Studies on Octylphenoxy Surfactants. 8. Effects of Ethylene Oxide Chain Length on Sorption of 2-(1-Naphthyl)acetic Acid by Isolated Tomato Fruit Cuticles†

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The effects of eight polyethoxy (EO) derivatives of octylphenol (OP) with 3 (OP + 3EO), 5 (OP + 5EO), 7.5 (OP + 7.5EO), 9.5 (OP + 9.5EO), 12.5 (OP + 12.5EO), 16 (OP + 16EO), 30 (OP + 30EO), and 40 (OP + 40EO) ethyleneoxy groups on sorption of 2-(1-naphthyl)acetic acid (NAA) by cuticles enzymatically isolated from mature tomato (*Lycopersicon esculentum* Mill. cv. Sprinter) and pepper (*Capsicum annuum* L.) fruits were studied at pH 3.2 and 25 °C. The time to reach NAA sorption equilibrium by tomato fruit cuticular membranes (CM) and dewaxed CM (DCM) was not affected by EO chain length (0.1% w/v). Sorption equilibrium for pepper fruit CM and DCM was not reached by 432 h, including control (no surfactant) treatments. In general, surfactants at 0.1% or 1.0% (w/v) concentration suppressed NAA sorption by tomato and pepper fruit CM and DCM, and this suppression was inversely related to EO chain length. An exception to this suppression/EO chain length relationship was observed with OP + 5EO and OP + 7.5EO, where a marked increase in NAA sorption by tomato fruit CM was observed at 0.1%. This enhancement of NAA sorption was not observed with tomato fruit cuticles after the removal of cuticular waxes. Pretreatment of tomato fruit CM with octylphenoxy surfactants (0.1%) did not cause significant changes in NAA sorption.

INTRODUCTION

Recently, considerable attention has been focused on the relationship(s) between surfactant chemistry and foliar absorption of active ingredients. Studies have focused on surfactant penetration and/or interaction with active ingredients using both whole plant (Hamburg and McCall, 1988; Lownds and Bukovac, 1983; Lownds et al., 1987; Silcox and Holloway, 1989; Stevens and Bukovac, 1987a,b) and isolated plant cuticle systems (King, 1982; Shafer and Bukovac, 1986, 1987b, 1988). Since the cuticle is the prime barrier to penetration of foliar-applied nonvolatile compounds (Bukovac et al., 1981) and sorption is an important early event in membrane penetration (Nobel, 1974), sorption by isolated cuticles may provide insight into the mechanism(s) of surfactant action during foliar penetration.

Surfactant (OP + 9.5EO) has been shown to alter the pattern of NAA sorption by tomato fruit cuticles (Shafer and Bukovac, 1989). This effect was concentration dependent. Below the critical micelle concentration (cmc), OP + 9.5EO had little effect on NAA sorption. However, above the cmc, NAA sorption was inversely related to concentration. These results were observed over wide ranges of pH and NAA concentration. Two explanations were offered for this response: (a) blocking of NAA sorption sites by sorbed OP + 9.5EO and/or (b) surfactant micelle solubilization or "trapping" of NAA molecules, which decreases the concentration of NAA in the intermicellar solution available for sorption.

To broaden our database and gain further insight into the nature of active ingredient/surfactant/cuticle interactions, we utilized a homologous series of octylphenoxy surfactants to assess the effect of hydrophile (EO) chain length on NAA sorption. The results of our study are presented herein.

EXPERIMENTAL PROCEDURES

Plant Material/Cuticle Isolation. Locally field grown mature tomato (*Lycopersicon esculentum* Mill. cv. Sprinter) and pepper (*Capsicum annuum* L.) fruits free of visual defects were selected for reasons previously discussed (Shafer and Schönherr, 1985). Disks, 20 mm in diameter, were punched from the fruit, and the cuticles were isolated by a procedure previously described (Orgell, 1955; Shafer and Bukovac, 1989). The cuticles were air-dried and stored at 23 °C until used.

Isolated cuticles will be referred to as cuticular membranes (CM). CM extracted for 3 days with at least 10 changes of chloroform–methanol (1:1 v/v) at 50 °C to remove cuticular waxes, i.e., soluble cuticular lipids (SCL), will be termed dewaxed cuticular membranes (DCM).

