mn}) and micelle−water partition coefficient (K_{mc}) of naphthalene and 1-naphthol with the surfactants were calculated by using the equation (*25*)

$$S_w{}^*/S_w = 1 + X_{mn}K_{mn} + X_{mc}K_{mc} \qquad (1)$$

where S_w* is the apparent water solubility of solutes at the surfactant concentration of X and S_w is the intrinsic water solubility of solute without surfactants; X_{mn} and X_{mc} are the equilibrium concentrations of the surfactant as monomer and micelle ($X_{mn} = X$, $X_{mc} = 0$, if $X \le$ CMC; K_{mn} = CMC, $K_{mc} = X -$ CMC, if $X >$ CMC), respectively. The CMC, X_{mn}, and X_{mc} values for naphthalene with three surfactant solutions (SDBS, CTMAB, and Tween 20) and for 1-naphthol with SDBS are presented in **Table 1**.

The solubility enhancement effects by surfactant solutions are closely related to the properties of solutes and surfactants. The K_{mn} values of naphthalene for three surfactants are much lower than the K_{mc} values, whereas for 1-naphthol, K_{mn} with SDBS is similar to K_{mn}. For SDBS, K_{mc} of naphthalene (481 L/mg) is higher than that of 1-naphthol (292 L/mg), whereas K_{mn} of 1-naphthol (227 L/mg) is much higher than that of naphthalene (62 L/mg). These observations indicate that naphthalene has a greater tendency in partitioning into the surfactant micellar phase, whereas 1-naphthol is favorable to stay in water and surfactant monomer phase for its more hydrophilic nature in

Table 1. Selected Properties of the Surfactants in this Study and the Critical Micelle Concentration (CMC) of Surfactants and Partition Coefficients of Surfactant Monomers (K_{mn}) and Micelles (K_{mc})

surfactant	formula	MW[a]	compound	K_{mn}(L/mg)[b]	K_{mc}(L/mg)[c]	CMC (mg/L)
SDBS	$CH_3(CH_2)_{11}C_6H_4SO_3Na$	348.5	naphthalene	62.1	481	783
			1-naphthol	227	292	719
CTMAB	$C_{16}H_{33}(CH_3)_3NBr$	364.4	naphthalene	277	3212	151
Tween 20	$C_{58}H_{113}O_{26}$	1226.5	naphthalene	419	1517	93

[a] MW, molecular weight, g/mol. [b] K_{mn} is a partition coefficient between surfactant monomers and water. [c] K_{mc} is a partition coefficient between surfactant micelles and water.

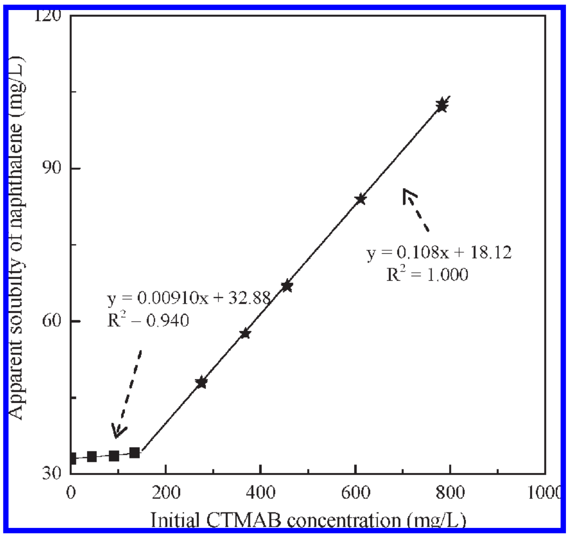

Figure 1. Solubility enhancement curve of naphthalene in the presence of CTMAB.

comparison with naphthalene. For naphthalene, K_{mn} and K_{mc} values of CTMAB and Tween 20 are much higher than those of SDBS (see **Table 1**), suggesting that micellar phases of CTMAB and Tween 20 are more hydrophobic than that of SDBS. The CMC value follows the order SDBS (~700 mg/L) > CTMAB (151 mg/g) > Tween 20 (93 mg/L). These properties (K_{mn}, K_{mc}, and CMC) of surfactants should play a regulating role in the surfactant effects on the affinity of plant cuticle with HOCs.

