Effect of Surfactants on Pressure Infiltration of Calcium Chloride Solutions into 'Golden Delicious' Apples

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ADDITIONAL INDEX WORDS. CaCl_2 , *Malus domestica*, postharvest, surface active agents

ABSTRACT. The effects of 36 organosilicone and conventional carbon-based surfactants on postharvest infiltration of radiolabeled and unlabeled Ca solutions into 'Golden Delicious' apples (*Malus domestica* Borkh) were examined to devise a more efficient pressure infiltration technique to increase fruit Ca concentration. Radiolabeled Ca infiltration and the proportional increase in fruit Ca estimated by fruit weight gain from Ca solutions of known concentration were significantly enhanced by a range of surfactants having different chemical structures. Tween 60 and 80; Triton X-45, X-100, X-114, X-305, and X-405; and Silwet L-77 and L-7604 enhanced Ca infiltration. The two organosilicone surfactants, Silwet L-77 and Silwet L-7604, known for their greater capacity to lower the surface tension of solutions than conventional carbon-based surfactants, were the most effective at augmenting Ca infiltration. Applications of surfactants to fruit were as or more effective when used as a pretreatment rather than mixing the surfactant with the Ca solutions. The pressure necessary to increase Ca to levels considered sufficient to maintain fruit firmness and resist decay during storage could be lowered in fruit treated with organosilicone surfactants. Sequential postharvest surfactant and Ca treatments may be a practical means of increasing the Ca concentration in apples.

Increasing the Ca content of apples decreases the incidence of bitter pit, scald, water core, and internal breakdown (Yuen, 1994), maintains fruit firmness and quality (Mason et al., 1975), and reduces decay caused by postharvest pathogens (Conway et al., 1992). To control physiological disorders on the tree, a series of Ca-containing tree sprays has gained commercial acceptance for increasing fruit Ca concentration. However, even a full regiment of preharvest Ca treatments adds only a modest amount of Ca to the apples, not enough to reduce significantly many postharvest physiological and pathological disorders (Yuen, 1994). To increase fruit Ca concentration further, it is necessary to treat the fruit directly after harvest with a Ca solution. Experimentally, postharvest infiltration of Ca by treating fruit in Ca solutions under positive atmospheric or hydrostatic pressure gradients can effectively introduce more Ca into fruit flesh than preharvest sprays (Mehuriuk and Moyls, 1989; Scott and Wills, 1977). However, inadequate Ca infiltration is still a problem with some lots of fruit, and nonuniform or excessive infiltration of Ca, resulting in fruit injury, is a problem for others (Conway et al., 1994a).

The mechanisms involved in Ca infiltration into fruit from postharvest treatments are not fully understood. The surface of apples is covered with a thick, waxy cuticle interrupted by lenticels

and sometimes by russeted areas. The cuticle is the major barrier to the penetration and escape of a wide range of solutes and water (Forbes and Watson, 1992). While Ca diffusion through the cuticle is a relatively slow process (Glenn and Poovaiah, 1985), significant amounts of Ca are adsorbed onto apple fruit cuticles (Chamel, 1983). The degree that adsorbed Ca penetrates the cuticle and affects internal Ca concentration during storage has not been investigated. However, the high levels of Ca infiltration observed during short-term (≤ 3 min) postharvest treatments with Ca solutions indicate mass flow through lenticels (Betts and Bramlage, 1977) or other openings in the waxy cuticle (Roy et al., 1996). Calcium infiltration has been reported to vary with the number and nature of the various penetration sites (Yuen, 1994). For more uniform and enhanced Ca infiltration, the fruit surface should be uniformly exposed to the Ca solutions. Mixing surfactants such as Agral, Tween 20, or Silwet L-77 into Ca dipping solutions has been shown to increase the number of penetration sites covered on the fruit surface resulting in increased Ca infiltration into apples (Yuen, 1994). While not fully understood, a few surfactants have been reported to decrease Ca infiltration (Roy et al., 1996; Yuen, 1994).

To date, the choice of which surfactant to use is made by a trial and error procedure, due to the complex nature of their interactions with target surfaces and lack of understanding of their mode of action (Tadros, 1995). The present study examines the efficacy of a broad range of surfactants for enhancing Ca infiltration.

