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STUDIES ON THE PROPERTIES OF ISOLATED TOMATO FRUIT CUTICLES: SELECTED CUTICULAR PHYSICOCHEMICAL CHARACTERISTICS AND CUTICULAR SORPTION AND DESORPTION OF A NONIONIC SURFACTANT

presented by

Peter Donald Petracek

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Horticulture

Major professor

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STUDIES ON
CUTICULA

STUDIES ON THE PROPERTIES OF ISOLATED TOMATO FRUIT CUTICLES: SELECTED CUTICULAR PHYSICOCHEMICAL CHARACTERISTICS AND CUTICULAR SORPTION AND DESORPTION OF A NONIONIC SURFACTANT

by

Peter Donald Petracek

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Department of Horticulture

1991

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ABSTRACT

STUDIES ON THE PROPERTIES OF ISOLATED TOMATO FRUIT CUTICLES: SELECTED CUTICULAR PHYSICOCHEMICAL CHARACTERISTICS AND CUTICULAR SORPTION/DESORPTION OF A NONIONIC SURFACTANT

by

Peter Donald Petracek

Physicochemical properties and surfactant sorption and desorption characteristics were determined for cuticular membranes (CM) enzymatically isolated from mature tomato fruit. Sorption of N_2 by both CM and dewaxed CM (DCM) was a linear function of pressure. Studies of cuticular rheology showed that the cuticle swelled in the presence of water. The rate of and extent to which swelling occurred was not affected by cuticular waxes or by surfactant. Response to a transient load suggested that elasticity and susceptibility to fracture were greater for cuticles that were hydrated or from which waxes had been extracted. The cuticle can be characterized as a viscoelastic polymer that is intercalated with waxes and whose physicochemical properties change in response to a plasticizing effect of water. CM rheology in aqueous solution was not affected by 1.0% Triton X-100 (TX-100). The sorption isotherm of TX-100 was characterized by two plateaus. Sorption of TX-100 was not reversible providing evidence for hysteresis. Hysteresis was apparent by the presence of buffer extractable and buffer non-extractable fractions. The buffer extractable fraction was not affected by pH of desorbing solution, but was drastically altered by NaCl and urea. Methanol was an effective desorbing solution. The buffer non-extractable fraction was readily removed by exchanging with surfactants of similar structure or by desorption with solvents less polar than water. Kinetic and thermodynamic studies demonstrated a weak temperature dependence for sorption and desorption processes. Rates of sorption and desorption increased with temperature, but activation energies were low. Diffusion coefficients calculated from sorption and desorption experiments agreed with those determined by steady state diffusion studies. Kinetic analysis suggest that sorption is a first order

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process at sorbate concentrations below the critical micelle concentration (CMC). At sorbate concentrations above the CMC, sorption may be limited by the number of sites or surfactant monomer concentration. The extent of sorption of TX-100 increased with temperature and, thus the process is entropy-driven. Desorption hysteresis was characterized by a decrease in the rate of desorption as the number of stepwise desorptions was increased. Partition coefficients increased with an increase in number of stepwise desorptions.

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Above all, I wish to thank my wife, Bridget, for her love and support.

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The journal-article format was adopted for this dissertation in accordance with departmental and university requirements. Section II was prepared and styled for publication in *New Phytologist*. Sections III and IV were prepared and styled for publication in *Plant Physiology*.

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INTRODUCTION

Foliar application of systemic agrochemicals is an effective but inefficient method of transferring an active ingredient (a.i.) from bulk solution to the plant. In practice, only a small percentage of the applied chemical reaches the reaction site. Consequently, (1) the producer applies unnecessarily high dosages of a.i. to achieve the desired response thereby increasing production cost and (2) the a.i. not retained by the plant may be a hazard to the applicator or a contaminant in the environment. By increasing the efficiency of transfer of foliar applied a.i. to the active site, chemical usage, production costs, and environmental contamination could be reduced.

The process of transferring the a.i. from solution to active site involves a complex sequence of events:

(1) Dispersion or dissolution of the a.i. in an aqueous carrier.

(2) Atomization of the spray solution and the transport of the droplets to the plant surface.

(3) Interaction of spray droplet and a.i. with the cuticle.

(4) Transfer of a.i. from droplet or deposit to the cuticle.

(5) Transfer of a.i. across the cuticle.

(6) Desorption of the a.i. from the cuticle and diffusion through the epidermal cell walls.

(7) Transport of a.i. through the plasmalemma into the cell or diffusion through the apparent free space.

(8) Eventually, entry into the vascular tissue and transport to other parts of the plant.

Accordingly, the efficiency of foliar application may be limited by one or more of these events.

The cuticle is the foremost barrier in the sequence of a.i. transport. The cuticular membrane (CM) is a protective covering of aerial parts of all terrestrial plants. It consists of a polyester matrix

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with associated waxes. The major constituents of the matrix are esterified long chain fatty acids and alcohols. The waxes, which are both embedded in the matrix and deposited on the outer morphological surface, are mostly long chain alkanes and alcohols. The hydrophobicity of these components restricts adsorption and subsequent penetration, particularly of polar molecules. Cuticular penetration is also impeded physically by the lack of sufficiently large pores through the membrane.

Surfactants are frequently used to enhance the efficiency of foliar applied chemicals. This enhancement may be due to increased water solubility of nonpolar chemicals, improved wetting of plant surfaces, and increased permeability of the cuticle. While some general principles of surfactant interactions with a variety of substrates are known, there is a lack of understanding of how surfactants associate with the plant cuticle.

Triton X-100 (TX-100, OP + 9.5 EO, α-[4-(1,1,3,3,-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-ethanediyl)) is a nonionic surfactant that is commonly used in agrochemical formulations. Recently, studies have focused on TX-100 interactions with plant cuticles.

First, TX-100 sorption by enzymatically isolated tomato fruit cuticles (Shafer and Bukovac 1987) has shown that:

(1) Cuticular sorption capacity plateaus for low surfactant concentration. However, this capacity increases for relatively high concentrations.

(2) Waxes in the cuticle significantly reduce surfactant sorption.

(3) pH in the acidic range has no effect on sorption.

Second, an examination of foliar uptake and translocation of surfactants (Silcox and Holloway 1986; Stevens and Bukovac 1987) and surfactant-induced phytotoxicity (Lownds and Bukovac 1988) has shown indirectly that TX-100 penetrates through the cuticle.

Third, studies with ^{14}C TX-100 have established directly that the surfactant diffuses through isolated cuticles (Petracek and Bukovac 1989), and that the removal of waxes and an increase in temperature both dramatically increase the permeability of the cuticle to the surfactant.

The objective of this dissertation was to gain a better understanding of the mode of action of

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surfactants. The research objectives focused on the physicochemical properties related to surfactant/cuticle interactions. Specifically, the experiments were designed to:

(1) Characterize selected physical and morphological properties of the cuticle and relate them to transport phenomena.

(2) Determine how two components of transport, sorption and desorption, are affected by surfactant concentration and environment.

(3) Develop an explanation of surfactant/cuticle interactions based on the thermodynamics and kinetics of sorption and desorption.

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SECTION I: BACKGROUND AND THEORY

This section provides a brief description of the plant cuticle and a review of pertinent principles of surfactant chemistry and the sorption process that have been used to interpret the data.

Physicochemical properties of the plant cuticle

The cuticular membrane (CM) is a thin polymer that covers all aerial plant organs. The CM serves as a barrier to protect the plant against excessive water loss, UV radiation, and invasion by pathogens and insects. While the physicochemical properties of the CM vary with plant maturity and species, many common characteristics exist (Martin and Juniper 1970; Cutler et al. 1982).

The CM is composed of a cutin matrix with waxes embedded in (cuticular) and deposited on (epicuticular) the matrix. The cutin consists largely of esterified hydroxylated fatty acids of which 10,16-dihydroxyhexadecanoic acid is the predominant component (Baker et al. 1982; Holloway 1982a). The waxes are comprised mostly of long chain alkanes, alcohols, aldehydes, and fatty acids with lesser quantities of triterpeniods and flavanoids. Trace amounts of polysaccharides and amino acids may also be present (Kolattukudy 1981; Baker et al. 1982; Holloway 1982a). Based on its constituents, the CM can be classified as a hydrophobic and nonreactive polyester with associated waxes. Its reactivity is diminished further since most carboxyl groups are esterified with hydroxylated fatty acids (Kolattukudy 1981). Nevertheless, CM of some species may have free epoxy groups available for covalent bonding (Riederer and Schönherr 1986; Shafer and Bukovac 1987).

While the morphology and related nomenclature of the cuticle are disputed, most researchers agree that the CM is essentially a layered structure (Holloway 1982b). In cross section, the CM appears to blanket the outer epidermal cell wall. In some species, pectic material of the subcuticular lamella

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is layered between the epidermal cell wall and the CM. This layer can be chemically or enzymatically degraded thus permitting isolation of the CM. The CM itself consists of the secondary cuticle (cuticular or cutinized layer), the primary cuticle (cuticle proper or cuticularized layer) with embedded waxes, and epicuticular wax from the innermost to outermost layer.

The precise chronology of CM development is unclear. During the growth of an epidermal cell, the primary cuticle apparently develops first. This layer remains flexible and expands with the enlargement of the underlying epidermal cell. According to one hypothesis, growth-induced stretching of the cuticular matrix stimulates monomer synthesis, insertion into the matrix, and polymerization. During the maturation of an epidermal cell, the secondary cuticle thickens, thus making the CM more rigid (Sargent 1976; Kolattukudy 1981). Wax precursors are thought to be located predominately in the primary cuticle (Sargent 1976). Here the precursors polymerize and either remain embedded in the matrix or are extruded to the matrix surface by some unknown mechanism. Once on the surface, waxes may acquire forms that vary from crystalline to amorphous (Holloway 1982b).

CM thickness varies from less than 0.25 μm for young tissue to several millimeters for some tropical plants. More commonly, leaf CM thicknesses are between 0.25 to 2 μm while the range for fruit CM is about ten-fold greater. The CM often projects between the anticlinal walls of adjacent epidermal cells to form wedge-like structures called cuticular pegs. In some instances CM development in mature fruit may be so extensive that the epidermal cells and some underlying cells become encased in cuticle (Esau 1977; Holloway 1982b).

Three physical characteristics are of particular interest with respect to the study of cuticular transport processes: (1) porosity, (2) polar pathways, and (3) mechanical properties.

First, the porosity of the cuticle may be classified by pore diameter. Large pores (> 1 μm), which extend across the CM, are associated with stomatal and other gas exchange structures (Miller 1983). These structures are absent in some CM, however, including the tomato fruit CM that were used in the experiments described in this dissertation. The potential effect of large pores on transport therefore will not be discussed. Macropores (> 50 nm diam.) and mesopores (2 - 50 nm diam.), which

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should be large enough to be seen by electron microscopy, are not evident in CM (Holloway 1982b). Micropores (< 2 nm diam.) in the CM have been examined by the diffusion of small polar organic molecules (Schönherr 1976). From these studies, CM micropores were determined to be about 1 nm in diameter. For comparison, an extended molecule of TX-100 is about 4 - 5 nm long and about 0.2 nm wide (Robson and Dennis 1977).

