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Studies on Octylphenoxy Surfactants[1]

III. SORPTION OF TRITON X-100 BY ISOLATED TOMATO FRUIT CUTICLES

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ABSTRACT

Sorption characteristics of a polyethoxy (EO) derivative of octylphenol (OP) were determined for enzymically isolated mature tomato (*Lycopersicon esculentum* Mill. *cv* Sprinter) fruit cuticles at 25°C. Sorption was followed using ^{14}C-labeled OP + 9.5EO (Triton X-100). Solution pH (2.2–6.2) did not affect surfactant sorption by tomato fruit cuticular membranes (CM). Surfactant concentration (0.001–1.0%, w/v) had a marked impact on sorption. Sorption equilibrium was reached in 24 hours for OP + 9.5EO concentrations below the critical micelle concentration (CMC), whereas 72 to 120 hours were required to reach equilibrium with concentrations greater than the CMC. Regardless of when equilibrium was attained, initial sorption of OP + 9.5EO occurred rapidly. Partition coefficients (*K*) of approximately 300 were obtained at pre-CMC concentrations, whereas at the highest concentration (1.0%), *K* values were approximately 15- to 20-fold lower. Sorption was higher for dewaxed CM (DCM) than for CM. At OP + 9.5EO concentrations below the CMC, the amount (millimoles per kilogram) sorbed by CM and DCM increased sharply as the CMC was reached. After an apparent plateau in the amount sorbed at concentrations immediately below and above the CMC, sorption by CM and DCM increased dramatically with OP + 9.5EO concentrations greater than the CMC (0.5 and 1.0%). In contrast, sorption of OP + 5EO (Triton X-45) by CM and DCM differed from one another at relatively high (0.5 and 1.0%) concentrations, where sorption by DCM increased with increasing concentration, but plateaued for the CM. Sorption of OP + 9.5EO was also related to CM concentration, with an inverse relationship existing between sorption and CM at concentrations less than 3.33 milligrams per milliliter.

Surfactants are amphipathic molecules which alter energy relationships at interfaces, thereby reducing surface (gas-liquid) and interfacial (liquid-liquid and liquid-solid) tensions (17). This characteristic is the primary basis for their widespread use in agrochemical formulations and in spray application (6). Numerous data have been generated on the effects of surfactants on foliar absorption of biologically active compounds (1). Although surfactants have been reported to increase, have no effect, or decrease foliar absorption of active ingredients (25, 29), little emphasis has been focused on the role of surfactants in this process or on their absorption and metabolism (28).

The length of the EO[3] chain of an OP-based nonionic surfactant may markedly affect surfactant-enhanced penetration (26, 27). Direct measurements show that penetration of active ingredients into leaf tissue decreased in the presence of an OP surfactant as the EO chain length was increased (27). There was no evidence that these surfactants enhanced penetration of the active ingredient by disrupting the fine-structure of the epicuticular wax on corn leaves (26). Detailed information on the mechanism of surfactant-enhanced penetration or on the nature of surfactant interaction with the CM is limited.

The CM is the primary barrier to the penetration of foliar-applied compounds (2). It is a nonliving, lipophilic, heterogeneous membrane that covers all aerial plant organs (2). Cutin, a polyester of long chain hydroxylated fatty acids, constitutes the matrix of the CM, and is impregnated and covered on the outer morphological surface with SCL (9). For a review of cuticle chemistry and composition, see Ref. (9).

Since cuticular penetration is a prerequisite for foliar absorption and surfactants may markedly modify cuticular penetration, an understanding of the nature and degree of surfactant interaction with the CM may provide a basis for improving the efficacy of agrochemicals. To elucidate these effects, we have focused on two primary components of foliar absorption, namely (a) surfactant effects on the interaction of a selected growth regulator with the CM (23) and (b) surfactant interaction with the CM.

Initially, our studies focused on characterizing sorption of surfactants by CM. This was an appropriate starting point in examining surfactant/CM interaction, since sorption is an important component of membrane (cuticle) permeability to foliar-applied compounds (*e.g.* active ingredient, surfactant) (12). The results of our study on two polyethoxy derivatives of OP are the subject of this report.