Materials and Methods

'Golden Delicious' apples were harvested in the preclimacteric stage (ethylene production $< 0.1 \mu\text{L}\cdot\text{kg}^{-1}$ and the climacteric rise in CO_2 production had not yet begun) from a commercial orchard and randomized. Fruit were rinsed with water to remove surface residual material from preharvest sprays and dried. All fruit were stored at 0°C and, as needed, removed from storage and allowed to warm to $21 \pm 1^\circ\text{C}$. Nine to twenty-eight fruit were dipped for 30

Received for publication 25 July 1996. Accepted for publication 19 Dec. 1996. We gratefully acknowledge Peter J.G. Stevens and George A. Policello, OSi Specialties; Gregory Grant, ICI Americas; and Edward Thacker, Union Carbide Corp., for many helpful discussions and suggestions during the course of this work. We also thank ICI Surfactants, Wilmington, Del., for samples of Atlox 8916TF, Brij 93 and 98, and Renex 30 and 36; OSi Specialties, Inc., Tarrytown, N.Y., for samples of Silwet L-77 and L-7604; Union Carbide Corp., Danbury, Conn., for samples of Tergitol 15-S-3, Triton X-35 and X-45; and Pennsylvania State University Analytical Services, University Park, Pa., for Ca analyses of freeze-dried samples of apple flesh. Use of a company name or product by the USDA does not imply approval or recommendation of the product to the exclusion of others that also may be suitable. The cost of publishing this paper was defrayed in part by the payment of page charges. Under postal regulations, this paper therefore must be hereby marked advertisement solely to indicate this fact.

Table 1. Hydrophile-lipophile balance (HLB) number and chemical description of polyoxyethylene-containing surfactants.

Surfactant	Chemical description	HLB
Polyoxyethylene sorbitan fatty acid and resin acid esters		
Atlox 8916TF	Polyoxyethylene sorbitan esters of mixed fatty and resin acids	15.4
Tween 20	Polyoxyethylene (20) ² sorbitan monolaurate	16.7
Tween 40	Polyoxyethylene (20) sorbitan monopalmitate	15.6
Tween 60	Polyoxyethylene (20) sorbitan monostearate	14.9
Tween 80	Polyoxyethylene (20) sorbitan monooleate	15.0
Tween 85	Polyoxyethylene (20) sorbitan trioleate	11.0
Polyoxyethylene alkyl ethers		
Brij 30	Polyoxyethylene (4) lauryl ether	9.7
Brij 35	Polyoxyethylene (23) lauryl ether	16.9
Brij 52	Polyoxyethylene (2) cetyl ether	5.3
Brij 56	Polyoxyethylene (10) cetyl ether	12.9
Brij 72	Polyoxyethylene (2) stearyl ether	4.9
Brij 76	Polyoxyethylene (10) stearyl ether	12.4
Brij 93	Polyoxyethylene (2) oleyl ether	4.9
Brij 98	Polyoxyethylene (20) oleyl ether	15.3
Renex 30	Polyoxyethylene (12) tridecyl ether	14.5
Renex 36	Polyoxyethylene (6) tridecyl ether	11.4
Tergitol 15-S-3	Polyoxyethylene (3) mixed fatty acid ethers	8.3
Tergitol 15-S-9	Polyoxyethylene (9) mixed fatty acid ethers	13.3
Polyoxyethylene tetramethylbutylbenzene ethers		
Triton X-35	Polyoxyethylene (3) tetramethylbutylbenzene	7.8
Triton X-45	Polyoxyethylene (5) tetramethylbutylbenzene	10.4
Triton X-100	Polyoxyethylene (10) tetramethylbutylbenzene	13.5
Triton X-114	Polyoxyethylene (8) tetramethylbutylbenzene	12.4
Triton X-305	Polyoxyethylene (30) tetramethylbutylbenzene	17.3
Triton X-405	Polyoxyethylene (40) tetramethylbutylbenzene	17.9
Polyoxyalkylene-modified polydimethylsiloxane		
Silwet L-77	Polyoxyalkylene-modified heptamethyl-trisiloxane	13.0
Silwet L-7604	Polyoxyalkylene-modified polydimethyl-siloxane	≈17

²Numbers in parentheses refer to the average number of polyoxyethylene units in the surfactant molecule.