Radioisotope. 2-(1-Naphthyl)[1-^{14}C]acetic acid (specific activity 2.3 GBq mmol^{-1}; Amersham) with a radiochemical purity of 98%, as determined by thin-layer radiochromatography, was used.

Surfactants. 4-(1,1,3,3-Tetramethylbutyl)phenol (OP) condensed with 3 (OP + 3EO), 5 (OP + 5EO), 7.5 (OP + 7.5EO), 9.5 (OP + 9.5EO), 12.5 (OP + 12.5EO), 16 (OP + 16EO), 30 (OP + 30EO), and 40 (OP + 40EO) mol of ethylene oxide (EO) was used. The trade names (registered trademarks, Rohm and Haas Co.) for these surfactants are Tritons X-35, X-45, X-114, X-100, X-102, X-165, X-305, and X-405, respectively. The cmc values for these surfactants are 0.004, 0.005, 0.012, 0.019, 0.029, 0.039, 0.099, and 0.16% (w/v), respectively, and other selected chemical characteristics relevant to foliar penetration were reported elsewhere (Lownds, 1987; Stevens and Bukovac, 1987a). Except for OP + 3EO (lot L-2-8294), OP + 5EO (lot L-2-8160), and selected OP + 5EO and OP + 7.5EO samples obtained later in our studies (see Results and Discussion), production lot numbers were not available for the surfactant samples utilized.

These surfactants were commercial preparations, and no further purification was performed prior to usage. The EO number is an average value, with the ethoxymer mole ratio distribution following a Poisson distribution (Rothman, 1982;

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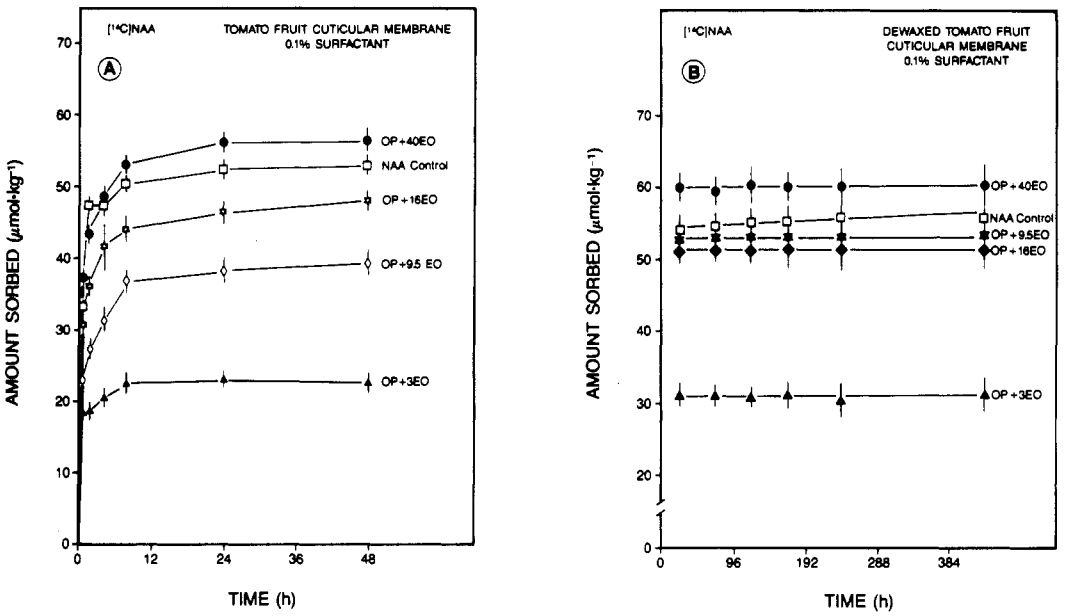

Figure 1. Effect of selected octylphenoxy surfactants (0.1%) on time course of NAA sorption by (A) tomato fruit cuticular membranes (CM) and (B) dewaxed tomato fruit cuticular membranes (DCM). Assay conditions: pH 3.2, 25 °C. Plots are means of five replications and their respective confidence intervals (P = 0.05).