Second, the hydrophobicity of the CM may require that polar compounds permeate by way of polar pathways. Schönherr and Bukovac (1970) found that association of mercury with the CM is localized. Later, their studies of ion permeation showed that the CM acts like a highly crosslinked ion exchange polymer that is selective for Ca^{2+} over K^+ or Na^+ (Schönherr and Bukovac 1973). They suggested that the exchange capacity is dependent on both ion size and charge. Further studies found that large polar molecules do not readily penetrate the CM. This indicated that if a polar pathway exists, then they act as pores that exclude molecules by size (Schönherr 1976). In a related hypothesis, nonpolar compounds are soluble in a large portion of the CM and are not size excluded (Schönherr and Schmidt 1979). The existence of polar pathways, however, could not be verified by electron microscopic staining (Wilson and Sterling 1976).

Third, factors that affect mechanical properties often also affect the diffusive properties of polymers (Meares 1965; Ferry 1980). These factors include the polymer density, the presence of fillers and plasticizers in the polymer, and temperature. Hartley and Graham-Bryce (1980) suggested that cuticular mechanical attributes such as swelling are related to permeability. Still, the study of CM mechanical properties has been limited. One exception has been the recent analysis of the CM by high resolution ^{13}C-NMR that characterized the cuticle as a flexible net-like structure whose motion is constricted by numerous crosslinkages (Zlotnik-Mazori and Stark 1988).

The tomato fruit CM has been used as a model CM because it is strong, readily available, easy to isolate, and because it lacks large pores (thus permitting diffusion experiments), epicuticular wax fine structure, and other specialized structures. The tomato fruit CM is about 95 percent cutin matrix and 5 percent wax. The matrix of the mature tomato fruit CM is approximately 90 percent polymerized

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10,16-dihydroxyhexadecanoic acid. The remaining fraction consists of similar hydroxylated fatty acids. Both epicuticular and cuticular waxes are mostly hydrocarbons and fatty acids. Small amounts of long chain alcohols, esters, triterprenoids, and the phenolic naringenin are also associated with cuticular waxes (Baker et al. 1982).

Light microscopy of tomato fruit CM illustrates that the epidermal and some hypodermal cells may be fully encapsulated by the cuticle. The CM is about 4 -10 μm thick in the region between the epidermal cell and the outer morphological surface. Further, staining of the tomato fruit CM with a cationic dye (methylene blue) reveals regions of lower dye affinity in the cuticular pegs and above the anticlinal walls (Bukovac et al. 1990). Lastly, when viewed with transmission electron microscopy, the cutin matrix generally appears to be reticulate (Wilson and Sterling 1976).

Since the cuticle is largely amorphous, no sharp diffraction patterns are found using X-ray diffraction (Wilson and Sterling 1976). Sorption of water by the cuticle imparts longer, wide angle spacings, indicating that water causes the membrane to swell. Finally, both tomato fruit CM and dewaxed tomato fruit CM are only slightly birefringent, with the intense yellow pigmentation of the cuticle confounding analysis. Orientation of cuticular waxes may contribute to the rotation patterns, which parallel the cuticular plane in the tomato fruit CM.

Surfactant chemistry and activity

Most surfactants are amphipathic; that is, they are composed of hydrophilic and hydrophobic (lipophilic) moieties. Ionic surfactants, such as soap, normally consist of a charged hydrophile and a long chain alkane hydrophobe. Nonionic surfactants, such as those commonly used in agrochemical formulation, often consist of a hydrophile that is a monodispersed chain of repeating oxyethylene groups and a hydrophobe comprised of hydrocarbons and alcohols. The effect of surfactant composition and size on relevant physical properties has been reviewed by Rosen (1989). A brief discussion of surfactant solution properties that are more relevant to foliar penetration follows.

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oxygen and the positive dipoles of hydrogen. Although hydrogen bonds are weak and short-lived in comparison with ionic or covalent bonds, they nonetheless provide substantial potential for interaction among water molecules. The resulting network of water molecules is sometimes termed the "flickering structure of water." In pure aqueous solution, water molecules in the bulk phase (interior phase) have low potential energies because they can freely form hydrogen bonds with all surrounding molecules. In contrast, molecules at a surface have high potential energies because their interactions are limited to adjacent molecules at the surface and with the water in the bulk. The difference in potential energies between the molecules at the surface and those in the bulk is the surface free energy or the amount of work required to bring a molecule to the surface. Similarly, surface tension, or surface free energy per unit area (γ) is the amount of work required to increase the surface one unit area.

When a surfactant initially dissolves in an aqueous solution, the free energy of the system increases because the hydrophobe does not readily interact with water. The free energy of the system is subsequently reduced as surfactant molecules migrate from the bulk phase to the surface. At the surface, the surfactant becomes oriented such that the hydrophiles remain in solution while hydrophobes are excluded from solution. Once the hydrophobe moiety is out of solution, it can readily interact with other hydrophobic moieties. The process of exclusion of a hydrophobic compound or moiety from water and interaction of hydrophobic groups is sometimes termed "hydrophobic interaction" (Ben-Naim 1980; Attwood and Florence 1983; Rosen 1989).

This model of surfactant migration can be extended to many systems in which there is an interface between two phases. For example, in a system with a water/cuticle interface, the surfactant would be expected to migrate to the nonpolar cuticle where the hydrophobe becomes associated with the cuticle while the hydrophile remains associated with water.

Perhaps the most important characteristic of surfactants is their ability to reduce surface tension at low concentrations. Figure 1 presents a simple model of molecular interactions at an interface:

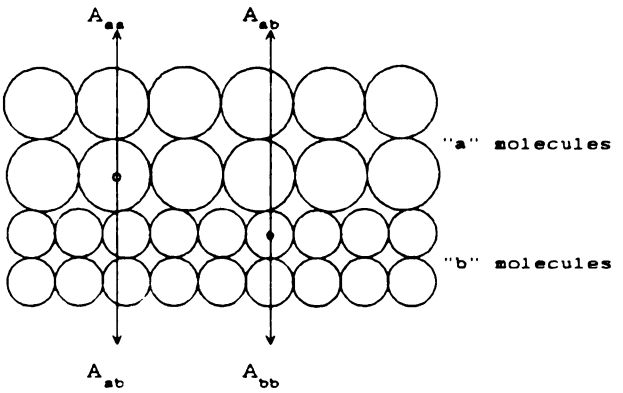

Figure 1. Molecular interactions at the interface of a two phase system (from Rosen 1989).

In a two phase system (*a* and *b*), A_a represents the increase in potential energy of the interfacial molecules over those in the bulk:

(1) $A_a = A_{aa} - A_{ab}$

where A_{aa} is the interaction energy of *a* molecules at the interface and in the bulk phase and A_{ab} is the interaction energy between molecules *a* and *b* across the interface. Note that A_{ab} is a term that contributes directly to the common observation that "likes dissolve likes." The increase in potential energy of *b* (A_b) is:

(2) $A_b = A_{bb} - A_{ab}$.

Thus, the total increase in potential energy or interfacial free energy (A_I) for the system is:

(3) $A_I = A_{aa} + A_{bb} - 2\,A_{ab}$.

A_I is the minimum amount of work required to create the interface. The interfacial free energy per unit area of the interface, or interfacial tension (γ_I) can be written as:

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where γ_a and γ_b are the surface free energies per unit area of *a* and *b* and γ_{ab} is the *a-b* interaction energy per unit area across the interface.

This equation provides a simplified, but useful way to explain the interaction of two phases. Below are examples of three relevant systems:

System 1: *a* interacts strongly with itself and *b* (e.g., water and methanol). A large γ_{ab} offsets a large γ_a, thus γ_I is small and the phases are miscible.

System 2: *a* interacts strongly with itself, but weakly with *b* (e.g., water and oil). γ_I will be large since γ_a is large and γ_{ab} is small. The large interfacial tension indicates that the phases are not miscible.

System 3: *a* is a gas and *b* is a liquid (e.g., air and water). The interactive forces of gas molecules generally are weak because they are spaced far apart and are capable of interacting with only weak dispersion forces. Therefore, γ_a and γ_{ab} are negligible and $\gamma_I = \gamma_b$.

In systems 2 and 3, immiscibility of the two phases is due to weak interaction between dissimilar molecules. Surfactant molecules, when added to a system with two immiscible phases, migrate to the interface between the phases. At the interface the hydrophobic portion of the surfactant interacts with the nonpolar phase while the hydrophilic portion interacts with the polar phase. The resulting "bridge" increases the γ_{ab} and thus reduces the interfacial tension. This explanation may also be valid for water/gas systems since gas molecules are nonpolar (Couper 1984; Rosen 1989).

An alternative view of surface tension reduction in aqueous systems is that surfactant molecules that accumulate at the interface do not interact with water as strongly as water interacts with itself. According to this model, surfactant acting as a water-structure breaker effectively reduces γ_b (Attwood and Florence 1983).

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As mentioned before, surfactants in aqueous solution tend to migrate and orient at the water-air interface with the hydrophobe oriented out of the solution. This adsorption and consequent reduction in surface tension are related as seen by Gibbs adsorption equation:

$$(5)\quad \Gamma = -\frac{1}{R\,T}\,\frac{d\gamma}{d\ln c}$$

where Γ is the excess surface concentration, c is the bulk surfactant concentration, R is the gas constant, and T is the absolute temperature. When the available sites at the surface become occupied (Γ_{max} is attained), the surfactant molecules associate with other surfactant molecules in the bulk phase of the solution. These individual surfactant molecules (monomers) orient such that the hydrophobes cluster to form a hydrophobic core while the hydrophiles are oriented to the solution. These aggregates of monomers are called micelles (Figure 2).

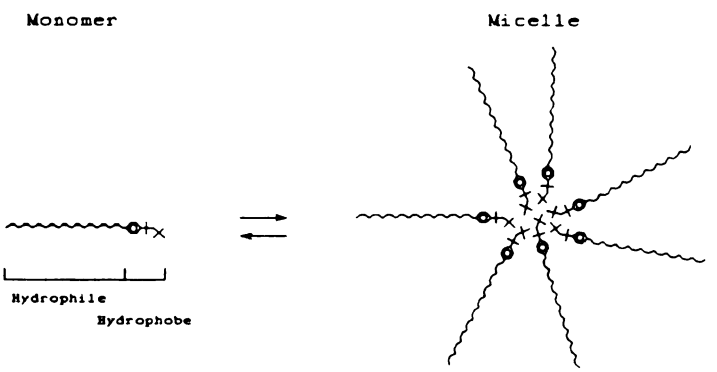

Figure 2. Micellization of a nonionic surfactant.