s in the following solutions at 21 ± 1 °C: distilled water, 50 mL·L⁻¹ ethanol, or a 2 g·L⁻¹ concentration (unless otherwise specified) of a surfactant (Tables 1 and 2) in distilled water or 50 mL·L⁻¹ ethanol. The fruit were allowed to dry, fresh mass (FM) was determined, and the calyxes of the fruit were sealed with 0.1 g of paraffin wax (to reduce subsequent solution infiltration through open calyxes of a small percentage of the fruit). The fruit were then pressure

infiltrated (3 min at 34 kPa unless otherwise specified) in a 20 g·L⁻¹ solution of CaCl₂·2H₂O without and with a 2 g·L⁻¹ concentration (unless otherwise specified) of a surfactant at 21 ± 1 °C. A 3-min treatment period causes near optimal Ca infiltration, a 34 kPa pressure gradient is the lowest pressure that consistently enhanced Ca infiltration, and a 20 g·L⁻¹ solution of CaCl₂ is near optimal for maintaining tissue water status (R. Saftner, unpublished data).

Table 2. Effect of experimental surfactants supplied as a pretreatment on estimated Ca infiltration into 'Golden Delicious' apples.

Surfactant	Estimated Ca infiltration ² (mg·kg ⁻¹ fresh mass)
None	70.4 a
Alkyl saccharide	
n-Dodecanoylsucrose	94.0 ab
n-Octylthioglucoside (OSG)	81.2 a
n-Octylglucoside (OG)	77.4 a
n-Octanoylsucrose	73.7 a
Alkyl sulfate	
Sodium dodecyl sulfate (SDS)	76.3 a
Betaine	
N-Dodecyl-N,N-dimethylglycine (Empigen BB)	108.9 b
3-[(Cholamidopropyl)dimethylammonio]-1-propanesulfonate (CHAPS)	24.6 c
Glucamides	
n-Nonanoyl-N-methylglucamide (MEGA-9)	75.0 a
n-Octanoyl-N-methylglucamide (MEGA-8)	74.6 a
n-Decanoyl-N-methylglucamide (MEGA-10)	68.8 a

²Values are means of observations from nine fruits. Means followed by the same letter are not significantly different at $P = 0.05$.

Fig. 1. The relationship of radiolabeled Ca infiltration (top) and Ca content (bottom) to estimated Ca infiltration determined on the basis of FM gain for 'Golden Delicious' apples pressure infiltrated in a 20 g·L⁻¹ CaCl₂ solution.

Following infiltration, fruit were blotted with paper towels and air dried for 20 min before FM was measured. Estimated Ca infiltration data were recorded on a FM basis (mg·kg⁻¹).

The relationship between the quantity of solution infiltrated into apples and the fruit Ca concentration was determined from 28-fruit lots. Following weight measurements, fruit were stored at 0 °C for 4 months to reproduce the usual storage conditions between Ca infiltration treatments and flesh Ca analyses previously done. After storage, flesh tissue samples were collected

Fig. 2. Effect of Atlox 8916TF and Tween-series surfactant treatments on estimated Ca infiltration into 'Golden Delicious' apples. Fruit were pretreated for 30 s with a 2-g·L⁻¹ solution of a surfactant or distilled water and then pressure infiltrated (3 min, 34 kPa) with a 20-g·L⁻¹ solution of CaCl₂ without and with the surfactant in the CaCl₂ solution. Black-filled bars, surfactant pretreatment, Ca treatment; gray-filled bars, water pretreatment, surfactant plus Ca treatment. Treatments: 1 = no surfactant control with reference line; 2 = Tween 85; 3 = Tween 60; 4 = Tween 80; 5 = Atlox 8916TF; 6 = Tween 40; and 7 = Tween 20. The means were separated at *P* = 0.05 using the Ryan-Einot-Gabriel-Welsch multiple range test. The hydrophile-lipophile balance (HLB) number of the surfactants is shown above the bars for each treatment.

and freeze-dried as previously described (Conway et al., 1994a). Dried tissue samples were then dry-ashed, dissolved 1:25 in 1 mol·L⁻¹ HCl and analyzed for Ca concentration by inductively coupled plasma emission spectrometry (model 61E; Thermo Jarrell Ash). Calcium concentration is reported on a dry-mass (DM) basis (mg·kg⁻¹). Each sample consisted of the flesh from seven apples, and four samples were obtained from each treatment.