Triton Surface-Active Agents, 1982). All concentrations were based on weight/volume.

Measurement of Sorption. Sorption was measured for the systems CM/buffer and DCM/buffer according to the procedure of Riederer and Schönherr (1984). Sodium citrate buffer (20 mM) at pH 3.2, containing 1 mM Na_3N, was used in all experiments.

Random samples (25–50) of CM or DCM disks were selected and cut into small (approximately 1 mm × 10 mm) strips (preliminary results showed no significant effect of strip size). Weighed subsamples (approximately 5 mg) were placed into 5-mL glass vials, and 1.5 mL of ^{14}C-labeled NAA (300–500 nM) buffered treatment solution was pipetted into each vial. 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 from the bulk solution, and radioactivity was determined by liquid scintillation spectrometry (LKB-Wallac LSC, Model 1211). Scintillation cocktail was composed of 1,4-dioxane (10 mL), containing 100 g of naphthalene and 5 g of diphenyloxazole (PPO) per liter. All samples were counted to a 2σ 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 NAA sorbed by CM or DCM was determined by subtracting the quantity of [^{14}C]NAA in the bulk solution from the amount originally present (Kipling, 1965).

Apparent partition coefficients (K^{pH}) were calculated by

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

K^{pH} values can be used herein to compare the effects of OP surfactants on equilibrium NAA sorption values since the experimental conditions (e.g., temperature, NAA concentration, pH) were held constant.

Radioassay of solutions in control vials, containing only [^{14}C]-NAA treatment solution (i.e., no CM or DCM strips), indicated that, except for OP + 3EO and OP + 5EO (see following paragraph), there was negligible (≤2%) loss of [^{14}C]NAA from the solutions. Therefore, the assumption is valid that the decrease of [^{14}C]NAA from the bulk solution represented that sorbed by the cuticle.

For the [^{14}C]NAA treatment solutions containing either OP + 3EO or OP + 5EO, a substantial (3–30%) "disappearance" of [^{14}C]NAA from the bulk solution was observed in control vials. The loss of radioactivity appeared to be associated with low water solubility of the surfactant and/or adsorption of surfactant to the glass vials, leading to lower NAA bulk solution concentrations. Equilibrium was achieved rapidly in control vials (unpublished results). Thus, the loss of [^{14}C]NAA was independent of the presence of cuticle, and corrections, based on the loss of [^{14}C]-NAA in the control vials, were made in the sorption calculations.

Surfactant Pretreatment of Cuticles. To determine if octylphenoxy surfactants produced irreversible effects on tomato cuticles that influence sorption, CM strips were treated with buffered (pH 3.2) 0.1% surfactant solutions. Weighed CM subsamples (approximately 5 mg) were placed into 5-mL vials and extracted with 1.5 mL of surfactant solution (no [^{14}C]NAA present) by shaking for 48 h as described earlier. CM strips were then removed, washed extensively with distilled water, and placed into clean vials containing 1.5 mL of fresh buffer (no [^{14}C]NAA or surfactant present) for an additional 48 h to desorb the surfactant. The CM strips were again washed with distilled water and dried in a desiccator at 30 °C until constant weight was achieved. NAA sorption in the absence of surfactant was determined on these pretreated CM subsamples as described earlier.

Statistics. All measurements were made with five replications per treatment. For the time course measurements, the same five replicates were sampled repeatedly. The results are presented as means with their 95% confidence intervals.

RESULTS AND DISCUSSION

The effects of polyethoxylated derivatives of octylphenol surfactants on NAA sorption by tomato fruit cuticles were dependent on EO content, concentration, and, with some surfactants, the presence of cuticular waxes.

Four octylphenoxy surfactants (0.1%) representing short (OP + 3EO), intermediate (OP + 9.5EO, OP + 16EO), and long (OP + 40EO) ethyleneoxy chain lengths were selected for our initial studies. None affected the time (48 h) required for NAA to reach sorption equilibrium with tomato CM (Figure 1A) and DCM (data not shown). A lack of surfactant effect on time to equilibrium would probably be observed for these surfactants at other concentrations (both pre- and post-cmc) since no effect was previously (Shafer and Bukovac, 1989) observed for OP + 9.5EO at pre- and post-cmc concentrations.