MATERIALS AND METHODS

Plant Material/Cuticle Isolation. Locally field-grown mature tomato (*Lycopersicon esculentum* Mill. *cv* Sprinter) fruit free of visual defects were selected for reasons previously discussed (24). Discs, 20 mm in diameter, were punched from the fruit and incubated at 35 ± 1°C in an aqueous mixture of pectinase (4%, w/v; ICN Nutritional Biochemicals), cellulase (0.4%, w/v; Sigma), and NaN_3 (1 mM) in 50 mM sodium citrate buffer at pH 4.0 (14). After 2 d and two changes of enzyme solution, the cuticle was separated from the outer cell walls of the epidermis. Adhering cellular debris was removed with a jet of distilled water and the cuticles were air-dried and stored at 23°C until used. Cuticles isolated by this procedure will be referred to as CM. CM extracted for 3 d with at least 10 changes of chloroform:methanol

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[3] Abbreviations: EO, ethylene oxide; OP, octylphenol; *K*, partition coefficient; CM, cuticular membrane; DCM, dewaxed cuticular membrane; SCL, soluble cuticular lipids; CMC, critical micelle concentration.

(1:1, v/v) at 50°C to remove SCL will be termed DCM.

Surfactants. 4-(1,1,3,3-tetramethyl)Butylphenol (OP) condensed with either 5 (OP + 5EO) or 9.5 (OP + 9.5EO) mol EO was used. Trade names (registered trademarks, Rohm and Haas Co.) for these two nonionic surfactants are Triton X-45 and Triton X-100, respectively. These surfactants were a mixture of oligomers, where the EO number represents an average value and the ethoxymer mol ratio distribution follows a Poisson distribution. Selected properties relevant to foliar penetration have been previously reported (26).

Radioactive ring-labeled [U-^{14}C]OP + 9.5EO (28.1 MBq·g^{-1}) was used as a tracer for OP + 9.5EO. The radiolabel distribution among the oligomers was not known. Radio-TLC, using silica gel (0.25 mm) with water saturated methyl ethyl ketone as running solvent (18), demonstrated that OP + 9.5EO was a mixture of ethoxymers.

Measurement of Sorption. Sorption was measured for the systems CM/water and DCM/water using the procedure of Riederer and Schönherr (16). Distilled H_2O (pH 5.8 ± 0.5), containing 1 mM NaN_3 to prevent bacterial and fungal growth, was used in all experiments unless noted otherwise. Citrate buffer (20 mM), containing 1 mM NaN_3, was used for the pH-controlled experiments.

Random samples (25–50) of CM or DCM discs were selected and sliced into small (approximately 1 × 10 mm) strips (preliminary results showed no significant effect of strip size). Weighed subsamples (approximately 5 mg, except where noted) were placed in 5 ml glass vials and 1.5 ml of ^{14}C-labeled OP + 9.5EO (approximately 48 μM) was pipetted into each vial. Total initial surfactant concentration for all experiments was 0.1%, except for the concentration experiments using 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0% (w/v). The vials were closed with Teflon-lined screw caps and shaken horizontally in a water bath at 25 ± 0.5°C.

At designated time intervals, 100 μl aliquots were removed and radioactivity determined by liquid scintillation spectrometry (LKB-Wallac LSC, model 1211). Scintillation cocktail was composed of 1,4-dioxane (10 ml), containing 100 g naphthalene and 5 g diphenyloxazole (PPO) L^{-1}. All samples were counted to a 2 σ error of approximately 1.0% and corrected for background. Since quenching was constant throughout the course of these experiments, all calculations were performed with CPM values.

The amount of ^{14}C-labeled surfactant sorbed by CM or DCM was determined by subtracting the quantity of ^{14}C-label in the dosing solution from the amount originally present (10). Radioassay of solutions in control vials, containing only ^{14}C-labeled OP + 9.5EO surfactant (total concentration 0.1%), indicated no significant loss (less than 2.0%) in ^{14}C-label concentration over the experimental periods. Therefore, the assumption was made that the decrease in ^{14}C-label in the bulk solution represented that sorbed by the CM or DCM. When appropriate, K values were calculated using the following equation:

$$K = \frac{\text{^{14}C-label in cuticle phase [Bq·kg^{-1}]}}{\text{^{14}C-label in aqueous phase [Bq·kg^{-1}]}}. \quad (1)$$

There was a rapid decrease (up to 25%) of radioactivity in control vials from solutions at low concentrations (less than 0.1%), presumably due to adsorption to the vials. This loss was inversely proportional to concentration and an equilibrium was achieved within 24 h (WE Shafer, MJ Bukovac, unpublished data), demonstrating that vial leakage did not occur. Therefore, we assumed that the ^{14}C-label loss was independent of the cuticle and the sorbate concentration was corrected for this loss in making sorption calculations. If loss was not independent of the presence of the CM, our sorption values (and K values) would be underestimated because sorption by the CM would decrease surfactant concentration in the bulk solution, thereby decreasing the surfactant available for sorption to the glass vials.