The critical micelle concentration (CMC) is the lowest concentration at which micelles form for a given surfactant/solvent system.

The shape and size of the micelle is determined by the characteristics of both the surfactant and the solvent. Triton X-100 (TX-100; α-[4-(1,1,3,3,-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-

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ethanediyl)) in aqueous solution, for example, forms relatively small oblate ellipsoidal micelles at concentrations near the CMC (Robson and Dennis 1977; Paradies 1980). Some surfactants form large lamellar sheets at high concentrations (Rosen 1989). At very high concentrations (> 50 percent w/v), the surfactant may gel to form a water-emulsifying network (Greenwald and Brown 1954).

The CMC marks a dramatic change in surfactant partitioning. Below the CMC the surfactant tends to adsorb to the interface. Above the CMC the excess surfactant monomers aggregate in solution. Since surface tension is dependent on Γ [eqn (5)], reduction in surface tension ceases at the concentration where Γ is maximized (CMC). A plot of log surfactant concentration vs. surface tension produces a curve with a sharp break coinciding with the CMC. Additionally, micelle formation causes abrupt changes in other solution properties such as detergency, conductivity, and osmotic pressure (Adamson 1982; Rosen 1989).

Factors other than concentration also affect surfactant behavior in aqueous solution. Since ionic and nonionic surfactants may react very differently to changes in the environment, this discussion focuses on nonionic surfactants with polyoxyethylene hydrophiles (polyethoxylate surfactants).

In solid state, the polyethoxy chain forms a helix such that the O-C-C-O units are *trans-gauche-trans* in conformation. However, O-C bonds are free to rotate in water. Consequently, the chain takes on random conformations (Matsuura and Fukuhara 1985). In aqueous solution, hydrogen bonds form between the two free electron pairs of the oxygen atom in the polyoxyethylene chain and the hydrogen of water. An increase in temperature decreases the strength of this interaction thus causing the dehydration of the hydrophile. Consequently, interaction increases among surfactant molecules thus favoring micelle formation. If dehydration of the hydrophile is extensive, the surfactant may become water insoluble and the solution appears turbid. The temperature at which this occurs is called the cloud point temperature (Rosen 1989).

When simple salts are added to an aqueous solution, the attracting forces among water molecules are enhanced. For solutions of polyethoxylate surfactants this increase in water structure reduces hydrophile hydration and promotes hydrophobe exclusion. As with an increase in temperature,

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In contrast to simple salts, urea is considered a "breaker" of water structure. Addition of urea in high concentration (> 1 M) causes a decrease in micellization. This presumably is due to an increase in the hydration of the hydrophile and reduction in the forces that exclude the hydrophobe (Rosen 1989). In related experiments, urea increased the cloud point of polyethoxylate surfactants (Han et al. 1989). This suggested that urea improved the hydration of hydrophile thus overcoming the effect of dehydration at higher temperatures.

For surfactants without readily dissociable protons (e.g., TX-100), solution properties are typically not affected by a change in pH. Regardless, solution pH may play a role in sorption and desorption if other components of the system are affected by hydrogen ion concentration (Couper 1984; Rosen 1989).

The effect of solvent composition on surfactant properties may be explained, in part, by changes in solvent-solute interaction energies (γ_{ab} from an earlier discussion). Previously, we noted that the unique properties of surfactants depend on the concurrence of hydrophobe exclusion from and hydrophile solubilization in water. In a solvent slightly less polar than water (e.g., methanol), solubility of the hydrophobe increases while that of the hydrophile decreases. As a result, the occurrence of phenomenon that depend on the amphipathic balance of forces such as micellization, may be reduced or eliminated (Rosen 1989). In very non-polar solvents (e.g., cyclohexane), the hydrophobe is solvent soluble and the hydrophile is excluded from the solvent. Thus, surfactant forms inverse micelles in which the hydrophile orientates towards the aggregate core (Kumar and Balasubramanian 1979).

Sorption isotherm analysis

So far, we have focused on intermolecular interactions in solvent-solute systems. Now we will discuss the effect of addition of a third component, the sorbent.

The term "sorption" is used to include material (sorbate) that is retained at the surface (adsorbed) and that penetrates and is retained in the interior (absorbed) of a substance (sorbent). In

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spite of its importance in many common processes such as catalysis and diffusion, the sorption process is not well understood. This section is intended to provide a brief review of several aspects of sorption pertinent to the tomato fruit CM system. General reviews of sorption, adsorption in particular, are found elsewhere (Kipling 1965; de Boer 1968, Hartley and Graham-Bryce 1980a and 1980b; Adamson 1982; Myers and Belfort 1984). Desorption theory is also covered briefly by these authors and is discussed more extensively by Beeby (1979).

The simplest model of sorption is that the sorbate molecule impinges, is retained by, and is released from a sorbent surface in a continuous sequence. The amount sorbed (σ) can be described by the equation:

(6) $\sigma = n \tau$.

In general n (number of molecules striking the sorbent per unit time per unit area) is dependent on the amount and velocity of sorbate. Tau (τ, residence time of the molecule on the surface) is dependent on the strength of the sorbate-sorbent intermolecular forces (de Boer 1968).

This model is valid for adsorption in a simple system, such as gas sorption to a metal surface. The parameters n and τ, although difficult to determine, sufficiently describe the intermolecular interactions of the two-component system. When a solvent phase is included, however, the description of the system becomes more complicated since all three components (sorbate, sorbent, and solvent) interact.

Knowledge of the interactions between all molecules of a sorption system may neither be possible nor necessary. Instead, most sorption research is conducted to answer questions about the forces that are most important to the system. One fundamental question is whether the sorbate-sorbent interaction is chemical (chemisorption) or physical (physisorption) sorption. Chemisorption occurs when sorbate and sorbent bond covalently, ionically, or metallically. These interactive forces are strong, thereby resulting in high sorption activation energies and irreversible sorption. Physisorption refers to

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processes where sorbate-sorbent interact through weak van der Waals (dispersion) forces such as dipole-dipole interaction or hydrogen bonding. Physisorption is usually a reversible process with relatively low sorption activation energies (Barrow 1979; Adamson 1982; Laidler 1987).

Typically, thermodynamic and/or kinetic studies are used to determine the strength and mechanism through which two entities interact. In sorption systems, however, several types of interactions may be occurring simultaneously. Therefore, additional approaches are necessary.

One useful alternative is to determine a sorption isotherm. Sorption isotherms are plots of the amount of sorbate remaining in the gas or solvent phase (x-axis) vs. the amount sorbed to a solid at equilibrium (y-axis) and at constant temperature. The sorption of a solute from solution has been classified into four types based on isotherm curve shape (Giles et al. 1960): (1) C curve - linear, (2) L curve - asymptotic and concave toward the x-axis, (3) S curve - sigmoidal, and (4) H curve - high affinity. Since the sorption of organic compounds to the cuticle is often described by C (linear) and L (Langmuir) isotherms (Bukovac et al. 1990), these two isotherm types will be stressed in the following sections (Figure 3).

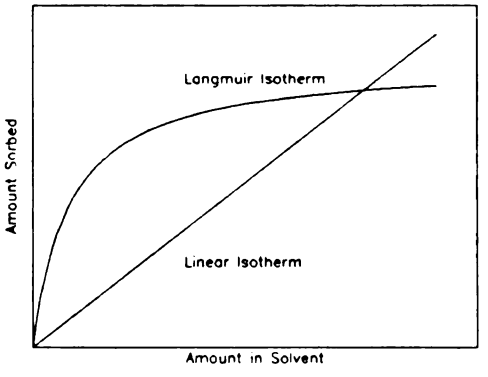

Figure 3. Examples of linear and Langmuir isotherms.

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Linear isotherms

For linear isotherms, the amounts of sorbate in solvent and sorbed at equilibrium are directly proportional. The most common explanation of the linear isotherm is the constant partitioning theory. This theory describes sorption as the partitioning of a sorbate (A) between the solvent (A_{solv}) and sorbent (A_{sorb}) phases.

(7) $A_{solv} \rightleftharpoons A_{sorb}$.

The mass balance of this process is:

(8) $A_{total} = A_{solv} + A_{sorb}$

where A_{total} is the total amount of sorbate in the sorption system. At equilibrium, the partition coefficient K is defined as:

(9) $$K = \frac{A_{sorb}/Wt}{A_{solv}/Vol}$$

where Wt is the weight of the sorbent and Vol is the volume of solvent. By rearranging eqn (9) we get:

(10) $A_{sorb}/Wt = K\, A_{solv}/Vol$.

Eqn 10 simply restates that for a linear isotherm, the y-intercept is zero (nothing is sorbed at concentration of zero) and the slope of the line K is constant for all concentrations. Under restricted circumstances, a linear sorption isotherm suggests that Henry's Law is obeyed. The partition coefficient, under these conditions, is termed Henry's constant (Adamson 1982).

We would like to express both A_{solv} and A_{sorb} in terms of the constants A_{total}, K, Wt, and Vol.

Solving eqn (9) for A_{so}

(11) $A_{sorb} = \frac{A_{solv}}{V}$

Substituting eqn (11) in

(12) $A_{solv} = \frac{A}{1 + K}$

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Solving eqn (9) for A_{sorb} gives:

$$(11)\quad A_{sorb} = \frac{A_{solv}\ Wt\ K}{Vol}\ .$$

Substituting eqn (11) into eqn (8) and solving for A_{solv} gives:

$$(12)\quad A_{solv} = \frac{A_{total}}{1 + K\ Wt/Vol}\ .$$

By substituting eqn (12) into eqn (11) and solving for A_{sorb} we obtain:

$$(13)\quad A_{sorb} = \frac{A_{total}\ K\ Wt/Vol}{1 + K\ Wt/Vol}\ .$$

Theoretically, if K is known for sorbate in a given solvent-sorbent system, the exact amount of sorbate in each phase can be calculated by equations (12) and (13).

The above derivation can be used to demonstrate the effect of sorbent heterogeneity on sorption. If the sorbent is composed of n classes of sorption site strengths, the sum of the amounts sorbed by each class is the total amount sorbed:

$$(14)\quad A_{sorb} = A_{sorb\ 1} + A_{sorb\ 2} + \ldots = \sum_{i=1}^{n} A_{sorb\ i}\ .$$

The amount sorbed to any class of sites can be expressed in terms of A_{solv} and K assuming (a) there is no interference with sorption among site classes and (b) the number of sites of any class is not

limiting. Combining eq

(15) $A_{sorb} = \frac{A_{solv}}{V}$

Similarly, by combining

(16) $A_{sorb} = \frac{}{1 + W}$

and:

(17) $A_{sorb} = \frac{A_{total}}{1 + W}$

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equation into eqn (12):

(18) $A_{solv\,1} = \frac{A_{total}}{(1 + K}$

limiting. Combining eqns (11) and (14) yields:

$$(15)\quad A_{sorb} = \frac{A_{solv}\ Wt\ K_1}{Vol} + \frac{A_{solv}\ Wt\ K_2}{Vol} + \ldots = \frac{A_{solv}\ Wt \sum_{i=1}^{n} K_i}{Vol}\ .$$

Similarly, by combining eqn (14) with eqns (12) and (13) we obtain eqns (16) and (17), respectively:

$$(16)\quad A_{sorb} = \frac{A_{total}}{1 + Wt/Vol \sum_{i=1}^{n} K_i}$$

and:

$$(17)\quad A_{sorb} = \frac{A_{total}\ Wt/Vol \sum_{i=1}^{n} K_i}{1 + Wt/Vol \sum_{i=1}^{n} K_i}\ .$$

Thus, partitioning of a sorbate between a solvent and a heterogeneous sorbent can be described by relatively simple equations.