In contrast to the time course data, the four octylphenoxy surfactants influenced the amount of NAA sorbed by CM and DCM. Sorption values (μmol kg^{-1}) for NAA with CM at 48 h, in the presence of 0.1% OP + 3EO, OP

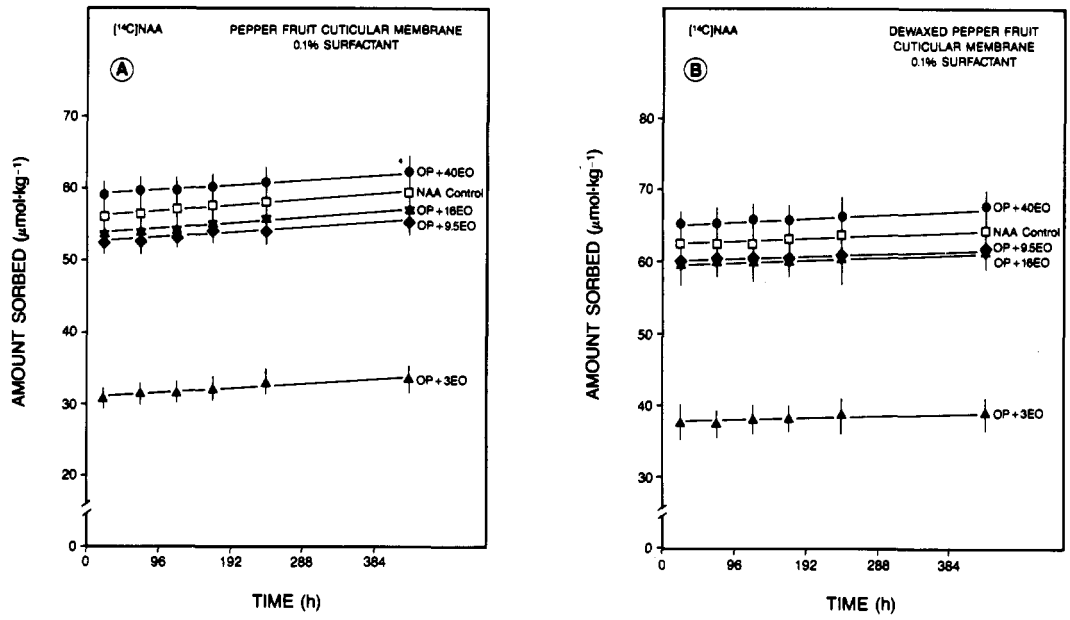

Figure 2. Effect of selected octylphenoxy surfactants (0.1%) on time course of NAA sorption by (A) pepper fruit cuticular membranes (CM) and (B) dewaxed pepper fruit cuticular membranes (DCM). Assay conditions: pH 3.2, 25 °C. Plots are means of five replications and their respective confidence intervals ($P = 0.05$).

+ 9.5EO, OP + 16EO, and OP + 40EO, were 41, 75, 91, and 107% of the control value, respectively (Figure 1A). The corresponding percentage values for tomato DCM were 48, 86, 94, and 108%, respectively (Figure 1B).

For octylphenoxy surfactants, EO content and critical micelle concentration (cmc) are positively related (*Triton Surface-Active Agents*, 1982). At 0.1% concentration, OP + 3EO, OP + 9.5EO, and OP + 16EO were above their cmc values. Therefore, on the basis of known surfactant behavior, these surfactant solutions would consist of a mixture of micelles and monomers. The capacity of OP + 9.5EO micelles to solubilize NAA has already been demonstrated (Heredia and Bukovac, 1990; Shafer and Bukovac, 1989), and the reduction in NAA sorption observed in this study (Figures 1 and 2) is most likely related to OP + 3EO, OP + 9.5EO, and OP + 16EO micelles solubilizing NAA, thus lowering the intermicellar NAA concentration. The magnitude of this reduction is a function of both NAA and micelle concentration; the lower the NAA:micelle ratio, the greater the reduction.