Since no ^{14}C-labeled OP + 5EO was available, a spectrophotometric assay was used. Radiolabel companion studies were compared with this technique for OP + 9.5EO. This allowed us to assess the accuracy of the UV technique by comparing sorption values for OP + 9.5EO obtained with the UV and radiotracer methods.

Maximum UV absorbance for both OP + 5EO and OP + 9.5EO, in 30% ethanol (to overcome low OP + 5EO water solubility for the spectrophotometric assay), occurred at 276 nm (3). Standard curves for both surfactants over the concentration range of 100 to 700 μM were obtained. The linear regression equations ($r > 0.99$) relating A and concentration (C, μmol·L^{-1}) were: $\hat{A} = -0.076 + 0.00161(C)$ and $\hat{A} = -0.014 + 0.00134(C)$ for OP + 5EO and OP + 9.5EO, respectively.

The procedure for determining sorption was as previously described, except that for the time-course measurements with OP + 5EO, approximately 13.5 mg of CM or DCM and 4.0 ml of dosing solution was used. The initial OP + 5EO concentration was 0.1%, except for the concentration experiment using 0.05, 0.1, 0.5, and 1.0% (w/v). Accurate, reproducible quantification of OP + 5EO at initial treatment concentrations below 0.05% was not possible in our system. Aliquots (500 μl) were taken, diluted with ethanol (final concentration 30% ethanol) and absorbance measured (Gilford Spectrophotometer, model 2600).

Preliminary experiments indicated that the two surfactants were extracting small amounts of a constituent(s) from the cuticles, particularly from the CM, absorbing at 276 nm. This interfered with measurement of the surfactant concentration remaining in the bulk solution. A correction factor was used for adjusting for this interference based on analysis of vials containing cuticle and 0.1% (w/v) nonanol (C_{9-11} linear primary alcohol) condensed with 10 mol EO. The assumption was made that OP + 5EO or OP + 9.5EO extracted similar quantities of UV absorbing constituents as the C_{9-11} + 10EO surfactant. Corrections were made for both OP surfactants at 0.1%, and for OP + 5EO at the other concentrations used. In addition to correction for UV interference, corrections were made for the rapid loss (up to 15%) of OP + 5EO observed in control vials, as described earlier. This loss was presumably due to adsorption and/or low water solubility.

Both the ^{14}C-label and spectrophotometric techniques for determining OP + 9.5EO sorption yielded results not significantly different (Table I). Similar results were obtained for pepper fruit cuticles (data not shown). Based on these results, it was concluded that ^{14}C-labeled OP + 9.5EO was an effective tracer for nonradioactive OP + 9.5EO and that the spectrophotometric technique was reliable. However, there was generally greater variability in the data obtained using the spectrophotometric method (Table I) and lower sensitivity and accuracy in measuring OP + 5EO sorption at low concentration.

No attempt was made to correct initial dosing surfactant (OP + 5EO or OP + 9.5EO) concentration in anticipation of surfactant loss. Therefore, for the data presented herein, the effective concentrations of the dosing solution may be less than initially prepared.

Table I. *A Comparison of Quantity of OP + 9.5EO (0.1%, w/v) Sorbed by Isolated Tomato Fruit CM as Determined by UV Absorbance and Radiochemical (^{14}C) Methods*

The amount sorbed (72 h) was determined at pH 5.8 and 25°C for tomato fruit CM and DCM. Data are means of five replications with their respective confidence intervals (P = 0.05).

Cuticular Membrane	UV Method	^{14}C Method
	mmol·kg^{-1}	
CM	36 ± 10	45 ± 8
DCM	86 ± 8	89 ± 6

Statistics. All experiments were made with five replications per treatment. For the time-course measurements, the same five replicates were monitored over the time periods indicated. The results are presented as means with their respective 95% confidence intervals.

RESULTS

Time-Course of OP + 9.5EO Sorption. Time-course of OP + 9.5EO sorption ($mmol \cdot kg^{-1}$) by tomato fruit CM is shown in Figure 1. At initial concentrations below the CMC (CMC = 0.019%), sorption equilibrium was achieved by 24 h. For solutions where the initial concentration exceeded the CMC, sorption equilibrium was reached by 72 to 120 h. Greater amounts of OP + 9.5EO were sorbed with increasing bulk solution concentration. Sorption of OP + 9.5EO occurred rapidly and extraction of SCL from CM resulted in significantly greater sorption (Fig. 2).