For correlation of radiolabeled Ca infiltration to Ca infiltration estimated by fruit weight gain, ⁴⁵CaCl₂ (specific activity, ≈10 GBq/g, Du Pont NEN, Boston) was added to CaCl₂ solutions to a final concentration of 20 g·L⁻¹ and ⁴⁵Ca infiltration was determined from nine-fruit lots. Following ⁴⁵Ca infiltration, fruit were dipped in 0.5 mol·L⁻¹ HCl for 30 s: this treatment effectively removes labeled Ca adhering and bound to the waxy cuticular surface (R. Saftner, unpublished data). Flesh Ca was determined by liquid scintillation counting, using whole fruit excluding seeds blended for 30 s with an equal volume of distilled water. Aliquots corresponding to 10% of the initial FM were air-dried at 65 °C before dry-ashing at 700 °C for 16 h. The ash was dissolved in 1 mL of 0.5 mol·L⁻¹ HCl and mixed with 15 mL of scintillation cocktail for analysis.

The Ca infiltration data were analyzed as a one-factor General Linear Models Procedure (SAS Institute, Cary, N.C.). To correct for variance heterogeneity, the data were log-10 transformed before analysis. The surfactant means were separated at the 5% significance level using the Ryan-Einot-Gabriel-Welsch multiple range test, which controls type I experiment-wise error rate. This multiple range test is more conservative than Duncan's multiple range test, which only controls the type I comparison-wise error rate. The means, in their original units of mg·kg⁻¹ FM, are presented. Unless stated otherwise, only results significant at *P* = 0.05 are discussed.

Results

There was a significant positive linear correlation (*r* = 0.99) between radiolabeled Ca infiltration and Ca infiltration estimated by fruit FM gain where Ca infiltration was varied by changing the pressure gradient between 0 and 137 kPa (Fig. 1A). The slope of the regression line was 0.98 and essentially passed through the origin (*y*-intercept = 0.3). While not as clearly defined, surfactant-enhanced radiolabeled Ca infiltration also was positively correlated to Ca infiltration estimated by FM gain of the

Fig. 3. Effect of Brij-, Renex-, and Tergitol-series surfactant treatments on estimated Ca infiltration into 'Golden Delicious' apples. Treatment conditions and statistical analysis are as identified in the legend to Fig. 2 except that 50 mL·L⁻¹ ethanol solution was used instead of distilled water in surfactant solutions. Black-filled bars, surfactant pretreatment in 50 mL·L⁻¹ ethanol solution, Ca treatment; gray-filled bars, water pretreatment, surfactant plus Ca treatment in 50 mL·L⁻¹ ethanol solution. Treatments: 1 = no surfactant control with reference line; 2 = Brij 72; 3 = Brij 93; 4 = Brij 52; 5 = Tergitol 15-S-3; 6 = Brij 30; 7 = Renex 36; 8 = Brij 76; 9 = Brij 56; 10 = Tergitol 15-S-9; 11 = Renex 30; 12 = Brij 98; and 13 = Brij 35. The hydrophile-lipophile balance (HLB) number of the surfactants is shown above the bars for each treatment.

fruit (data not shown). There also was a significant positive linear correlation ($r=0.98$) between Ca concentration and nonradioactive Ca infiltration estimated by FM gain (Fig. 1B). In this case, the y-intercept of the regression line was at 203 mg·kg⁻¹ DM, similar to the Ca concentration (210 ± 30 mg·kg⁻¹ DM) of untreated fruit. The slope of the regression line was 7.4 and reflected the difference between the dry and fresh masses of the fruit used (data not shown). Therefore, the Ca concentration of the fruit is the sum of the native Ca concentration of the fruit and the estimated Ca infiltration as determined by FM gain.

Thirty-six surfactants applied either as a pretreatment or by mixing with the CaCl₂ solutions were tested for their ability to affect Ca infiltration estimated by FM gain, and determined by direct measurement of radiolabeled Ca infiltration or nonradioactive Ca concentration. However, direct measurements of Ca infiltration were done to confirm the validity of Ca infiltration data estimated by FM gain, and only the surfactant effect on estimated Ca infiltration is presented. The surfactants were selected to cover a range of chemical classes and the hydrophile-lipophile balance (HLB) range from 4.9 to 17.9, which would be from nonpolar to polar on the scale of 0 to 20 usually described (Myers, 1988). Two organosilicone surfactants were specifically