Desorption can also be explained by the constant partition theory. After sorption, the sorbate solution is discarded. The total amount of sorbate in the system during desorption is equal to the amount present in the sorbent at sorption equilibrium. At desorption equilibrium, the amount of sorbate in solvent ($A_{solv\ 1}$) can be found by setting A_{total} to A_{sorb} in eqn (13) and substituting this equation into eqn (12):

$$(18)\quad A_{solv\ 1} = \frac{A_{total}\ K\ Wt/Vol}{(1 + K\ Wt/Vol)^2}\ .$$

Likewise, the amount of

(19) $A_{sorb\ 1} = \frac{A_{total}}{(1 +$

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Likewise, the amount of sorbate in the sorbent can be found by a similar substitution:

$$(19)\quad A_{\text{sorb 1}} = \frac{A_{\text{total}}\,(K\ \text{Wt/Vol})^2}{(1 + K\ \text{Wt/Vol})^2}\ .$$

This series can be expanded for serial desorptions. The total amount of sorbate in the system for each desorption step is equal to the amount present in the sorbent at equilibrium of the previous desorption. Thus, for x desorptions, the amount of sorbate in either phase can be determined:

$$(20)\quad A_{\text{solv x}} = \frac{A_{\text{total}}\,(K\ \text{Wt/Vol})^x}{(1 + K\ \text{Wt/Vol})^{x+1}}$$

and:

$$(21)\quad A_{\text{sorb x}} = \frac{A_{\text{total}}\,(K\ \text{Wt/Vol})^{x+1}}{(1 + K\ \text{Wt/Vol})^{x+1}} - \frac{A_{\text{sorb}}\,(K\ \text{Wt/Vol})^x}{(1 + K\ \text{Wt/Vol})^x}\ .$$

In principle, a plot of the number of stepwise desorptions vs. the logarithm of the amount sorbed should be linear with slope dependent on the partition coefficient. Since desorption and extraction processes are similar, it is then not surprising that eqn (21) is analogous to the equation that describes two-phase extractions (Skoog and West 1979).

Finally, if sorption is a completely reversible process, then sorption and desorption isotherms should be described by the same equations. In theory, the partition coefficient of sorption (eqn (9)) should equal that of desorption (eqn (21) divided by eqn (20)). In practice, this is not always true. When sorption and desorption isotherms are not coincidental, the curves are termed "non-singular" and the process "hysteretic." Sorption hysteresis has been shown for sorbents that are microporous or polymeric. Hysteresis requires an irreversible event to occur during sorption (Kipling 1965). This topic

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Langmuir isotherms

The constant partitioning theory assumes that the number of sites available for sorption is infinite. As a result, the complications due to the site filling process are disregarded. When the amount sorbed is not linearly related to the solvent concentration but approaches an asymptote, we must consider a sorption model in which the number of sites is finite. A model frequently used is Langmuir's equation of adsorption.

The Langmuir model was originally developed to explain the adsorption of gases to ideal surfaces and describe the formation of a monolayer. The equation has been subsequently derived several ways and has been applied to many sorption systems (Adamson 1982). The derivation in this section was generated to permit comparison with the constant partitioning theory for the linear isotherms.

By Langmuir's theory, we assume that: (1) the number of sites is finite, (2) the binding strengths of these sites are equal and not influenced by molecules already sorbed, (3) sorption is reversible, and (4) no multilayers are formed (de Boer 1968; Adamson 1982). The maximum number of sites available for the sorption of sorbate A ($A_{sorb\ max}$) is the sum of occupied (A_{sorb}) and unoccupied ($Site_{unoccupied}$) sites:

$$(22)\quad A_{sorb\ max} = Site_{occupied} + Site_{unoccupied} = A_{sorb} + Site_{unoccupied}\ .$$

The relationship between occupied and unoccupied sites is:

$$(23)\quad A_{solv} + Site_{unoccupied} \underset{k2}{\overset{k1}{\rightleftharpoons}} A_{sorb}$$

where k_1 and k_2 are the rate constants for sorption and desorption, respectively. Note that this process

is similar to that described by eqn (7) with the addition of unoccupied sites as an added variable. The rate equations are:

(24) Rate of sorption = k_1 [A_{solv}] [$Site_{unoccupied}$]

and:

(25) Rate of desorption = k_2 [A_{sorb}]

where [A_{solv}] and [A_{sorb}] are the concentrations of sorbate A in the solvent and sorbent phases, respectively, and [$Site_{unoccupied}$] is the concentration of unoccupied sites. At equilibrium, the rate of sorption equals the rate of desorption. Therefore:

(26) k_1 [A_{solv}] [$Site_{unoccupied}$] = k_2 [A_{sorb}]

or:

$$(27)\quad \frac{k_1}{k_2} = \frac{[A_{sorb}]}{[A_{solv}]\,[Site_{unoccupied}]} = b$$

where b is an affinity constant. Thus:

$$(28)\quad b = \frac{[A_{sorb}]}{[A_{solv}]\,([A_{sorb\ max}] - [A_{sorb}])} = \frac{[A_{sorb}]}{[A_{solv}]\,[A_{sorb\ max}] - [A_{solv}]\,[A_{sorb}]}\ .$$

Multiplying both sides by the denominator yields:

(29) [A_{sorb}] = b ([A_{solv}] [$A_{sorb\ max}$] - [A_{solv}] [A_{sorb}]) .

A form of Langmuir's equation is found by multiplying eqn (29) through by b and solving for $[A_{sorb}]$:

$$(30)\quad [A_{sorb}] = \frac{b\,[A_{sorb\ max}]\,[A_{solv}]}{1 + b\,[A_{solv}]}\ .$$

At low concentrations, the $b\,[A_{solv}]$ term is negligible. The amount sorbed is then linearly related to the concentration and is dependent on the affinity (b) and the number of sites available for sorption ($[A_{sorb\ max}]$). At higher concentrations, the $b\,[A_{solv}]$ term becomes significant and the amount sorbed approaches the number of sites available. Note that the fraction of sites occupied (θ) can be found by dividing eqn (30) by $[A_{sorb\ max}]$:

$$(31)\quad \theta = \frac{[A_{sorb}]}{[A_{sorbmax}]} = \frac{b\,[A_{solv}]}{1 + b\,[A_{solv}]}\ .$$

One application of Langmuir's equation is the determination of surface area from a sorption isotherm. To do this, a form of Langmuir's equation is used to calculate the number of molecules required to form a monolayer of sorbate molecules on the sorbent surface. By dividing eqn (30) by $[A_{solv}]$ and inverting we obtain a Langmuir plot:

$$(32)\quad \frac{[A_{solv}]}{[A_{sorb}]} = \frac{1 + b\,[A_{solv}]}{b\,[A_{sorbmax}]} = \frac{1}{b\,[A_{sorbmax}]} + \frac{[A_{solv}]}{[A_{sorbmax}]}\ .$$

A Langmuir plot of $[A_{solv}]$ vs. $[A_{solv}]/[A_{sorb}]$ gives a slope of $[A_{sorb\ max}]$ and a y-intercept of $b/[A_{sorb\ max}]$. By assuming that $[A_{sorb\ max}]$ represents coverage of the entire surface and by knowing the area occupied by each molecule (σ_a), surface area (S.A.) of the sorbent can be calculated:

$$(33)\quad \text{S.A.} = [A_{sorbmax}]\,\sigma_a\,N_o$$

where N_o is Avogadro's number. For surfactants, σ_a is derived from the number of molecules in a monolayer at the liquid-air interface (eqn (6): Γ_{max}) (Adamson 1982).

Surface area determination by Langmuir plots should be interpreted cautiously. The Langmuir theory originally was derived as a mechanistic explanation of adsorption of gas molecules to homogeneous surfaces and made no provisions for such complications as pore filling or absorption. Fortunately, the success of the theory in determining surface area depends not on the mechanism of sorption, but on the formation of a molecular monolayer.

Application of Langmuir's equation to surfactant sorption data for surface area determination requires further consideration. Typically, surfactant sorption reaches a plateau slightly above the CMC regardless of surfactant or sorbent (Clunie and Ingram 1983). The resulting sorption isotherm is usually explained by the sorption site filling model. This interpretation may be complicated for surfactants, since micelles, which form at concentrations above the CMC, could act as a third phase. By an alternative model, the third phase would compete with the sorbent and solvent phases for surfactant molecules, thus producing an asymptote above the CMC on the sorption isotherm (Kipling 1965).

Langmuir type adsorption is in some respects similar to hormone receptor and simple enzyme binding. Although hormone receptor and enzyme binding are site specific, all three processes are analyzed as reversible reactions that are first order with respect to the amount of sorbate (substrate) and the number of available sorbent sites. For example, Scatchard plot analysis, a method used to measure binding affinity and capacity, is a simple rearrangement of Langmuir's equation. Scatchard's equation is found by dividing both sides of eqn (29) by $[A_{solv}]$ and multiplying through by b:

$$(34)\quad \frac{[A_{sorb}]}{[A_{solv}]} = b\,[A_{sorbmax}] - b\,[A_{sorb}]\ .$$

Langmuir's equation can also be transformed into a form of the Eadie-Hofstee equation (Kinniburgh 1986). However, analyzing adsorption kinetics as a simple enzymatic reaction may be inappropriate. The rate equation for a one-substrate enzymatic reaction, the Michaelis-Menton equation, is derived for

a two-step process. The substrate binds to the enzyme in the first step and is converted to a new compound in the second (Creighton 1984). By analogy, adsorption consists of only the first step. Still, Jennissen (1986) found that protein-Sepharose adsorption kinetics fit the Michaelis-Menton rate equation and suggested that in this case adsorption was a two-step process.

Combination linear and Langmuir isotherms

To this point, we have examined linear isotherms using the constant partitioning theory and asymptotic isotherms using Langmuir's theory. We now focus on how the two theories may be combined to: (1) define the effects of surface heterogeneity on sorption, and (2) provide an alternative interpretation of the linear sorption isotherm.