Given that octylphenoxy surfactants are mixtures of various ethoxymers (Rothman, 1982; *Triton Surface-Active Agents*, 1982) and that short-chain ethoxymers may differ dramatically, in terms of chemical behavior, from long-chain ethoxymers (Trogus et al., 1979), it seems reasonable to assume that micelles from these octylphenoxy surfactants present different microenvironments to NAA and thus differ in their NAA solubilization capacity. Our approach did not permit us to directly address this question, since at a given concentration the micelle population, and probably micelle structure, varies depending on the cmc. Regardless of differences in micelle solubilization capacity, it remains to be determined whether correction for NAA solubilization by surfactant micelles would lead to sorption values similar to that of pre-cmc values.

At 0.1% concentration, OP + 40EO was below its cmc and it did not suppress sorption (Figures 1 and 2). Thus, OP + 40EO surfactant monomers and NAA molecules did not associate and therefore interacted independently with CM or DCM (actually OP + 40EO resulted in sorption values slightly higher than control values, presumably due to enhanced cuticle wetting). The lack of NAA/surfactant monomer complex formation is consistent with findings for NAA and OP + 9.5EO (Shafer and Bukovac, 1988).

The effects of octylphenoxy surfactants (0.1%) on NAA sorption by CM or DCM were apparent early in the sorption process (Figure 1A) and persisted for extended periods of time (Figures 1B and 2). Dewaxing CM led to greater sorption by both tomato and pepper cuticles (Figures 1B and 2B). Greater sorption by DCM has been demonstrated previously (Riederer and Schönherr, 1984; Shafer and Bukovac, 1987a), and this effect has been attributed to increased accessibility of NAA to the cutin matrix once the SCL are removed. Sorption equilibrium for NAA with pepper CM and DCM was not reached with any treatment even after 432 h (Figure 2). While this general phenomenon has been observed previously with auxins (Riederer and Schönherr, 1986; Shafer and Bukovac, 1987a) and has been attributed to the presence of epoxide bonds in certain cuticles (e.g., pepper fruit cuticles) which slowly react with the carboxyl groups of auxins, octylphenoxy surfactants had no qualitative effect on this response.

On the basis of initial results with OP + 3EO, OP + 9.5EO, and OP + 16EO (Figures 1 and 2), NAA solubility in, or association with, octylphenoxy surfactant micelles appeared to be inversely related to EO content. These results were similar, in principle, to the data from pharmaceutical studies, where an inverse relationship between solubility of barbiturates or benzoic acid derivatives and EO content of poly(oxyethylene) stearate surfactants was observed (Goodhart and Martin, 1962; Gouda et al., 1970).

To more completely characterize the relationship between EO content and NAA sorption by tomato CM and DCM, eight octylphenoxy surfactants differing in EO content were compared at 0.1% (Figure 3) and 1.0% (Figure 4). At 0.1% concentration, sorption was, in general, again found to be positively related to EO content, except where OP + 5EO and OP + 7.5EO caused a dramatic increase in sorption by CM. This general EO effect is consistent with that observed for isolated pepper fruit and *Ficus* leaf cuticles (Shafer et al., 1989). These data provide evidence for a direct octylphenoxy surfactant/NAA/CM (or, more specifically, SCL) interaction. Al-

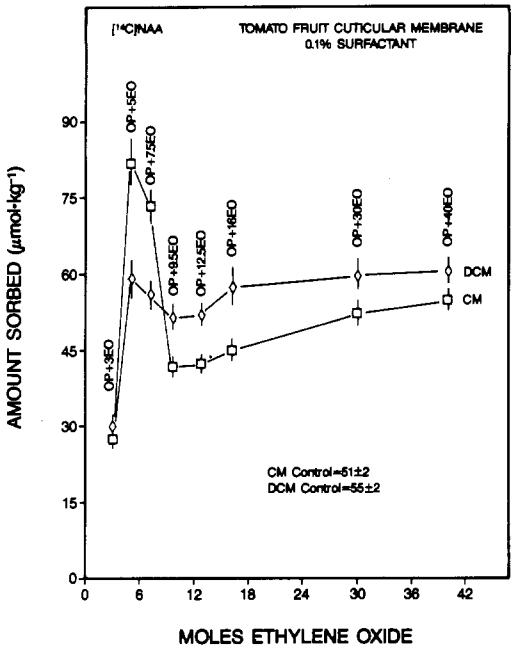

Figure 3. Effect of ethyleneoxy (EO) chain length for octylphenoxy surfactants (0.1%) on NAA sorption by tomato fruit cuticular membranes (CM) and dewaxed cuticular membranes (DCM) at 48 h, pH 3.2, and 25 °C. Plots are means of five replications and their respective confidence intervals ($P = 0.05$).