Influence of Surfactants on the Sorption of HOCs by Apple and Tomato Cuticles. Sorption isotherms of naphthalene and 1-naphthol by AC and TC with the presence of anionic SDBS, cationic CTMAB, and nonionic Tween 20 are demonstrated, respectively, in **Figures 2**, **3**, and **4**. The Freundlich model regression parameters of isotherms, the calculated apparent sorption coefficients (K_d*), and intrinsic sorption coefficients (K_d) are listed in **Tables 2** and **3**. Intrinsic sorption coefficients (K_d) of plant cuticle were gained through the equation

$$K_d = Q/C_e = K_d^* \times C_e^*/C_e = K_d^* \times (1 + X_{mn}K_{mn} + X_{mc}K_{mc}) \quad (2)$$

where the meanings of the used parameter were all as mentioned above; K_{mn} and K_{mc} were obtained by the solubility enhancement experiments; X_{mn} and X_{mc} were calculated according to the initial surfactant concentration (X_0). The ratios of K_d^*/K_{d0} and K_d/K_{d0} were calculated to evaluate the surfactant effects, where K_{d0} is the sorption coefficient of plant cuticles without the presence of surfactants. The K_d^*/K_{d0} ratio indicates the apparent effect of the coexisting surfactant on the sorption performance of plant cuticles, consisting of the negative effect of surfactant solution by solubility enhancement and the positive effect of the cuticle-sorbed surfactant by plasticizing. The K_d/K_{d0} ratio represents the change of the intrinsic nature of plant cuticles, caused to the cuticle-sorbed surfactant via forming a new partition medium or softening the cuticular waxes. The effects of surfactants on the sorption of organic contaminants to plant cuticles are assumed to be related with the type of surfactant, the initial concentration (X_0) of a given surfactant, the properties of organic contaminants, and the nature of cuticles.

Effects of SDBS on the Affinity of Apple and Tomato Cuticles. One of the noticeable effects of SDBS on the sorption of both cuticles is the variations of the linearity of sorption isotherms. Without the presence of SDBS, sorption isotherms of naphthalene by both tomato and apple cuticles were practically linear (Freundlich $N \approx 1$), indicating the main sorption mechanism is partition. For 1-naphthol, the nonlinearity of sorption isotherms of both cuticles increased with the presence of SDBS, as Freundlich N decreased (except for tomato cuticle, with SDBS at 305 mg/L). However, for naphthalene, this effect is not obvious. The change of N values for naphthalene to tomato cuticle is quite slight, whereas the change of N on apple cuticle seems a little irregular (**Table 2**). The increasing nonlinearity of sorption behavior for 1-naphthol in the presence of SDBS may be attributed to the plasticizing effect of the cuticle-sorbed SDBS, which can decrease the tortuosity and viscosity of cuticular waxes and increase the porosity of the cuticle to enhance the accessibility of plant cuticle to sorbate and offer more adsorption sites and specific interaction domains on the outer surface (*8*, *16*). Nevertheless, sorption isotherms of naphthalene by tomato cuticle were all practically linear with the presence of SDBS (Freundlich $N \approx 1$, **Table 2**), showing that the major sorption mechanism was still partition. Hence, the nonlinear sorption of 1-naphthol in the presence of SDBS is supposed to be that cuticle-sorbed SDBS induces the specific interaction (such as hydrogen binding) between the cuticle sorbent and 1-naphthol involving the −OH group.

The other important effect of SDBS is on sorption capacity (K_d* and K_d) of tomato and apple cuticle. For 1-naphthol, the apparent sorption coefficients (K_d*) for both cuticles first increase slightly and then decrease a little with further increase of SDBS (**Figure 2** and **Table 2**). When the initial SDBS concentration is only 58 mg/L, significantly less than the CMC (~700 mg/L), K_d* values of tomato and apple cuticle increase by 28 and 15%, respectively. Interestingly, the intrinsic sorption coefficients (K_d) of tomato and apple cuticle increase by 29 and 16%, respectively, which approach the enhancement of K_d*. These observations indicate that the slight sorption enhancement is mainly attributed to the cuticle-sorbed surfactants that increase the partition medium for 1-naphthol and decrease the barrier properties of the waxes by softening its crystalline nature (plasticizing effect),