Langmuir's theory assumes that the binding strengths of all sites on the sorbent are equal. The assumption of such homogeneity is perhaps questionable even for ideal surfaces. Heterogeneity may be attributed not only to physical imperfections and chemical impurities, but also the non-specific nature of sorption. That is, all possible sorption sites are not identical. In turn, their respective binding strengths may also vary. When Langmuir's theory is applied, heterogeneity may not be a problem because the various affinities may be compensated for by their respective numbers of sites. If the sorbent consists of a few sites with high affinity and many sites with low affinity, however, the sorption isotherm may appear somewhat asymptotic at low concentrations and linear at high concentrations. Vieth and Sladek (1965) suggested this "dual sorption" type of isotherm is simply a mathematical summation of linear and Langmuir isotherms for the two types of sites.

A more common alternative for describing sorbent heterogeneity is Freundlich's equation:

$$(35)\quad [A_{sorb}] = k\,[A_{solv}]^{1/n}$$

where k and n are empirical constants that are related to sorbent capacity and sorption intensity, respectively (Kipling 1965; Adamson 1982). Although Freundlich's equation conforms well to data for

many sorption systems, the constants are useful for comparison only among similar systems.

The properties of linear and Langmuir isotherms were combined by Giles et al. (1974) to provide an alternate explanation to linear sorption isotherms. The constant partition theory requires that the number of sorption sites be unlimited. Giles et al., however, postulated that there are a finite number of sites available for sorption as assumed in Langmuir's theory. They also suggested that the sorbent becomes "unzippered" by the sorption of a sorbate molecule, thus creating more new available sites. Consequently, $[A_{sorb\ max}]$ must increase by an expansion factor (B) with increasing concentration of sorbate in the solvent:

$$(36)\quad [A_{sorbmax}] = [Site_o]\ (1 + B\ [A_{solv}])$$

where $[Site_o]$ is the concentration of sorption sites available at zero concentration. Substituting eqn (36) into eqn (30) (Langmuir's equation) gives:

$$(37)\quad [A_{sorb}] = \frac{b\ [Site_o]\ (1 + B\ [A_{solv}])\ [A_{solv}]}{1 + b\ [A_{solv}]}\ .$$

The derivation of this hypothesis can be extended to determine the value of B. We can describe the number of occupied sites by combining eqn (22) and eqn (36):

$$(38)\quad [A_{sorbmax}] - [Site_{unoccupied}] = [Site_o]\ (1 + B\ [A_{solv}]) - [Site_{unoccupied}] = [A_{sorb}]$$

Giles et al. (1974) assumed that the number of unoccupied sites remained constant ($Site_{unoccupied} = Site_o$), thus eqn (38) becomes:

$$(39)\quad [A_{sorb}] = [Site_o] + [Site_o]\ B\ [A_{solv}] - [Site_o] = [Site_o]\ B\ [A_{solv}]\ .$$

By setting eqn (37) equal to eqn (39), we find that B = b. Hence,

(40) $[A_{sorb}] = [Site_o]\ b\ [A_{solv}]$.

By this hypothesis of sorbent expansion, the slope of the linear isotherm is a product of affinity and the number of unoccupied sites.

A comparable derivation of a linear isotherm from Langmuir's equation may be made for a model in which the affinity, rather than the number of accessible sites, changes with concentration. In this case:

$$(41)\quad b = \frac{b_o}{1 - b_o\,[A_{solv}]}$$

where b_o is the affinity between sorbate and sorbent at zero concentration. This equation indicates that affinity increases with concentration. The models for either accessibility or affinity changes with concentration provide a basis for understanding other concentration-dependent sorption phenomena such as hysteresis.

Gas sorption

The sorption of simple gases is mentioned in this discussion of solute sorption for two reasons. First, early theory of adsorption, such as that of Langmuir, was derived for gases. Second, gas sorption can be used to characterize some physicochemical properties of a sorbent (Adamson 1982; Gregg and Sing 1982).

Brunauer et al. (1940) identified five types of adsorption isotherms for gases:

Type I: Characteristic of non-porous surfaces. A Langmuir isotherm in which a monolayer is filled.

Type II: Characteristic of a surface with micropores (pores that are the size of or slightly smaller than the sorbate). Essentially a Langmuir isotherm at low pressure. All

pores are filled and multilayers are formed at high pressures.

Type III: Characteristic of a system in which molecular interactions result in cooperative sorption. This is exemplified by water sorption in which multilayers are formed at a critical pressure.

Type IV: Characteristic of a surface with mesopores (pores that are about the same size or slightly larger than the sorbate). Similar to Type II sorption except a second sorption maximum (plateau) is reached at high concentrations.

Type V: Similar to Type III sorption except a sorption maximum is reached at high pressures.

The BET (Brunauer, Emmett, and Teller) theory of adsorption describes adsorption as the summation of all adsorption events regardless of affinity or order in which they occur (Brunauer et al. 1938). Unlike Langmuir's theory, multilayer formation is considered in the analysis of the isotherm. One important application of the BET theory is to determine surface area of a solid. This is done by calculating the number of molecules in a monolayer and determining the surface area based on the area occupied by each molecule. Consequently, the validity of application depends on monolayer formation (Types I, II, and IV) (Adamson 1982; Gregg and Sing 1982). Sorbate porosity may be calculated from gas adsorption data using the Kelvin equation. This equation relates the amount adsorbed for a given pressure to the number of pores of a given radius. Gregg and Sing (1982) suggest that porosity analysis using the Kelvin equation is valid only for sorbents with Type IV sorption isotherms.

›rption/desorption kinetics and thermodynamics

Sorption/desorption kinetics and thermodynamics are studied to: (1) provide fundamental ⁻mation about the mechanisms and forces associated with sorbate/sorbent interactions, and (2) ·mine permeation properties. In this dissertation, sorption/desorption kinetics and thermodynamics been interpreted, in part, by theories used for analyzing simple chemical reactions. This approach ·een criticized largely because it oversimplifies what may be a series of complex events. However,

the alternatives are not viable because they either complicate the theory without alleviating the fundamental problems (Skopp 1986) or can not be readily applied to a surfactant/polymer system (Grunze and Kreuzer 1987).

Kinetics

The rates of sorption and desorption can be analyzed by rate equations derived from several models. The components of the system determine which model is appropriate. In general, the interaction of sorption/desorption is either predominantly (1) adsorption or (2) absorption and the rate of interactive process is limited by either (1) diffusion or (2) the interaction itself. Consequently, several fundamental models of sorption can be hypothesized.

The simplest model is that of adsorption in which diffusion is not limiting. A general reaction for the sorption/desorption process can be written as:

$$(42)\quad A_{solv} + A_{solv} + \cdots \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_{sorb} + A_{sorb} + \cdots$$

where k_1 and k_2 are the rate constants for sorption and desorption, respectively. This equation describes sorption/desorption as a reversible process or a pseudo-reaction. The rate of reaction for an irreversible process, is:

$$(43)\quad -\frac{d[A]}{dt} = k\,[A]^n$$

ere [A] is the concentration of the driving force ([A_{solv}] for sorption and [A_{sorb}] for desorption), /dt is the change in driving force with time (t), k is the rate constant for sorption or desorption, the exponential term n is the order of reaction or molecularity. Note that if the process is first r (n=1), eqn (43) effectively describes simple mass transfer of a compound from one phase to her (Cussler 1988).

The confounding effect of sorption/desorption reversibility is minimal when the amount of product is small, since the probability of "back reaction" is low. Therefore, the initial rate of reaction ($d[A]_o/dt$) can be used to determine the order of reaction. Eqn (43) is linearized by converting to logarithms:

$$(44)\quad \ln -\frac{d[A]_o}{dt} = \ln k + n \ln [A]_o \ .$$

The order of reaction is obtained from the slope and the rate constant from the y-intercept of a plot of $\ln [A]_o$ vs. $\ln (-d[A]_o/dt)$. The rate constants for all concentrations can now be obtained since the order of reaction is known.

As sorption or desorption equilibrium are approached, both forward and reverse processes occur. The processes are described by a reversible first order reaction:

$$(45)\quad A_{solv} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_{sorb}$$

and a rate equation that accounts for both forward and reverse processes:

$$(46)\quad \frac{d[A]}{dt} = - k_1 [A] + k_{-1} [B]$$

In this case, [A] is the driving force, [B] is the product, and k_1 and k_{-1} are the forward and reverse rates of reaction, respectively. Integration yields:

$$(46)\quad \ln \frac{[A] - [A]_\infty}{[A]_o - [A]_\infty} = k\ t$$

where $[A]_\infty$ is the concentration of A at equilibrium and k is the sum of k_1 and k_{-1}. For reversible, first-

order processes that are limited by the rate of reaction rather than diffusion, plots of t vs. $\ln(([A]-[A]_\infty)/([A]_0-[A]_\infty))$ are linear with slopes equaling the rate constant (Shoemaker et al. 1981; Laidler 1987).

Sorption and desorption may be controlled by diffusion for both adsorbing or absorbing systems. If sorption is limited to surface events (adsorption), boundary layers, which form near the surface of the sorbent in poorly-stirred systems, may limit sorption/desorption. As a result sorbent diffusion through unstirred layers may be slow relative to the rates of forming sorbate-sorbent interactions. If the sorbate penetrates the sorbent (absorption), diffusion may also regulate sorption/desorption processes. In these cases sorption/desorption kinetics may be more meaningfully analyzed by Fick's 2nd law of diffusion which relates sorbate concentration in the sorbent to position and time. A "Fickian" system is one in which a plot of the fraction of material sorbed or desorbed vs. the square root of time is linear through the time when at least one half of the material is sorbed or desorbed ($t_{1/2}$). For homogeneous sorbents in which partition and diffusion coefficients are not concentration dependent, the diffusion coefficient (D) can be determined:

$$(47)\quad D = \frac{0.049\ l^2}{t_{1/2}}$$

where l is the thickness of the sorbent (Crank 1975; Rogers 1985; Cussler 1988).

The above solutions describe sorption/desorption kinetics for relatively simple systems. Complications to the interpretation of sorption/desorption kinetics data, such as chemical reactions and sorbent heterogeneity, are common but beyond the scope of this introduction (see Crank and Park 1968; Hopfenberg 1974; Crank 1975; Cussler 1988).

Lastly, the effect of temperature on the rate of sorption or desorption is determined by plotting

the data (1/temperature vs. ln k) to fit the Arrhenius equation:

$$(45)\quad \ln k = -\frac{E_a}{R\,T} + \ln C$$

where E_a is the activation energy and C is the pre-exponential factor (Shoemaker et al. 1981; Laidler 1987). For polymer sorbents, the activation energy of sorption/desorption is hypothetically the amount of energy required to create a hole through which the sorbate can diffuse. Additionally, the pre-exponential, an index of the degree of entropy, may indicate the amount of polymeric side chain movement (Crank and Park 1968; Hopfenberg 1974).