Effect of OP + 9.5EO Concentration. The relationship between K values and surfactant concentration ($mol \cdot kg^{-1}$) for OP + 9.5EO and tomato fruit CM and DCM at sorption equilibrium (264 h) is illustrated in Figure 3. K values for both CM and DCM decreased dramatically as the CMC was approached and/or exceeded. Maximum K values were obtained for both CM and DCM at surfactant concentrations of 38 and 33 μM, respectively (initial concentration of 0.005%). Greater differences in sorption between CM and DCM occurred at surfactant concentrations below the CMC. At the highest concentration examined (initial concentration of 1.0%), differences between K values for CM and DCM were not significantly different. The equilibrium surfactant concentrations were 15.1 and 15.0 mM for the CM and DCM, respectively, representing a 15- to 20-fold decrease in K values over the OP + 9.5EO concentration range examined.

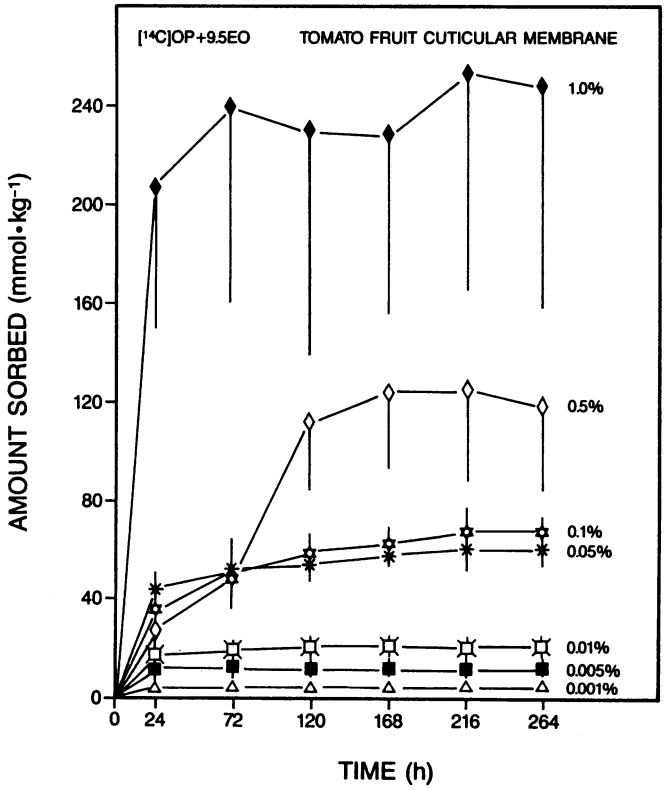

FIG. 1. Time-course of OP + 9.5EO sorption by tomato fruit CM. Concentrations (w/v) shown represent initial values. Assay conditions: pH 5.8, 25°C. Means of five replications and their respective confidence intervals (P = 0.05). Where confidence intervals are not shown, they were smaller than data symbol.