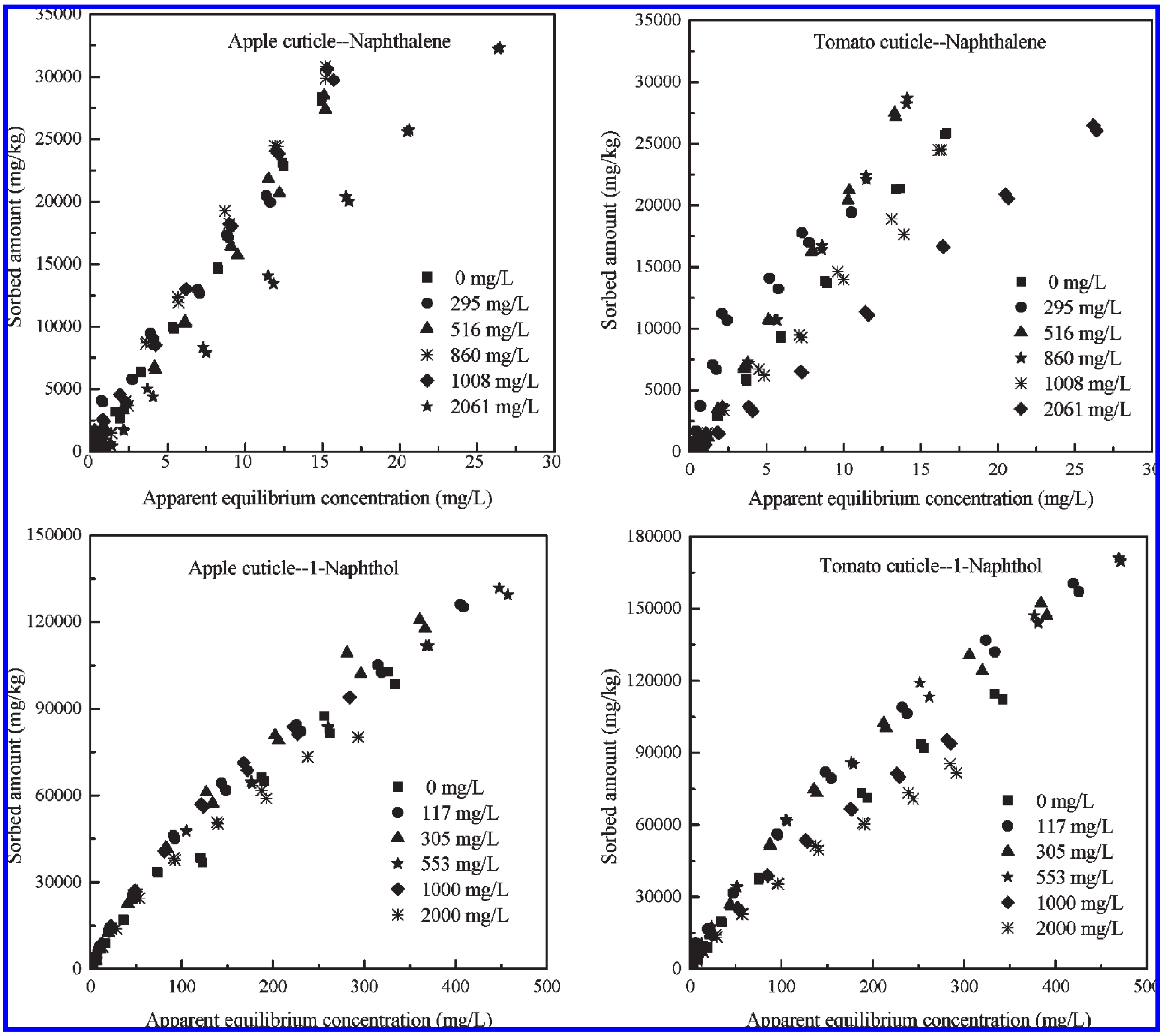

Figure 2. Sorption isotherms of 1-naphthol and naphthalene by apple and tomato cuticles in the presence of SDBS.