Thermodynamics

We begin by assuming that sorption and desorption processes are reversible and first order with respect to the amount of sorbate: (1) in solution for sorption or (2) associated with the polymer for desorption:

$$(7)\quad A_{solv} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_{sorb}$$

This reaction implies that constant partitioning is occurring and that the number of unoccupied sites is not limiting. First-order rate equations can be written for this process:

$$(47)\quad \text{Rate of sorption} = k_1\,[A_{solv}]\ .$$

and:

$$(48)\quad \text{Rate of desorption} = k_2\,[A_{sorb}]\ .$$

Note that in comparison with the sorption rate equation for asymptotic (Langmuir) partitioning [eqn

(24)], the sorption rate equation for constant partitioning does not include the term for concentration of unoccupied sites. Desorption rate equations, however, are identical for asymptotic and constant partitioning [cf. eqn (25)].

At equilibrium, the sorption and desorption rates are equal:

$$(49)\quad k_1 [A_{solv}] = k_2 [A_{sorb}] .$$

Since k_1 and k_2 are constants, their ratios are constant:

$$(50)\quad K = \frac{k_1}{k_2} = \frac{[A_{sorb}]}{[A_{solv}]}$$

where K is the equilibrium coefficient [cf. eqn (9)]. In dilute solutions K is equal to the ratio of chemical activities. Therefore, the change in Gibbs free energy (ΔG) of the system can be written as:

$$(51)\quad \Delta G = - R T \ln K .$$

When the affinity of the sorbate is greater for sorbent than solvent, $K > 1$ and ΔG is negative.

Further, ΔG for a system can be expressed in terms of changes in enthalpy (ΔH) and entropy (ΔS):

$$(52)\quad \Delta G = \Delta H - T \Delta S .$$

Substituting eqn (51) into eqn (52) gives:

$$(53)\quad \ln K = -\frac{\Delta H}{R T} + \frac{\Delta S}{R} .$$

From eqn 53, note that a plot of 1/T vs. ln K yields ΔH and ΔS (Barrow 1979; Hartley and Graham-

Bryce 1980b; Riederer and Schönherr 1986).

Eqns 51, 52, and 53 summarize the equilibrium energetics of a system. Several generalizations follow:

(1) The extent to which a reaction occurs (K) depends on the degree to which the reaction reduces the free energy (G) of the system.

(2) Negative ΔH values, representing release of heat, contribute favorably to reducing the free energy of a system. Positive ΔS values, representing increased entropy, also contribute favorably to reducing the free energy of a system. Consequently, a reaction can be driven by sufficiently large negative ΔH values and/or positive ΔS values.

(3) As ΔH approaches zero, the apparent influence of temperature on partitioning becomes increasingly less.

The energetics of sorption and desorption also can be viewed in terms of these equations. These relationships are useful in the following discussion on the effect of temperature on sorption. If sorption decreases with increasing temperature, ΔH is negative. An example of this is gas adsorption. When gas molecules such as N_2 and He adsorb to a surface, they tend to form weak exothermic (negative ΔH) interactions with the surface. At the same time adsorption reduces the entropy (negative ΔS) or freedom of motion for the sorbate. Gas adsorption occurs because the enthalpy contribution is greater than the opposing entropy contribution. This example of enthalpy-driven adsorption is sometimes termed "classic adsorption" (Kipling 1965; Laidler 1987). Sorption of naphthaleneacetic acid (NAA) and 2,4-dichlorophenoxyacetic acid (2,4-D) by cuticles are also examples of enthalpy-driven sorption.

If sorption increases with increasing temperature, ΔH is positive. An endothermic process such as this also can proceed spontaneously (ΔG is negative) if a positive entropy contribution predominates over the enthalpic contribution. Typically, sorption is associated with a decrease in entropy due to the loss in sorbate mobility. However, increased entropy during sorption may occur if solvent molecules associated with either sorbate or sorbent are released during the process. For instance, sorption of methylene blue by the cuticle may be driven by entropy gained due to dehydration of sorbate or sorbent

(Bukovac et al. 1990).

While the sorption/desorption thermodynamics constants determined by the above method provide indications of the strength of sorbate-sorbent interactions, their utility is limited by several complicating factors. First, the process initially considered for the derivation of the thermodynamics constants (eqn 7) focuses on movement of the sorbate between solvent and sorbent phases. However, eqn 7 does not consider potentially important interactions such as those between solvent molecules and the sorbent. If solvent interactions are included in the process, an alternative reaction for sorption can be rewritten:

(54) Sorbate-Solvent + Solvent-Sorbent = Sorbate-Sorbent + Solvent-Solvent

This reaction is the sum of four interactions:

(55a) Sorbate-Solvent = Sorbate + Solvent

(55b) Solvent-Sorbent = Solvent + Sorbent

(55c) Sorbate + Sorbent = Sorbate-Sorbent

(55d) Solvent + Solvent = Solvent-Solvent

By Hess's Law, thermodynamic constants determined for the entire process are the sum of the values r the individual processes. Therefore, temperature affects the overall process not only through ption (eqn 55c), but also solubilization (eqn 55a) and the formation of solvent-sorbent and solvent- ent complexes (eqns 55b and 55d, respectively). This complicates the interpretation of sorption nodynamics. For instance, sorption of stearic acid from benzene to nickel has been attributed to nbination of weakening of sorbate-sorbent interaction and an increase in sorbate-solvent solubility ling 1965). Note that sorbate-sorbate, sorbent-sorbent, and sorbate-solvent-sorbent interactions lly are not considered in the sorption thermodynamics because they typically are weak ($\Delta H \approx 0$).

Interaction among surfactant molecules may be substantial and could contribute to sorption or desorption thermodynamics. Surfactant hydrophobes might form weak exothermically favorable interactions by self-association (Tamamushi 1983; Rosen 1989).

Second, eqn 51 relates the concentrations of sorbate in solution and sorbent with the change in free energy. In theory, this relationship is valid only for ideal solutions (i.e. sorbate concentration is proportional to activity). For concentrated solutions, activity coefficients or fugacities can be used to correct for deviations from non-ideal behavior. For many systems, however, activity coefficients are not known and/or applicable. In the case of surfactants, the understanding of sorption thermodynamics is confounded by micelle formation. Another consideration is whether the sorbent acts as an ideal solution at all concentrations. Discussions of the thermodynamics of non-ideal solutions are found elsewhere (e.g., Barrow 1979; Mackay and Shiu 1981).

Finally, the interpretation of temperature effects on sorption may be confounded by physicochemical changes in the sorbent. With respect to the plant cuticle, sorption may be altered by temperature-dependent phase changes (Eckl and Gruler 1980). Alternatively, sorption may induce irreversible changes in sorbent structure as in water sorption to proteins (Bryan 1987).

In this chapter I have briefly discussed the focal points of the dissertation: properties of the cuticular membrane and surfactant solutions and the processes of sorption and desorption. These topics will be further examined in the following chapters to provide a better understanding of cuticle-surfactant interactions.

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SECTION II: CUTICULAR TRANSPORT PROPERTIES: 1. PHYSICAL CHARACTERIZATION OF AND OCTYLPHENOXY SURFACTANT SORPTION BY ISOLATED TOMATO (*LYCOPERSICON ESCULENTUM* MILL.) FRUIT CUTICLE

Summary

Several physical characteristics and sorption properties of the nonionic octylphenol (OP) polyethoxylate surfactant Triton X-100 (TX-100, OP+9.5EO) were determined for cuticular membranes (CM) enzymatically isolated from mature tomato (*Lycopersicon esculentum* Mill. cv. Pik Red) fruit. Sorption isotherms for N_2 gas for both CM and dewaxed CM (DCM) were nearly linear, indicating that N_2 partitioned into the matrix rather than filling sites on the surface or in pores. N_2 sorption/desorption was hysteretic for both CM and DCM. In stress-strain studies, the cuticle responded as a viscoelastic polymer. Hydration caused both CM and DCM to expand and become more elastic and susceptible to fracture. This strongly suggests that water plasticized the cuticle. Dewaxing of the CM caused similar changes in elasticity and fracturing, indicating that wax is a supporting filler in the matrix. Sorption of TX-100 by the cuticle did not significantly affect its rheological properties. Sorption isotherms for TX-100 were characterized by two plateaus, suggesting that surfactant sorption is concentration dependent. This dependence may be due to either a limited number of available sorption sites or of sorbate molecules.

Key words: Rheology, swelling, desorption, hysteresis, permeability.

Introduction

The CM is the thin, hydrophobic polymer that covers the aerial parts of terrestrial plants (Martin and Juniper 1970; Cutler et al. 1982) and acts as the primary barrier to the movement of molecules between the plant and its environment (Bukovac et al. 1981). While CM permeability has been examined frequently (for recent reviews, see Kirkwood 1987; Schönherr and Riederer 1989), the process of permeation is not well understood.

Permeation of any polymer can be viewed as a series of interactions of the penetrant, including sorption by, diffusion through, and desorption from the polymer. All interactions among penetrant, solvent, and polymer molecules potentially affect the rate of and the extent to which these events occur. From a simplistic view, however, the predominant factors affecting polymer permeation are the size and polarity of the penetrant and the polarity and mobility of the polymer chain (Crank and Park 1968; Comyn 1985). While penetrant size is a constant and polarity may be altered by changes in pH and ionic strength, polymer permeability may be affected by altering polymer chain mobility, particularly through the inclusion of plasticizers. For this reason, the relevant study of rheology as characterized by the response of the polymer to mechanical stress may provide insight into how polymer permeability can be modified.

Surfactants are commonly used to enhance the performance of foliar applied chemicals (Foy and Smith 1969). This enhancement may be due to (1) improved dispersion of hydrophobic compound in solution, (2) increased wetting and spreading of the spray droplet on the leaf cuticle, and (3) altered permeability of the cuticle. The third mode of action is intriguing, especially in light of recent studies showing that surfactants enhance cuticular permeability to water (Riederer and Schönherr 1990) and 1-naphthaleneacetic acid (NAA, Knoche personal communication).

Surfactant effects on the cuticle can be studied by examining interactive processes of a surfactant/isolated cuticle system. Of particular interest are the cuticular transport properties of Triton X-100 (TX-100; OP+9.5EO), a nonionic polyethoxylate surfactant that is commonly used in spray

formulations. First, sorption of TX-100 to isolated tomato fruit cuticles is characterized by a complex sorption isotherm, similar to the sorption isotherm for materials such as metals and carbon black (Abe and Kuno 1962). Sorption of TX-100 reaches a maximum near the critical micelle concentration (CMC), presumably because the monomer, the sorbing species of surfactant, reaches a maximum concentration at the CMC (Clunie and Ingram 1983). Further, as the concentration approaches 1.0 % (w/v), cuticular sorption again increases dramatically (Shafer and Bukovac 1987). In contrast with TX-100, cuticular sorption isotherms for 2,4-dichlorophenoxyacetic acid (2,4-D, Morse 1971), NAA (Shafer et al. 1988), and benzyladenine (BA, Appendix IV) are linear over a wide concentration range. In related studies, permeation of isolated cuticles by TX-100 is concentration dependent (Appendix V) whereas that of NAA (Knoche personal communication) and BA (Petracek et al. unpublished) is not. Finally, extraction of cuticular waxes significantly increases cuticular sorption (Shafer and Bukovac 1987) and permeation (Petracek and Bukovac 1989) of TX-100.