Fig. 4. Effect of Triton X-series surfactant treatments on estimated Ca infiltration into 'Golden Delicious' apples. Treatment conditions and statistical analysis are identified in the legend to Fig. 2. Black-filled bars, surfactant pretreatment, Ca treatment; gray-filled bars, water pretreatment, surfactant plus Ca treatment. Treatments: 1 = no surfactant control with reference line; 2 = Triton X-35; 3 = Triton X-45; 4 = Triton X-114; 5 = Triton X-100; 6 = Triton X-305; and 7 = Triton X-405. The hydrophile-lipophile balance (HLB) number of the surfactants is shown above the bars for each treatment.

tested because of their ability to reduce surface tension and aid penetration of aqueous agrochemical solutions through small apertures on the fruit surface. Results are presented by chemical classes of surfactants as identified in Tables 1 and 2.

Six (five Tweens and Atlox 8916TF) surfactants belonging to the polyoxyethylene sorbitan fatty acid and resin acid esters were tested as a group (Fig. 2). Only Tween 60 and 80 stimulated Ca infiltration.

Twelve (8 Brij, 2 Renex, and 2 Tergitol) surfactants of the chemical class polyoxyethylene alkyl ethers were tested as a group in the presence of 50 mL·L⁻¹ ethanol. Ethanol was required for emulsification of the nonpolar, water-insoluble surfactants, e.g., those having HLB numbers <10. An ethanol concentration of 50 mL·L⁻¹ had no effect on Ca infiltration (data not shown). The nonpolar surfactants, Brij 52, 72, and 93, having HLB numbers <6, inhibited Ca infiltration (Fig. 3). The surfactant effect was up to 33%

stronger when supplied as a pretreatment rather than by mixing with the Ca infiltration solution. None of the more-polar surfactants of this chemical class consistently stimulated Ca infiltration (Fig. 3).

Triton surfactants are polyoxyethylene-containing surfactants with an ether linkage to the rather compact hydrophobic moiety, tetramethylbutylbenzene (Table 1). Except for the nonpolar, water-dispersible Triton X-35, the Triton surfactants enhanced Ca infiltration at least when the surfactant was used as a pretreatment (Fig. 4). Of the conventional carbon-based, polyoxyethylene-containing surfactants used in this study, Triton X-100 and X-114, with HLB numbers of 13.5 and 12.4, respectively, were the best at enhancing Ca infiltration. Both stimulated Ca infiltration ≈50%.

The effect of 10 other conventional carbon-based surfactants on Ca infiltration is shown in Table 2. With the possible exception of n-dodecanoylsucrose, the alkylsaccharide- and glucamide-containing surfactants did not enhance Ca infiltration. n-Dodecanoylsucrose increased Ca infiltration ≈30%. The only cationic surfactant tested in this study was sodium dodecyl sulfate and it did not affect Ca infiltration. The two zwitterionic, betaine-containing surfactants affected Ca infiltration, with Empigen BB increasing and CHAPS decreasing Ca infiltration. Unlike the other

Fig. 5. The effect of organosilicone surfactant concentration on estimated Ca infiltration into 'Golden Delicious' apples. Except for surfactant concentration, treatment conditions and statistical analysis are as identified in the legend to Fig. 2. Surfactant treatments are Silwet L-77 (A) and Silwet L-7604 (B). (●) Surfactant pretreatment; (○) surfactant plus Ca.

surfactants tested, the zwitterionic surfactants appeared to injure apple fruit tissue, causing skin discoloration and lenticel pitting.

Two organosilicone surfactants, Silwet L-77 and L-7604, were specifically tested for their effect on Ca infiltration because they can reduce the surface tension of aqueous solutions and increase the wetting and spreading rate of the aqueous agrochemical solutions across plant surfaces to a greater degree than conventional carbon-based surfactants (Knoche, 1994). The effect of organosilicone surfactant concentration on Ca infiltration is shown in Fig. 5. Silwet L-77 and L-7604 stimulated Ca infiltration at all concentrations tested, pretreatments with these surfactants being up to 28% more effective than when mixed with the Ca infiltration solution. Calcium infiltration was enhanced as surfactant concentration was increased. These surfactants increased Ca infiltration between 1.7- and 3.1-fold, with Silwet L-77 (HLB 13.0) having a stronger effect than the more polar L-7604 (HLB ≈ 17). A concentration dependence of conventional carbon-based, Triton-series surfactants on Ca infiltration was not observed (data not shown).