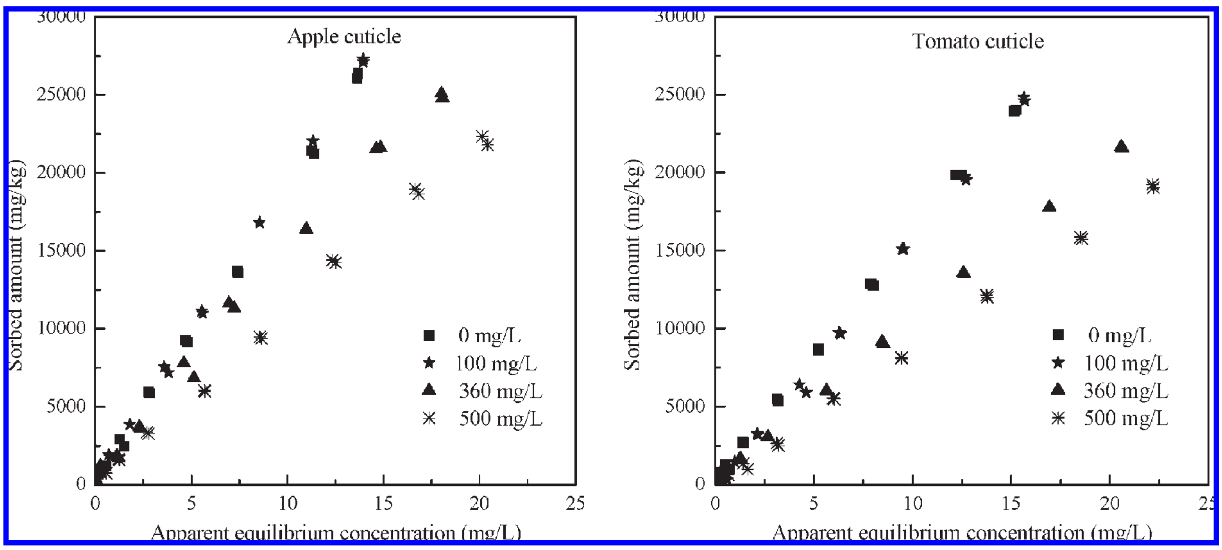

Figure 3. Sorption isotherms of naphthalene by apple and tomato cuticles in the presence of CTMAB.

whereas the solubilization effect of SDBS could be neglected at such low concentration. However, with further increase of SDBS concentration, the contribution of solubilization effect became more important, which would diminish the partition amount of solutes onto plant cuticles, especially when SDBS concentration was above the CMC. On the other

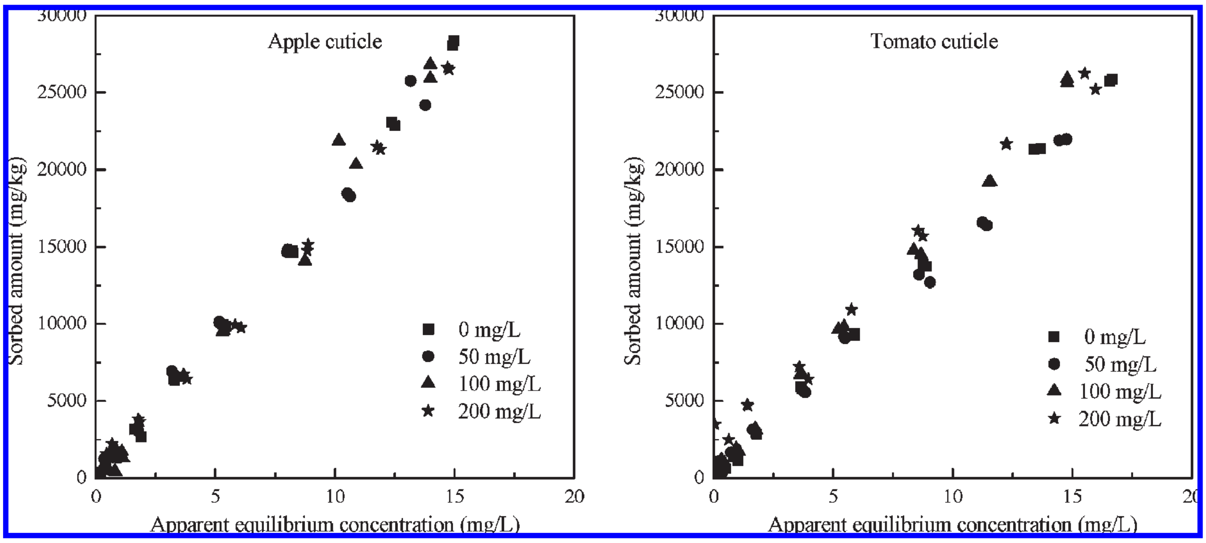

Figure 4. Sorption isotherms of naphthalene by apple and tomato cuticles in the presence of Tween 20.