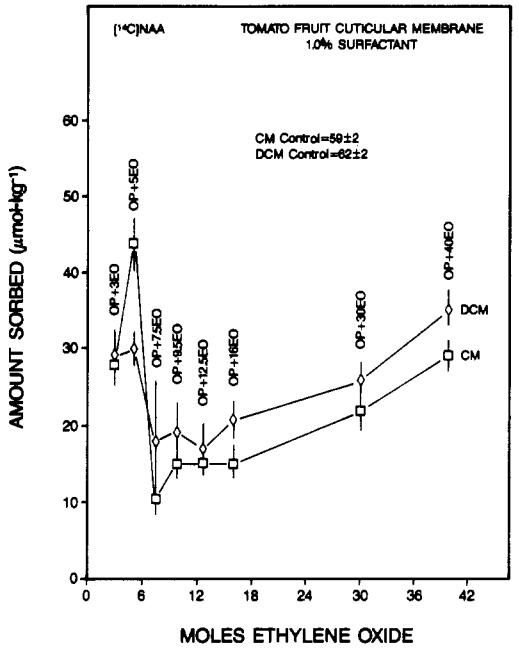

Figure 4. Effect of ethyleneoxy (EO) chain length for octylphenoxy surfactants (1.0%) on NAA sorption by tomato fruit cuticular membranes (CM) and dewaxed cuticular membranes (DCM) at 48 h, pH 3.2, and 25 °C. Plots are means of five replications and their respective confidence intervals ($P = 0.05$).

though water solubilities of OP + 5EO and OP + 7.5EO are low, this was not a factor since the response was only obtained with CM.

To expand our database on the enhancement effects with OP + 5EO and OP + 7.5EO, additional surfactant samples representing different production lots were evaluated. Two samples each of OP + 5EO (lots 9422 and 9500) and OP + 7.5EO (lots 2-5059 and 2-8691) were tested at 0.1%, and all four treatments led to an increase in NAA sorption compared to control (NAA only) values (Table I). Follow-up studies with other OP + 5EO samples (lots L-2-1013 and L-2-3914), however, showed no enhancement

Table I. Apparent Partition Coefficients (K^{pH}) for NAA and Tomato Fruit Cuticular Membranes (CM), As Affected by 0.1% OP + 5EO (Triton X-45) or OP + 7.5EO (Triton X-114) from Different Production Lots, at 48 h, pH 3.2, and 25 °C

treatment	lot[a]	K^{pH} [b]
control (NAA only)		151 (145–157)
OP + 5EO	9422	276 (265–287)
	9500	272 (259–284)
OP + 7.5EO	2-5059	252 (242–262)
	2-8691	266 (260–272)

[a] Two samples from different production lots for each surfactant were provided by Dr. Gary Willingham, Rohm and Haas Co., Spring House, PA. [b] Mean of five replications with respective confidence interval limits ($P = 0.05$).

Table II. Effect of Octylphenoxy Surfactant Pretreatment (0.1%, 48 h) of Tomato Fruit Cuticular Membrane (CM) on Subsequent NAA Sorption (K^{pH} Values) at 48 h, pH 3.2, and 25 °C[a]

treatment	K^{pH} [b]
control (NAA only)	157 (134–180)
OP + 3EO (Triton X-35)	155 (145–165)
OP + 5EO (Triton X-45)	164 (152–175)
OP + 7.5EO (Triton X-114)	162 (158–165)
OP + 9.5EO (Triton X-100)	164 (161–168)
OP + 12.5EO (Triton X-102)	158 (143–174)
OP + 16EO (Triton X-165)	161 (155–167)
OP + 30EO (Triton X-305)	162 (159–165)
OP + 40EO (Triton X-405)	162 (152–173)