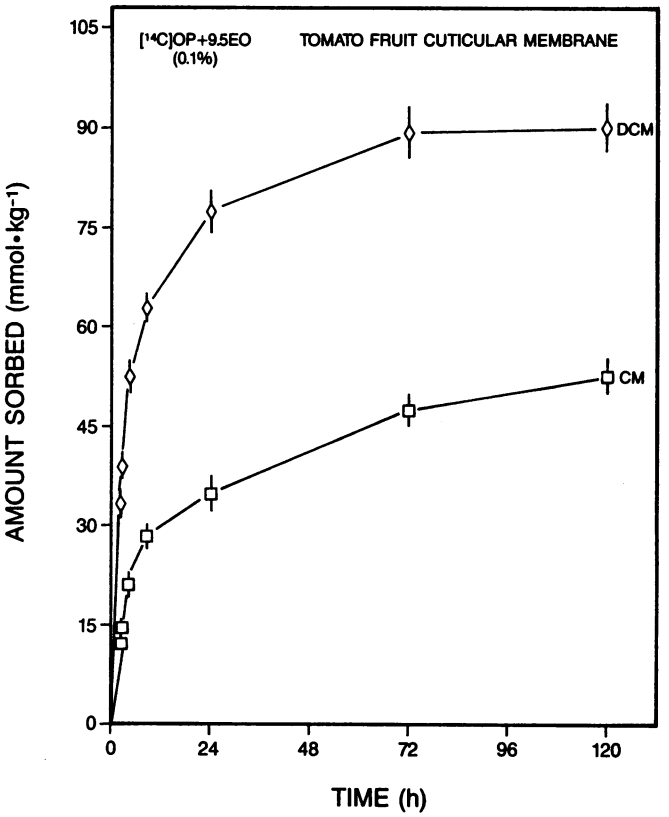

FIG. 2. Short-term time-course of OP + 9.5EO sorption by tomato fruit CM and DCM. Assay conditions: initial concentration of 0.1% (w/v), pH 5.8, 25°C. Means of five replications and their respective confidence intervals (P = 0.05). Where confidence intervals are not shown, they were smaller than data symbol.

Although K values for OP + 9.5EO in tomato fruit CM and DCM decreased with increasing concentration (Fig. 3), the total amount ($mol \cdot kg^{-1}$) of surfactant sorbed increased with increasing concentration (Fig. 4). Below and near the CMC, there was a rapid increase in the amount sorbed with increasing concentration. At concentrations above the CMC, sorption plateaued but increased again with a further increase in concentration (Fig. 4).

The amount of tomato CM present per ml of surfactant solution had a marked effect on OP + 9.5EO sorption (Fig. 5). Sorption was inversely related to amount of CM over the range of 0.33 to 2.67 $mg \cdot ml^{-1}$ and independent over the range of 3.33 to 5.33 $mg \cdot ml^{-1}$.

Effect of pH on OP + 9.5EO Sorption. There was no significant effect of pH (2.2–6.2) on sorption ($mmol \cdot kg^{-1}$) of OP + 9.5EO by tomato CM (Table II).

Time-Course of OP + 5EO Sorption. Time-course of OP + 5EO (0.1%) sorption by tomato CM and DCM was rapid at first, but equilibrium was not obtained even after 432 h (data not shown). Removal of SCL led to significantly greater sorption, but the time-course curve was similar as for CM. It was not established if sorption equilibrium was attained with 0.05, 0.5, and 1.0% OP + 5EO concentrations at 432 h.

Effect of OP + 5EO Concentration. The relationship between sorption ($mmol \cdot kg^{-1}$) and surfactant concentration for OP + 5EO and tomato fruit CM at 432 h is shown in Figure 6. At lower initial OP + 5EO concentrations (0.05 and 0.1%), sorption by CM and DCM increased rapidly with increasing concentration, with DCM values being slightly greater than for the CM. However, for the two highest initial OP + 5EO concentrations (0.5 and 1.0%), sorption by CM appeared to be independent of

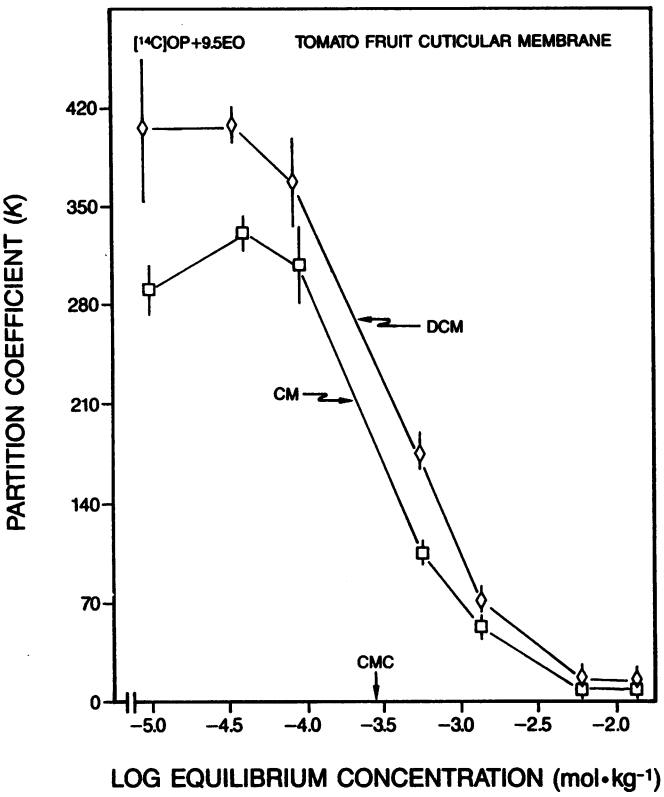

FIG. 3. Concentration-dependence of sorption (K values) of OP + 9.5EO by tomato fruit CM and DCM. Assay conditions: 264 h, pH 5.8, 25°C. Means of five replications and their respective confidence intervals (P = 0.05).