Table 2. Sorption Coefficients and Freundlich Model Parameters of 1-Naphthol and Naphthalene with Apple and Tomato Cuticle in the Presence of SDBS

sorbent	SDBS (mg/L)	$\log K_f$[a]	N[a]	Freundlich r^2	K_d*[b] (mL/g)	linear r^2	K_d[c] (mL/g)	K_d^*/K_{d0}[d]	K_d/K_{d0}[d]
				1-Naphthol					
apple cuticle	0	2.422 ± 0.125	1.069 ± 0.069	0.941	308 ± 9	0.986	308	1.00	1.00
	58	3.132 ± 0.016	0.779 ± 0.008	0.998	354 ± 11	0.984	359	1.15	1.16
	117	3.107 ± 0.017	0.772 ± 0.009	0.998	307 ± 11	0.978	316	1.00	1.02
	305	3.094 ± 0.020	0.784 ± 0.011	0.997	334 ± 12	0.978	357	1.08	1.16
	553	3.083 ± 0.018	0.771 ± 0.009	0.998	283 ± 8	0.985	319	0.92	1.03
	1000	3.082 ± 0.021	0.788 ± 0.012	0.997	337 ± 14	0.970	420	1.09	1.36
	2000	2.946 ± 0.029	0.812 ± 0.015	0.994	279 ± 11	0.974	428	0.90	1.39
tomato cuticle	0	2.892 ± 0.032	0.866 ± 0.018	0.994	339 ± 9	0.989	339	1.00	1.00
	58	3.336 ± 0.012	0.727 ± 0.006	0.999	433 ± 14	0.981	439	1.28	1.29
	117	3.382 ± 0.035	0.691 ± 0.017	0.991	376 ± 13	0.978	386	1.11	1.14
	305	2.885 ± 0.041	0.908 ± 0.022	0.991	392 ± 14	0.976	419	1.16	1.24
	553	3.140 ± 0.023	0.795 ± 0.012	0.997	363 ± 13	0.977	408	1.07	1.20
	1000	2.971 ± 0.021	0.828 ± 0.011	0.997	334 ± 9	0.986	416	0.98	1.23
	2000	2.901 ± 0.020	0.829 ± 0.011	0.997	288 ± 8	0.986	442	0.85	1.30
				Naphthalene					
apple cuticle	0	3.244 ± 0.015	1.018 ± 0.021	0.994	1868 ± 17	0.999	1868	1.00	1.00
	56	3.524 ± 0.013	0.764 ± 0.018	0.993	1810 ± 64	0.978	1865	0.97	1.00
	295	3.421 ± 0.043	0.837 ± 0.066	0.921	1777 ± 63	0.978	2062	0.95	1.10
	516	2.954 ± 0.057	1.323 ± 0.079	0.950	1836 ± 32	0.995	2350	0.98	1.26
	860	2.944 ± 0.078	1.419 ± 0.105	0.934	2076 ± 44	0.992	2253	1.11	1.21
	1008	3.528 ± 0.030	0.736 ± 0.038	0.958	1936 ± 23	0.997	2239	1.04	1.20
	2061	2.812 ± 0.054	1.246 ± 0.058	0.971	1258 ± 15	0.998	2091	0.67	1.12
tomato cuticle	0	3.151 ± 0.025	1.050 ± 0.033	0.984	1564 ± 6	1.000	1564	1.00	1.00
	56	3.148 ± 0.029	1.095 ± 0.038	0.986	1811 ± 52	0.985	1817	1.16	1.16
	295	3.482 ± 0.050	0.974 ± 0.077	0.908	4771 ± 256	0.968	4858	3.05	3.11
	516	3.181 ± 0.026	1.134 ± 0.036	0.986	2086 ± 23	0.998	2152	1.33	1.38
	860	3.243 ± 0.020	1.040 ± 0.028	0.990	2007 ± 18	0.999	2178	1.28	1.39
	1008	3.113 ± 0.019	1.045 ± 0.025	0.991	1445 ± 32	0.991	1671	0.92	1.07
	2061	2.731 ± 0.053	1.236 ± 0.058	0.966	1016 ± 8	0.999	1689	0.65	1.08