Silwet L-77 pretreatment at a concentration of 2 g·L⁻¹ reduced by ≈50% the pressure necessary to infiltrate a unit amount of Ca (Fig. 6). A Silwet L-7604 pretreatment at a concentration of 5 g·L⁻¹ had an equivalent effect (data not shown). The Ca concentration of apple fruit pretreated with 2 g·L⁻¹ Silwet L-77 and pressure infiltrated (34 kPa) with a 20 g·L⁻¹ solution of CaCl₂ was 1440 ± 120 mg·kg⁻¹ DM. When L-77 was dispersed into the CaCl₂ solution, the Ca concentration of the fruit was 1320 ± 140 mg·kg⁻¹ DM.

Discussion

Postharvest treatment of apples with CaCl₂ solutions and the resulting increase in fruit Ca concentration beneficially affect fruit during storage. A fruit Ca concentration of 250 mg·kg⁻¹ DM is considered sufficient to control Ca-related storage disorders

Fig. 6. Effect of applied atmospheric pressure gradients on Ca infiltration into water- and Silwet L-77-pretreated 'Golden Delicious' apples. The reference line indicates the amount of Ca infiltration required to raise the tissue Ca content to levels considered adequate to maintain fruit firmness and reduce decay during storage. (●) Surfactant pretreatment; (○) water pretreatment.

high Ca concentrations (>25 g·L⁻¹) can increase Ca concentration to optimal levels for storage, these treatments increase the risk of skin injury to commercially unacceptable levels. In this study, we did the first detailed investigation of surfactants and their use in augmenting Ca infiltration into apples using relatively mild (20 g·L⁻¹ CaCl₂, 34 kPa) procedures.

To measure Ca infiltration reliably and quickly into individual fruit, we verified that Ca infiltration under the conditions used in this study could be accurately estimated by FM gain of the fruit. Calcium infiltration estimated by FM gain was linearly correlated with radiolabeled Ca infiltration ($r = 0.99$, Fig. 1A) and Ca concentration ($r = 0.97$, Fig. 1B). Lee and Dewey (1981) had previously shown that Ca infiltration into 'Jonathan' apples could be accurately estimated by the same method.

Using FM gains to estimate Ca infiltration, we found that only 25% of the surfactants tested as pretreatments enhanced Ca infiltration, and their effectiveness in doing this could generally be predicted from their chemical nature. Of those that did, Tweens 60 and 80 (Fig. 2) and Triton X-45, X-305, and X-405 (Fig. 4) increased Ca infiltration between 25% and 50% and Triton X-100 and X-114 (Fig. 4) and Silwet L-77 and L-7604 (Fig. 5) enhanced infiltration by >50%. However, all of these surfactants were less effective at increasing Ca infiltration when mixed with the Ca infiltration solution in accord with findings that dissolved inor-

such as bitter pit and breakdown (Meheriuk and Moyls, 1989), while 800 to 1200 mg·kg⁻¹ DM is needed to reduce soft rot development and maintain firmness during storage (Conway et al., 1994a; Conway et al., 1994b). The 'Golden Delicious' fruit used in this study contained an endogenous Ca content of ≈210 mg·kg⁻¹ DM, a typical value for nontreated fruit but well below optimal levels for storage. While postharvest Ca treatments using high (103 kPa) pressure in combination with relatively

ganic salts decrease the solvation of surfactants particularly polyoxyethylene-containing surfactants and reduce surfactant solubility (or emulsion stability) in water (Tadros, 1995). As a surfactant and Ca mixture, only Triton X-100 and X-114 (Fig. 4) and Silwet L-77 and L-7604 (Fig. 5) retained the ability to enhance Ca infiltration. These four surfactants have in common a branched-chain hydrophobic moiety (Table 1) and are either dispersible (Triton X-100, Triton X-114, Silwet L-77) or soluble (Silwet L-7604) in water (OSi Specialties, Inc., 1995; Union Carbide Corp., 1993). Triton X-45, X-305, and X-405, effective as pretreatments, share these same characteristics (Union Carbide Corp., 1993). Tween 60 and 80, while soluble in water, have relatively long alkyl chains as the hydrophobic moiety (Table 1). Other surfactants tested with relatively long (Figs. 2 and 3) or short (Table 2) unbranched, alkyl chains as the hydrophobic moiety did not enhance Ca infiltration. Tween 80 and Triton X-100 have previously been shown to stimulate Ca infiltration into apples (Roy et al., 1996).