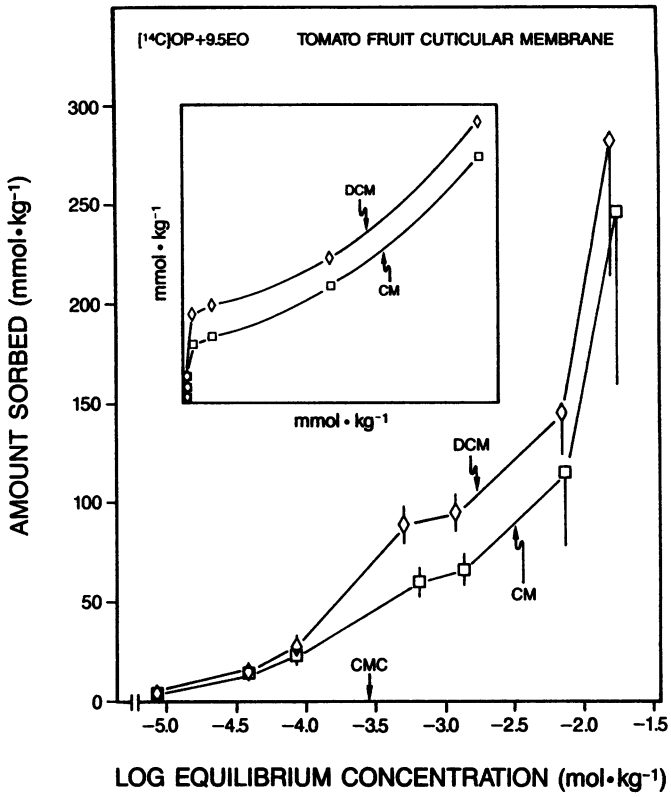

FIG. 4. Sorption isotherms for OP + 9.5EO and tomato fruit CM and DCM. Assay conditions: initial concentrations 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, and 1.0% (w/v), 264 h, pH 5.8, 25°C. Data points represent means of five replications. Where confidence intervals are not shown, they were smaller than the data symbol. Inset depicts isotherm on arithmetic scale.

concentration while sorption by DCM increased dramatically with increasing concentration.

DISCUSSION

Our data demonstrate that the nonionic surfactant OP + 9.5EO is rapidly sorbed by plant cuticles. The degree of sorption was related to various solution characteristics and the presence of waxes in the cuticle.

Solution pH was not a significant factor in sorption of OP + 9.5EO by tomato CM (Table II). Since tomato CM possess an isoelectric point of about pH 3.0 (20), possible changes in the cuticle relative to pH did not significantly affect sorption of OP + 9.5EO, and the absence of a pH effect on this nonionic surfactant was expected.

Sorption of OP + 9.5EO by tomato CM and DCM occurred rapidly (Fig. 2) and was dramatically influenced by sorbate and sorbent (CM) concentration (Figs. 1, 3, 4, 5). Sorption equilibrium was achieved more rapidly (24 h) with OP + 9.5EO concentrations below the CMC (CMC = 0.019%) than at concentrations above the CMC (72–120 h) (Fig. 1). The initial rapid sorption was most likely due to adsorption to the surface while the slow increase at higher (post-CMC) concentrations may be related to (a) increased accessibility of new sites within the cutin matrix and/or (b) changes in the ethoxymer distribution between the bulk solution and CM/DCM imposed by the presence of micelles.

Sorption of OP + 9.5EO increased with increasing bulk solution concentration over a thousand-fold range (Fig. 4). Initially, sorption increased rapidly with an increase in sorbate concentration, then at a decreasing rate followed by a third phase characterized by increased sorption with an increase in sorbate concentration (Fig. 4, inset). Although the plateau region is not well defined, the first region of the curve is typical of the Langmuir type. Here, the initial curve implies that as more sites become occupied it becomes increasingly more difficult to occupy additional sites. The upper portion of the curve showing increased sorption may be attributed to availability of new sorption sites and/or multilayer formation or sorption of micelles.