[a] The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e^{*N}$, where Q is the amount sorbed per unit weight of sorbent, mg/kg; C_e* is the apparent equilibrium concentration, mg/L; K_f [(mg/kg)/(mg/L)^N] is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature. r^2 is a regression coefficient. [b] K_d* is the apparent sorption coefficient ($K_d^* = Q/C_e^*$), calculated from the slope of linear isotherms in the presence of surfactants, where C_e* is the equilibrium concentration of sorbate in the presence of surfactants. [c] K_d is the intrinsic sorption coefficient $K_d = Q/C_e$, where C_e is the equilibrium concentration of sorbate in the water. [d] K_{d0} is the sorption coefficient of plant cuticle without surfactants.

hand, positive effects such as plasticizing effect would also promote, accounting for the enhancing amount of cuticle-sorbed SDBS during the increase of SDBS concentration (*24*). As mentioned above, effect of surfactant depends on the balance of the two opposite effects. Apparently, there was no distinctive change in the sorption capability (K_d*) of 1-naphthol during the increase of SDBS concentration. Even when the initial concentration of SDBS is as high

Table 3. Sorption Coefficients and Freundlich Model Parameters of Naphthalene with Apple and Tomato Cuticle in the Presence of CTMAB and Tween 20

sorbent	surfactant (mg/L)	$\log K_f$[a]	N[a]	Freundlich r^2	$K_d{}^{*}$[b] (mL/g)	linear r^2	K_d[c] (mL/g)	$K_d{}^{*}/K_{d0}$[d]	K_d/K_{d0}
				CTMAB					
apple cuticle	0	3.244 ± 0.015	1.018 ± 0.021	0.994	1868 ± 17	0.999	1868	1.00	1.00
	100	3.360 ± 0.008	0.927 ± 0.011	0.998	1931 ± 10	1.000	1985	1.03	1.06
	360	3.344 ± 0.034	0.811 ± 0.041	0.966	1402 ± 22	0.995	2401	0.75	1.29
	500	3.117 ± 0.011	0.932 ± 0.012	0.998	1096 ± 11	0.998	2369	0.59	1.27
tomato cuticle	0	3.151 ± 0.025	1.050 ± 0.033	0.984	1564 ± 6	1.000	1564	1.00	1.00
	100	3.166 ± 0.012	1.019 ± 0.015	0.997	1581 ± 15	0.999	1625	1.01	1.04
	360	3.219 ± 0.018	0.806 ± 0.020	0.990	1039 ± 5	1.000	1779	0.66	1.14
	500	3.070 ± 0.031	0.857 ± 0.035	0.974	858 ± 6	0.999	1855	0.55	1.19
				Tween 20					
apple cuticle	0	3.244 ± 0.015	1.018 ± 0.021	0.994	1868 ± 17	0.999	1868	1	1
	50	3.344 ± 0.027	0.906 ± 0.036	0.980	1801 ± 37	0.993	1839	0.96	0.98
	100	3.268 ± 0.015	0.991 ± 0.020	0.997	1918 ± 46	0.99	2014	1.03	1.08
	200	3.322 ± 0.031	0.921 ± 0.042	0.967	1760 ± 25	0.996	2113	0.94	1.13
tomato cuticle	0	3.151 ± 0.025	1.050 ± 0.033	0.984	1564 ± 6	1.000	1564	1	1
	50	3.349 ± 0.020	0.805 ± 0.026	0.984	1460 ± 21	0.996	1490	0.93	0.95
	100	3.330 ± 0.019	0.894 ± 0.026	0.988	1694 ± 18	0.998	1780	1.08	1.14
	200	3.420 ± 0.053	0.825 ± 0.066	0.929	1584 ± 45	0.986	1902	1.01	1.22