Our study had two objectives: (1) to further examine the physical properties of the cuticle to develop a better basis for understanding the mechanisms of cuticular penetration; (2) to prepare a detailed sorption isotherm for a nonionic surfactant TX-100 to help define the nature of surfactant-cuticle interactions.

Materials and methods

Plant material

Tomatoes were field grown locally free of pesticides. Sections of cuticle free of visible defects were excised from mature fruit, and disks (15 mm diam.) were cut with a cork bore. Enzymatic cuticle isolation was based on the technique of Orgell (1955) as modified by Shafer and Bukovac (1987). The excised tissue was incubated in a mixture of cellulase (0.2 % w/v, Sigma), pectinase (4 % w/v, ICN Nutritional Biochemicals), and NaN_3 (1 mM to prevent fungal and bacterial growth) in sodium citrate buffer (50 mM, pH 4.0) made up with distilled water. Enzyme solution was changed several times over

a two-week period, after which the isolated cuticles were repeatedly rinsed with distilled water. Cuticles were cleaned manually in distilled water, air dried, and stored at room temperature. Dewaxed cuticles (DCM) were prepared by batch extracting the soluble cuticular lipids with 10 exchanges of chloroform:methanol (1:1 v/v) at 50°C over 4 d. Cuticles used for scanning electron microscopy, specific weight, and wax content studies were air dried and held in a desiccator.

Chemicals

Citrate buffer solution: Buffer solution consisted of 20 mM sodium citrate (pH 3.2) with 1 mM NaN_3 included to inhibit bacterial and fungal growth.

Surfactant: TX-100 (α-[4-(1,1,3,3,-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-ethanediyl), Rohm and Haas) is an octylphenol surfactant condensed with EO (ethylene oxide) whose number of EO groups per molecule is an average of 9.5 and follows a Poisson distribution. Ring-labeled TX-100 ([U-^{14}C]OP+9.5 EO, 28.1 MBq g^{-1}, Rohm and Haas) was used for radiolabeled studies. TLC and radio-TLC (silica gel and 95:5 water saturated methyl ethyl ketone:methanol) showed that distributions of labeled and unlabeled surfactant molecules were similar. No further purification was performed.

Physical characterization

Scanning electron microscopy: Cuticles were mounted on aluminum stubs with a carbon suspension, coated with about 7 nm gold, and observed with a scanning electron microscope (JEOL JSM-35C SEM) at 15 kV. Photomicrographs were made with 665 positive/negative film (Polaroid). Freeze-fractured edges were prepared by fracturing isolated cuticles in liquid N_2. Cross-sectional areas for stress-strain calculations were estimated by weighing traces of cuticle cross-sections from the SEM viewing screen onto paper and converting weight to area. Five samples were examined for each of the five replicates used in the rheology experiments. For stress-strain calculations, only the cross-sectional area of cuticle between periclinal wall of the epidermal cell and the outer morphological surface were used to express stress (force/area).

Transmission electron microscopy: Strips of isolated cuticles were prestained with OsO_4, dried, and embedded in Spurr's Firm resin under 0.3 MPa vacuum for 48 h. Samples were sectioned with a diamond knife, collected on copper mesh grids, and stained with uranyl acetate and Reynold's lead. Specimens were examined with a Philips 201 microscope at 60 kV.

Wax content: Specific weight was determined by weighing 50 CM (15 mm diam disks) dried to constant weight in a desiccator. CM were then dewaxed, desiccated, and reweighed. Wax content was determined by difference between CM and DCM weights. Specific weight was expressed as the weight per planar area.

Density and N_2 gas sorption and desorption: Density was measured by He gas pycnometry for CM sections (approx. 0.7 g sample) at 25°C by Porous Materials, Inc. (Ithaca, NY). Density values represent the true volume or volume of cuticle not accessible to gas. The same CM sample was analyzed for N_2 gas sorption and desorption characteristics (-196°C) by a PMI Automated BET Sorptometer (Porous Materials, Inc., Ithaca, NY). Sorption and desorption isotherms were prepared by plotting the partial pressure of N_2 available vs. the amount sorbed per sorbent weight. The CM were dewaxed and densities and N_2 sorption and desorption determinations were repeated on the dewaxed samples. Comparison plots for N_2 gas sorption and desorption were prepared by plotting the amount in the CM vs. amount in the DCM for a given pressure.

Cuticular water holding capacity: Desiccated cuticles were weighed and equilibrated with buffer solution or buffer solution containing 1.0 % w/v of the surfactant TX-100. After 24 h, cuticles were removed from solution, blotted with filter paper to remove free standing water, and re-weighed.

Rheological properties: The rheological properties of the cuticle were measured using an extensiometer equipped with a linear-displacement transducer (Kutschera and Schopfer 1986). Dry cuticle strips (4 x 12 mm) were mounted between clips mounted on a piston attached to a stand and a wire on the balancing arm such that the cuticle formed a plane surface (Figure 1). Unintentional stretching of the cuticle was minimized by handling the cuticle carefully during mounting and positioning the balancing arm such that only minimal tension was placed on the cuticle during non-stretching phases.

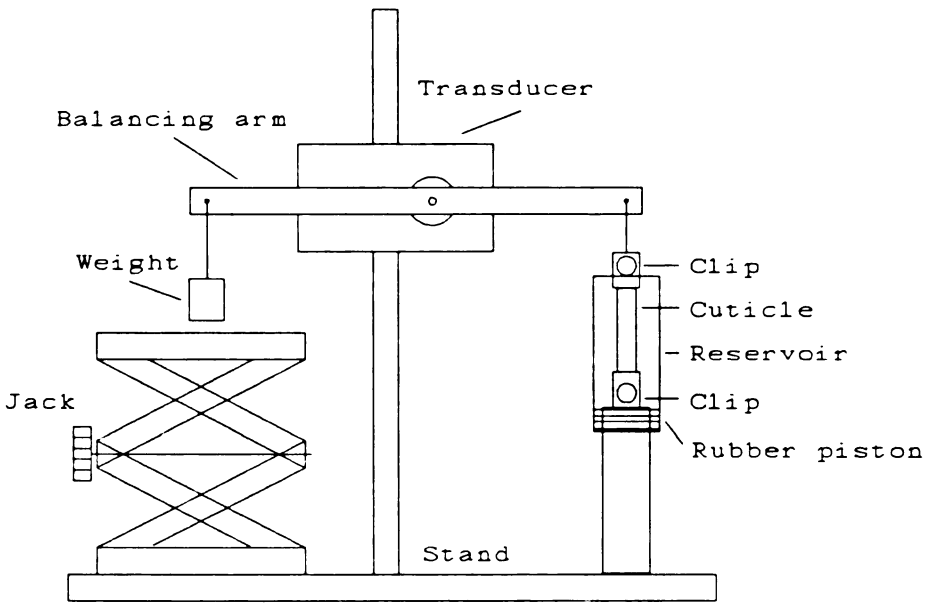


Figure 1. Extensiometer equipped with a linear displacement transducer.

After allowing the system to equilibrate, a reservoir was raised into position around the cuticle. The reservoir was either left empty or filled with buffer solution or buffer solution with 1.0 % (15.9 mmol kg^{-1}) TX-100. After re-equilibration (48 h), a transient load creep test was performed. For these experiments, a designated mass was loaded on the balancing arm for 5 min and then removed. The system was allowed to re-equilibrate and the process was repeated for the next mass in the series (3, 5, 8, 10, 13, 15, 18, 20 g ...) until the cuticle fractured. Extension due to transient load as well as hydration (expansion in the initial hours following solution treatment) were followed with a strip chart recorder. Total extension was expressed as the sum of reversible (elastic) and irreversible (plastic) extension (Figure 2).

Surfactant sorption

Sorption isotherms: Sorption experiments were performed as described by Shafer and Bukovac (1987). In brief, 5 mg of cuticle strips (approx. 2 mm x 10 mm) were weighed in 5 mL glass vials. Surfactant solutions were prepared in buffer. Initial concentrations of ^{14}C TX-100 (MW = 628, Rohm and Haas 1988) used for the sorption isotherm experiment were 0.005, 0.01, 0.05, 0.1, 0.3, 0.5, 0.67, 0.83, and 1.0 % (w/v) corresponding to 0.0795, 0.159, 0.795, 1.59, 4.77, 7.95, 10.6, 13.2, and 15.9 mmol kg^{-1}, respectively. Two of the nine concentrations were below the CMC of TX-100 (0.302 mmol kg^{-1} or 0.019 %, Rohm and Haas 1988). The cuticles were dosed with 1.5 mL surfactant solution and the vials were capped with Teflon-lined screw caps and shaken horizontally in a water bath at 25.0 ± 0.5°C. Upon equilibration (360 h), radioactivity in 100 μL aliquots was determined by liquid scintillation spectrometry (LKB-Wallac LSC model 1211). Aliquots were taken up in scintillation cocktail comprised of 1,4-dioxane (10 mL) with 100 g L^{-1} naphthalene and 5 g L^{-1} diphenyloxazole. Samples were counted to a 2 σ error of 1.0 % and corrected for background. The amount of surfactant in the cuticle was calculated by difference (Appendix I).

Sorption by wax: Waxes were extracted from enzymatically isolated tomato fruit cuticles as described above. Solvent volume was reduced by evaporating the solvent/waxes solution at 45°C. The

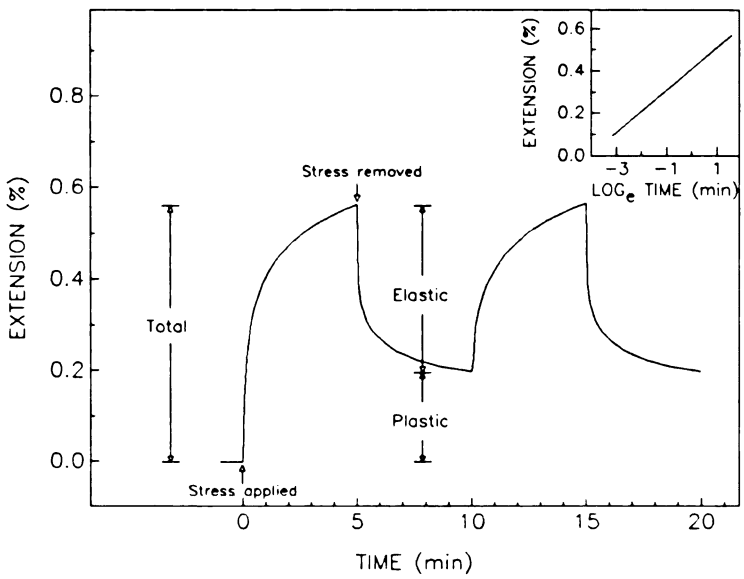


Figure 2. Trace of a recording for dry CM with 5 g weight (0.049 N force) applied. After 5 min the weight was removed and applied again after 5 min. Total extension (elastic + plastic) is a linear-logarithmic function of time (see inset).

remaining solution was pipetted into weighed 5 mL glass vials such that about 5 mg of wax were delivered to each vial. The solvent was then completely evaporated leaving a wax ring deposit on the bottom of the vial. For comparison, sorption of TX-100 was followed for CM and DCM using the method described above. Four concentrations of TX-100 were prepared in buffer solution. Surfactant solution (1.5 mL of 0.0159, 0.159, 1.59, and 15.9 mmol kg^{-1}) was delivered to vials in which waxes were present or absent (control). Vials were gently shaken for 12 d at 22°C. A yellow pigment was extracted by solutions of 1.59 and 15.9 mmol kg^{-1} surfactant. Additionally, suspended particulate matter was noted in vials containing 1.59 mmol kg^{-1} surfactant. The vials were left undisturbed for 4 d to allow particulate matter to settle. Sorbate solutions were sampled several times over 120 d to assure equilibrium had been established. Equilibrium sorbate concentrations in wax were calculated by difference and sorption partition coefficients (K), ratio of concentration of surfactant sorbed to that in solution at equilibrium, were calculated.