Some insight into the general sorption characteristics of OP + 9.5EO by CM and DCM may be gained by considering the chemical composition of surfactant solutions. Trogus *et al.* (30) suggested that surfactant solutions containing more than one ethoxymer may display unique sorption behavior because some of the ethoxymers possess greater tendencies to associate with lipophilic solids (*e.g.* cuticles) and/or to form micelles than other ethoxymers. As surfactant solution concentration increases, mol ratios of the various ethoxymers in monomeric and micellar forms continue to change. In the presence of CM or DCM, both micelles and cuticle could compete for the monomeric species. It seems reasonable that complex concentration-dependent interactions between the various ethoxymers and CM or DCM would occur in our system.

Further, Trogus *et al.* (30) suggested that a reduction in sorbent (cuticle) concentration would increase surfactant adsorption, apparently due to the delicate balance between the amount of each ethoxymer adsorbed and the concentration of sorbent present. Our data offered evidence of this inverse relationship (Fig. 5) and suggests that surfactant sorption by CM and DCM was dependent on multiple interactive processes.

The mechanism of sorption of the monomeric species of OP + 9.5EO by CM and DCM was not defined. Several mechanisms (*e.g.* ionic interactions, hydrogen bonding, van der Waals forces) of nonionic and/or ionic surfactant adsorption to various sor-

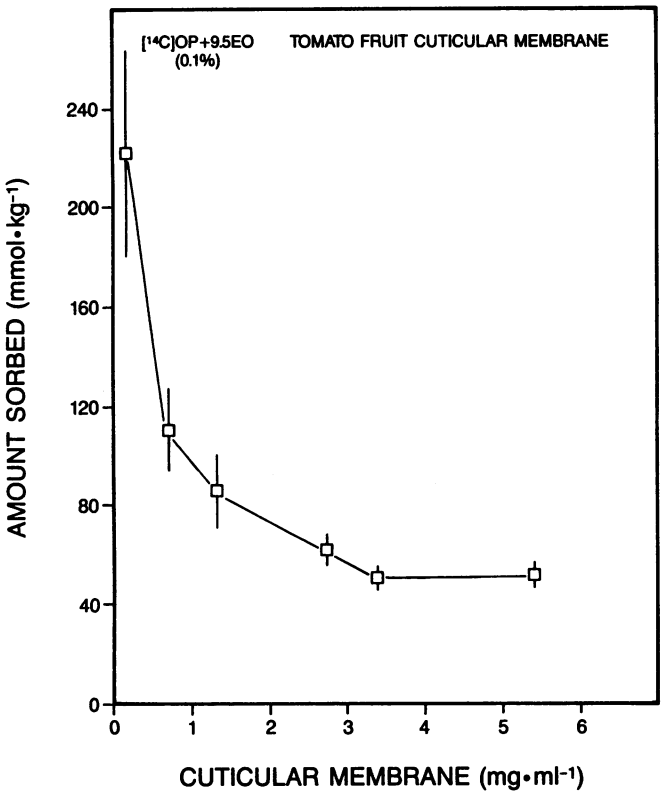

FIG. 5. Effect of sorbent concentration (tomato fruit CM) on sorption of OP + 9.5EO. Assay conditions: initial concentration of 0.1% (w/v), 120 h, pH 5.8, 25°C. Means of five replications and their respective confidence intervals (P = 0.05).