[a] The Freundlich parameters (K_f and N) were calculated using the logarithmic form of the equation $Q = K_f C_e{}^{*N}$, where Q is the amount sorbed per unit weight of sorbent, mg/kg; $C_e{}^{*}$ is the apparent equilibrium concentration, mg/L; K_f [(mg/kg)/(mg/L)^N] is the Freundlich capacity coefficient; and N (dimensionless) describes the isotherm curvature. r^2 is a regression coefficient. [b] $K_d{}^{*}$ is the apparent sorption coefficient ($K_d{}^{*} = Q/C_e{}^{*}$), calculated from the slope of linear isotherms in the presence of surfactants, where $C_e{}^{*}$ is the equilibrium concentration of sorbate in the presence of surfactants. [c] K_d is the intrinsic sorption coefficient $K_d = Q/C_e$, where C_e is the equilibrium concentration of sorbate in the water. [d] K_{d0} is the sorption coefficient of plant cuticle without surfactants.

as 2000 mg/L, $K_d{}^{*}$ decreases only 15 and 10% for tomato and apple cuticle, respectively. In such high concentration, many free aqueous surfactant micelles appeared, tending to decrease sorption significantly by increasing the apparent aqueous solubility of 1-naphthol. Actually, the sorption capacity ($K_d{}^{*}$) decreases only a little due to the obvious enhancement of the intrinsic sorption coefficients (K_d) of plant cuticles (K_d/K_{d0} = 1.30 vs 1.39, for tomato vs apple cuticle, see **Table 2**), counteracting the solubilization effect of SDBS.

For naphthalene, the effect of SDBS on the sorption behavior of tomato cuticle is much different from that of apple cuticle. In a wide range (X_0, 0−1008 mg/L), SDBS has little effect on the apparent sorption coefficient of naphthalene ($K_d{}^{*}/K_{d0} \approx 1$, see **Table 2**) by apple cuticle. However, $K_d{}^{*}$ of naphthalene by tomato cuticle is quite sensitive to the concentration of SDBS. Briefly, the $K_d{}^{*}$ values showed an obvious increase and then a decrease as the SDBS concentration increased. $K_d{}^{*}$ of naphthalene by tomato cuticle increased sharply ($K_d{}^{*}/K_{d0}$ = 3.05) as the initial concentration of SDBS was only 295 mg/L and then quickly decreased ($K_d{}^{*}/K_{d0}$ = 1.33) when SDBS was 516 mg/L (see **Table 2**). Similarly, when the initial concentration of SDBS was up to 2061 mg/L, the $K_d{}^{*}$ values of naphthalene for both cuticles decreased significantly, that is, 33% versus 35% for apple versus tomato cuticle, which were much higher than those of 1-naphthol.

The sharp decrease of $K_d{}^{*}$ for naphthalene compared with 1-naphthol is attributed to the higher solubilization effect of naphthalene for its more hydrophobic nature (K_{ow} = 1950) in comparison with 1-naphthol (K_{ow} = 501). However, the solubilization effect difference ($1 + X_{mn}K_{mn} + X_{mn}K_{mc}$) of the two solutes is actually too small to generate this huge difference. The main reason is that the intrinsic sorption coefficients (K_d) of 1-naphthol increase more than those of naphthalene (K_d/K_{d0} = 1.30−1.39 vs 1.08−1.12 for 1-naphthol vs naphthalene) when SDBS was at 2000 mg/L, attributed to the fact that SDBS could enhance the specific interaction between 1-naphthol and cuticles.

The distinct effect of SDBS on the sorption processes of apple and tomato cuticles is due to their different composition characteristics. Sorption of SDBS to the two cuticles is presented in **Figure 5**, demonstrating that the SDBS sorption by tomato cuticle is higher than that by apple cuticle. Apple cuticle membrane is a harder surface for surfactant than that of tomato cuticle, which is attributed to the fact that apple cuticle has more waxes (44.7 wt %) than tomato cuticle (6.5 wt %) and less cutin (34.6%) than tomato cuticle (69.5%)(*10*). Cutin components exhibit a liquid-like state due to low glass-transition temperature [$T_g \approx -40$ °C (*10*)]. Cuticular waxes have been extensively studied as a composite transport barrier system, consisting of two distinct phase, that is, amorphous and crystalline domains. Sorption and diffusion of nonwax molecules is supposed to take place in the amorphous phase and liquid-like zone (*3*, *15*). The differential scanning calorimeter (DSC) data for apple cuticular fractions demonstrated that the presence of waxes increase the cuticle's T_g, implying that waxes would be viewed as an antiplasticizer to cuticle (*10*). Thus, this antiplasticizer negates the surfactant's plasticizing effect, and the SDBS's plasticizing effect is not strong enough to soften the waxes in the apple cuticle, resulting in minor changes in sorption capacity with a large range of SDBS concentrations.