[a] See text for details of pretreatment procedure. [b] Mean of five replications with respective confidence interval limits ($P = 0.05$).

of NAA sorption at 0.1% within 48 h (data not shown). Recent studies have now shown that the maximum enhancement response from various OP + 5EO and OP + 7.5EO production lots is affected by slight shifts in surfactant concentration (e.g., 0.075% instead of 0.1%) and also by sorption time. These differences may be due to subtle shifts in ethoxymer distribution profiles from one lot to another. There is no evidence that the presence of any impurities in the production lots affect the enhancement response (R. G. Fader, personal communication).

All octylphenoxy surfactants, except OP + 3EO, yielded lower sorption values at 1.0% compared to those at 0.1% (Figures 3 and 4). Interestingly, in foliar absorption studies with selected herbicides, Smith et al. (1966) observed that, with octyl- or nonylphenol poly(oxyethylene) glycol ether surfactants, the EO chain length which yielded maximum herbicidal toxicity decreased as surfactant concentration increased. Since cuticular sorption/penetration is an early step in the foliar absorption process, it is tempting to speculate that a similar EO/concentration relationship exists for NAA uptake.

Pretreatment of tomato CM with 0.1% surfactant did not lead to significant changes in NAA sorption. Observations made by Stevens and Bukovac (1987a) of droplet residues on leaf surfaces using SEM techniques would support the concept that octylphenoxy surfactants do not solubilize epicuticular lipids.

There was some weight loss with CM (1–5%, data not shown) on extraction. King (1982), working with isolated cuticles from pear leaves, also reported a weight loss with isolated cuticles following treatment with three different types of surfactants. Thus, it appears that surfactants may extract constituents from cuticles, but this did not significantly affect the NAA sorptive properties of the cuticles used in our study.

While the suppression of NAA sorption by cuticles in the presence of OP + 3EO, OP + 9.5EO, OP + 12.5EO, OP + 16EO, and OP + 40EO micelles may be due to

blocking of sorption sites and/or solubilization of NAA by micelles (Heredia and Bukovac, 1990; Shafer and Bukovac, 1989), the mechanism(s) by which OP + 5EO and OP + 7.5EO micelles dramatically increased NAA sorption by CM is not clear. Two possible explanations for the enhancement effect deserve mention.

First, OP + 3EO, OP + 9.5EO, OP + 12.5EO, OP + 16EO, and OP + 40EO are sorbed, to varying levels, by plant cuticles (Shafer and Bukovac, 1987b; Shafer et al., 1989). If OP + 5EO and OP + 7.5EO were sorbed by, or associated with (e.g., multilayer formation), CM in a manner that "trapped" relatively large quantities of NAA on the CM (Gellan and Rochester, 1985; Harwell et al., 1985), then it would appear (on the basis of the difference method of calculating sorption) that more NAA was sorbed. An inconsistency with this suggestion is that increasingly higher surfactant concentrations (Figure 4) did not lead to increasingly greater levels of NAA sorption by CM for the OP + 5EO and OP + 7.5EO surfactant treatments.

A second explanation focuses specifically on surfactant/SCL interactions. Reports by Chambers and Possingham (1963) and Radler (1965) suggested that the enhanced drying rate of grapes, which had been treated with selected dipping emulsions or detergents, was due to a specific cuticular wax/emulsion association. This association apparently "bypassed" the hydrophobic wax barrier to water loss by allowing a hydrophilic continuum between the epidermal cells and the environment to develop. More recently, Geyer and Schönherr (1988) observed that deposits of some surfactants increased the water permeability of cuticles, although unusually high amounts of surfactant (up to 25 g of surfactant/m^2 of cuticle) were used. If OP + 5EO and OP + 7.5EO surfactants interacted with CM in a manner that "softened" or "opened up" the SCL, then such an alteration could provide more sites for NAA sorption. The specific concentration-dependent nature of the OP + 5EO and OP + 7.5EO enhancement effect remains to be elucidated.

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