Only surfactants with HLB numbers >12 enhanced Ca infiltration. In addition, there was the general tendency for the surfactant with the strongest stimulatory effect on Ca infiltration within any particular polyoxyethylene-containing class of surfactants to have an HLB number between 12.4 and 14.5. Surfactants with HLB numbers between 12.4 and 14.5 would be polar enough to be at least dispersible in water yet nonpolar enough to be reversibly adsorbed on or into hydrophobic plant surfaces. We also found that surfactants with HLB numbers <6 inhibited Ca infiltration (Fig. 3). Reduced Ca infiltration might be expected with surfactants of a low HLB number if the latter are adsorbed in large quantities or if they transiently solubilize components of the waxy cuticle, blocking pathways within the lenticel for Ca infiltration. This hypothesis is in accord with the observations that Brij surfactants with HLB numbers <6 and CHAPS, which has a nonpolar surface, inhibited Ca infiltration (Table 2, Fig. 3), altered surface wax structure, and reduced the number of open lenticels on the fruit (Roy et al., 1996; R. Saffner, unpublished data).

The two organosilicone surfactants, L-77 and L-7604, were the best surfactants tested at augmenting Ca infiltration. Calcium infiltration was enhanced as the concentration of the organosilicone surfactants was increased (Fig. 5). This is in accord with findings of their enhanced concentration-dependent wetting of and spreading across plant surfaces and infiltration of aqueous agrochemical solutions through apertures on plant surfaces (Knoche, 1994). The conventional carbon-based Triton-series surfactants did not show a concentration-dependent enhancement of Ca infiltration nor have they been reported to show concentration-dependent effects on wetting, spreading, or infiltration through plant apertures at concentrations between 0.5 and 5.0 g·L⁻¹ used in this study. The effectiveness of organosilicone surfactants at augmenting Ca infiltration is probably also related to their superior ability to lower the surface tension of agrochemical solutions relative to carbon-based surfactants (Knoche, 1994). Regardless of the mechanisms involved in surfactant efficacy, Silwet L-77 and L-7604 were superior to other surfactants at enhancing Ca infiltration.

Because of their superior performance, organosilicone surfactants reduced the applied atmospheric pressure gradient needed to infiltrate Ca to levels considered sufficient to maintain fruit firmness and resist decay during storage. Silwet L-77 pretreatment at a concentration of 2 g·L⁻¹ reduced by ≈50% the applied atmospheric pressure needed to infiltrate Ca to levels considered sufficient to maintain fruit firmness and to resist decay during storage (Fig. 6). A similar effect may occur at lower concentrations of Silwet L-77 (Fig. 5).

The sequential use of selected surfactants and Ca treatments may offer a practical means of increasing Ca content of apples

while reducing the potential for surface injury to the fruit. In general, as the concentration of CaCl₂ in the treatment solutions is increased, injury to the fruit surface also increases (Conway and Sams, 1983). A surfactant pretreatment with L-77 negates the need to increase the concentration of CaCl₂ above 20 g·L⁻¹ in the treatment solutions to obtain optimal Ca levels in the fruit cortex, thereby reducing the potential for skin injury. As discussed above, surfactant pretreatment with L-77 also allows for the use of a low (34 kPa) applied pressure gradient to effect an optimal increase in Ca content of apple fruit (Fig. 6), reducing the potential for pressure gradient-related injuries to the fruit.

More research is needed to reduce the potential of fruit injury related to postharvest Ca treatments. Preliminary data indicates that sequential postharvest treatments with surfactant, a CaCl₂ solution (20 g·L⁻¹ concentration, 34 kPa), a water rinse, and a surface coating significantly reduces or eliminates skin injury of apple fruit (R. Saffner, unpublished data). Besides efforts to eliminate fruit injury, further research is needed to evaluate the relative phytotoxicities of surfactants useful in postharvest Ca treatments, the effect of washing adsorbed surfactants and Ca off the fruit surface following postharvest Ca treatments, the efficacy of these procedures on a commercial scale, and the effect, if any, on fruit flavor.

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