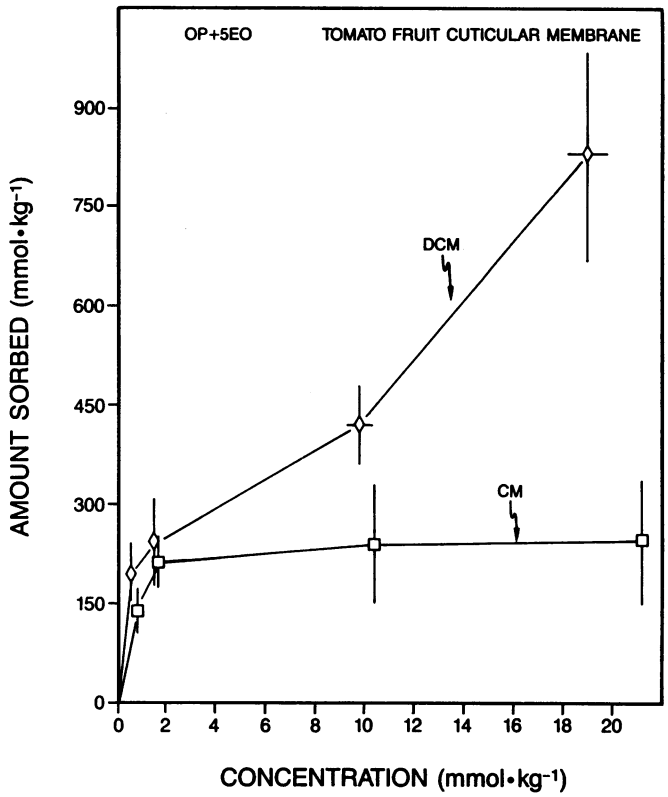

FIG. 6. Sorption isotherms for OP + 5EO by tomato fruit CM and DCM. Assay conditions: initial concentrations 0.05, 0.1, 0.5, and 1.0 (w/v), 432 h, pH 5.8, 25°C. Means of five replications and their respective confidence intervals (P = 0.05).

Table II. *Sorption (mmol·kg^{-1}) of OP + 9.5EO (0.1%, w/v) by Tomato Fruit CM as a Function of pH*

Amounts sorbed (264 h) were determined at 25°C. Data are means of five replications with their respective confidence intervals (P = 0.05).

pH	Quantity Sorbed
	mmol·kg^{-1}
2.2	47 ± 3
3.2	48 ± 4
4.2	45 ± 3
5.2	47 ± 4
6.2	45 ± 4

bents (*e.g.* silica, clay, graphite) have been described (1, 17). Given the chemistry of both OP surfactants and the CM, it is likely that hydrogen bonding was common to our system.

At surfactant concentrations above the CMC, sorption by CM and DCM was concentration dependent. This suggests that micelles may participate in surfactant sorption. A similar observation has been made with a nonionic surfactant on calcium carbonate (11). The nature of enhanced sorption at high concentrations in our system remains to be defined. In some systems (7), nonionic surfactants may form bilayers on silica when the concentration exceeds the CMC. Also, some evidence suggests that charged surfactants form admicelles (adsorbed micelles) on heterogenic surfaces (8). Although our system differed from those described, some insight into surfactant sorption by CM and DCM, at post-CMC concentrations, may be provided by these observations. At this point, we have not attempted to distinguish between adsorbed and absorbed surfactant or the involvement of micelles. This remains the focus of future studies.

Extraction of SCL consistently increased sorption of the OP surfactants, the effect being more pronounced at higher concentrations (Figs. 2, 4, 6). The SCL are present within the CM as a highly ordered layer (9) and on the outer morphological surface as crystalline and/or amorphous deposits (5, 9). Because of their highly ordered structure, they may be less sorptive than the cutin matrix and may cover potential sorption sites on or within the CM (13, 19, 22).

Removal of SCL appeared to have a greater impact on OP + 5EO sorption than on OP + 9.5EO sorption (Figs. 4, 6). The amounts of OP + 9.5EO sorbed by CM and DCM, as a function of concentration, were generally parallel to one another. For OP + 5EO, however, the amounts sorbed by DCM, compared to CM values, were dramatically greater at relatively high concentrations. Whether this is related to increased penetration of the cutin matrix by the smaller OP + 5EO molecule (average mol wt = 426), in contrast to OP + 9.5EO (average mol wt = 628), remains to be resolved. It is also interesting to note that sorption of OP + 5EO was greater than the sorption of OP + 9.5EO for either the CM or DCM at an initial concentration of 0.1%. Decreasing adsoprtion of surfactants by graphite (Graphon) with increasing size of the hydrophilic head group has been observed (4). It should be emphasized, however, that while sorption equilibrium was achieved for OP + 9.5EO in these studies, equilibrium for OP + 5EO was not reached (0.1%), even after 432 h (23).

In terms of surfactant/active ingredient/cuticle interactions, the orientation of adsorbed surfactant molecules with respect to the cuticular surface may be of importance. Ottewill and Walker (15) found that nonionic surfactant molecules were oriented vertically on polystyrene lattices. If OP surfactant molecules assumed a similar orientation as a monolayer on the CM or DCM, the hydrophilic moiety would be oriented farthest away from the CM or DCM surface. This orientation would impart on the CM or DCM a relatively more polar chemical environ-

ment. If multiple layers of surfactant molecules were adsorbed by the CM or DCM, then the overall surface chemistry would depend on complex solution/sorbed molecule/CM interactions. The prevailing chemical environment on the cuticular surface may then influence the sorption and subsequent penetration of an active ingredient through the plant cuticle.

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