Effects of CTMAB and Tween 20 on the Affinity of Apple and Tomato Cuticles. Sorption isotherms of naphthalene with CTMAB and Tween 20 show more nonlinearity than those without the presence of surfactants (**Table 3**), which is similar to the effect of SDBS on 1-naphthol sorption. Different from 1-naphthol, adsorption is employed to explain the increasing sorption nonlinearity for naphthalene in the presence of surfactants, because specific interaction between naphthalene (nonpolar) and cuticle can be neglected. Reasonably, the plasticizing effect of the cuticle-sorbed

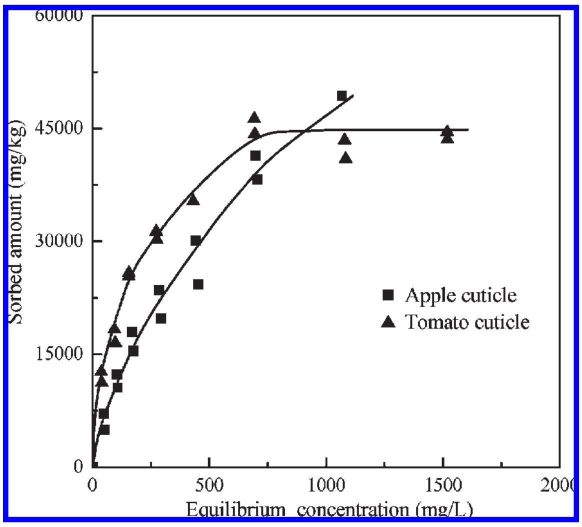

Figure 5. Sorption isotherms of SDBS by apple and tomato cuticles.

CTMAB/Tween 20 enhances the accessibility of cuticles to naphthalene and offers more adsorption sites on the outer surface (*8*, *16*).

Effects of CTMAB on the sorption of naphthalene by both cuticles are quite similar. Apparent sorption coefficients (K_d*) increased a little when the initial CTMAB concentration was 100 mg/L (K_d^*/K_{d0} = 1.01 vs 1.04 for tomato vs apple cuticle, see **Table 3**) and then decreased with further increase of CTMAB concentration. When the initial CTMAB concentration was 500 mg/L, K_d* of naphthalene decreased by 41 and 45% for apple and tomato cuticle, respectively. However, when the initial SDBS concentration was 516 mg/L, the K_d* values of naphthalene decreased by 2% and increased by 33% for apple and tomato cuticle, respectively. This great difference is attributed to the different properties of CTMAB and SDBS (see **Table 1**). The solubilization effect of CTMAB is much higher than that of SDBS at the same concentration due to the lower CMC value (151 vs 783 mg/L for CTMAB vs SDBS) and much higher surfactant−water partition coefficients (i.e., K_{mn} and K_{mc}) for CTMAB. With the increase of the initial CTMAB concentration, the intrinsic sorption coefficients (K_d) for both cuticles increase, indicating that cuticle-sorbed surfactants are effective in enhancing the sorption capability of plant cuticles despite the solubilization effect of the aqueous surfactant monomers and micelles. Tween 20 has little effect on the apparent sorption coefficient (K_d*) of naphthalene for both cuticles in the selected concentration (0−200 mg/L). However, the intrinsic sorption coefficients (K_d) for both cuticles increase with the increase of initial Tween 20 concentration, after a little decrease at 50 mg/L, further proving that cuticle-sorbed surfactants are effective accelerators in organic pollutant accumulation by plant cuticles.

In summary, influences of surfactant on the affinity of plant cuticles via alteration of their sorption mechanism and capabilities are dominated by the type and concentration of surfactant, the nature of cuticles, and the chemical properties of pollutants. Regardless of different influences of surfactant on the apparent sorption coefficient (K_d*), the intrinsic sorption coefficients (K_d) for fruit cuticles should be promoted with the coexisting surfactant in the agrochemical spray due to the plasticizing effects. This indicates that surfactant serves as an accelerator for organic pollutant accumulation onto plant cuticle, potentially threatening crop safety and then human health via the terrestrial food web.

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