Surface area: Cuticular surface areas TX-45 (Shafer and Bukovac 1987) and TX-100 were estimated from Langmuir plots of sorption data:

$$(1)\quad \frac{[A_{solv}]}{[A_{sorb}]} = \frac{1}{b \cdot [A_{sorbmax}]} + \frac{[A_{solv}]}{[A_{sorbmax}]}$$

where $[A_{solv}]$ and $[A_{sorb}]$ are the amounts in the solvent (solution), and sorbent (cuticle), repsectively, at equilibrium, $[A_{sorbmax}]$ is the amount sorbed in a monolayer, and b is an affinity constant (Adamson 1982). Only data points that comprise the first plateau were used since points from the second plateau

may constitute multilayer formation. The surface area (S.A.) was calculated by assuming that the surfactant is oriented perpendicularly with the hydrophile on the surface of the sorbent:

$$(2)\quad S.A. = [A_{sorbmax}] \cdot \sigma_a \cdot N_o$$

where σ_a is the area occupied by each molecule (0.42 and 0.51 nm^2 for TX-45 and TX-100, respectively Rohm and Haas 1988), and N_o is Avogadro's number. Cuticular surface area has been previously estimated by this approach using methylene blue as the probe molecule (Morse 1971).

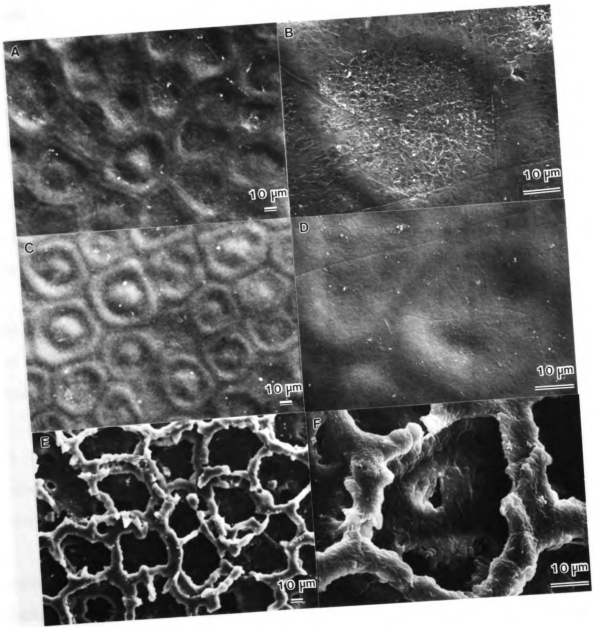
Surface area was also determined by the sorption of ethylene glycol using a technique described by Sor and Kemper (1959). In this case, desiccated cuticles (about 0.35 g) were weighed in glass vessels and coated with ethylene glycol. The vessels were placed in a vacuum chamber (2.7 Pa) supplied with an ethylene glycol buffer and weighed periodically. When the weight reached a constant value, it was assumed that only a monolayer of ethylene glycol remained on the cuticle surface. Surface area was calculated based on the area occupied by monolayer of ethylene glycol molecules.

Results

Physical characterization

The outer morphological surface of the CM was sparsely covered with wax platelets (Figure 3A and B), whereas that of the DCM lacked wax platelets (Figure 3C and D) and bore small grooves above the regions of the anticlinal walls. The cell-wall side was characterized by a network of cuticular pegs which produced a honeycomb-like appearance (Figure 3E). The cuticular pegs, or cutinaceous material that formed between the anticlinal walls of adjacent epidermal cells, demarcated regions of underlying epidermal cells (Figure 3F). The cell-wall side of the CM was not distinguishable from that of the DCM (not shown).

Figure 3. Scanning electron micrographs of isolated tomato fruit cuticles. Figures 3A, B and C, D are micrographs of the outer morphological surface of the cuticle with and without waxes, respectively. Figures 3E and F are micrographs of the cell wall side of the cuticle with waxes.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10 µm
B
10 µm
C
10 µm
D
10 µm
E
10 µm
F
10 µm

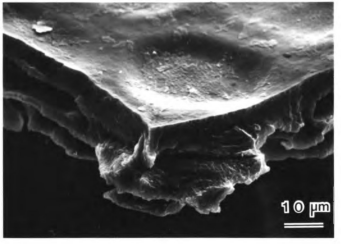
Cuticles which were freeze fractured perpendicular to the plane of the surface exhibited no consistent fracture location or pattern. However, fracturing sometimes produced jagged edges within the cuticle which extended nearly vertically through the matrix (Figure 4). The cuticle of mature tomato fruit was extensively developed, often encasing the epidermal cells and extended into the hypodermal cell region. Average thickness of the cuticle between the epidermal cell wall and the outer morphological surface was 7.0 μm (range 4.4 to 10.7 μm); average thickness for all regions was 10.5 μm (range 6.7 to 15.3 μm). The maximum thickness of the cuticle through the cuticular peg was estimated to be about 30 μm. The areas of the cuticle above the epidermal cells were depressed up to about 1 μm. This was presumably not an artifact of cuticular isolation or SEM preparation since similar indentations were found in fresh material observed by a SEM equipped with a cold stage (Appendix II). No pores (stomatal or otherwise) were observed under close examination of about 30 sections of cuticle (approx. 5 mm x 5 mm each).

Transmission electron micrographs indicated (Figure 5) that the cuticle was generally reticulate with dark tangentially- and radially-oriented striae appearing more predominantly near the epidermal cell lumen (cf. Wilson and Sterling 1976). In some cases, a region above the anticlinal wall was predominantly electron lucent.

The tomato fruit CM used in this study consisted of about 95 % matrix and 5 % waxes (Table I). CM density as determined by helium pycnometry was about 1200 kg m^{-3}. This was about 10 % higher than values obtained by water pycnometry (Schreiber and Schönherr 1990). Dewaxing did not alter the density.

Cuticular N_2 sorption isotherms (Figure 6) were nearly linear (r^2 = 0.984 and 0.989 for CM and DCM, respectively). However, note that both sorption isotherms were slightly convex to the x-axis, indicating that the isotherms had some Type III character. Nevertheless, since the sorption isotherms clearly showed no indication of N_2 forming a monolayer on the cuticle, BET analysis for surface area was invalid. Furthermore, the isotherm was not Type IV, and thus pore analysis by the Kelvin equation is also inappropriate. Interestingly, the desorption isotherm for CM had a shoulder around P/P_o = 0.6,

Figure 4. Scanning electron micrograph of a freeze-fractured transverse section of isolated tomato fruit cuticle.



tomato frui

Figure 5. Transmission electron micrographs of isolated dewaxed tomato fruit cuticular membrane. Figures 5B - D are enlargements of areas labeled in figure 5A.

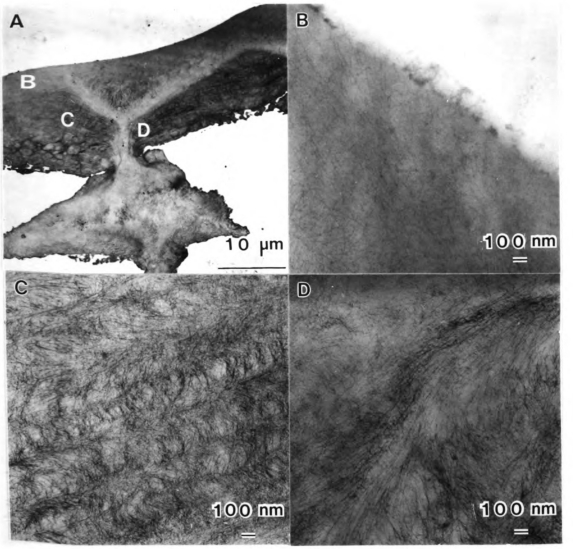

A
B
C
D
10 μm
B
100 nm
C
100 nm
D
100 nm

Table I. *Physical characteristics of tomato fruit cuticles.*

Cuticle	Wax (% weight)	Specific weight (kg m^{-2})	Density (g m^{-3})
CM	5.19	21.2	1.21
DCM		20.1	1.19

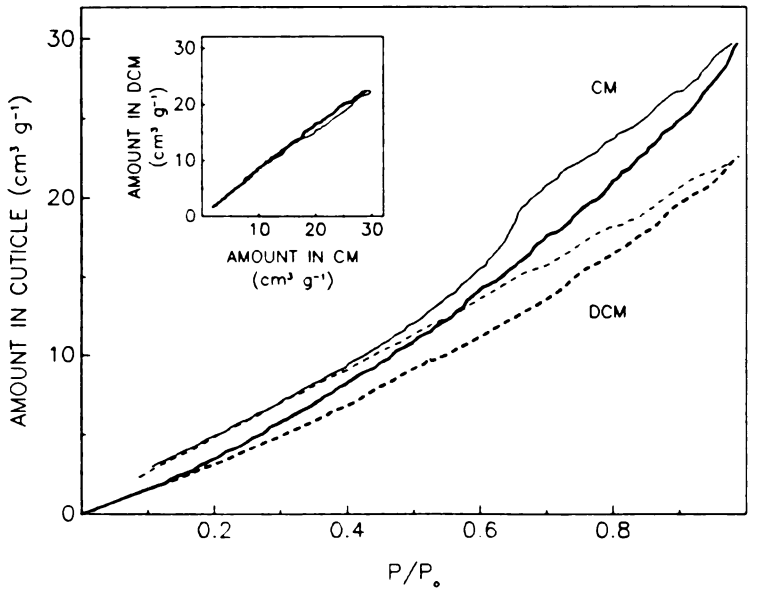


Figure 6. N_2 gas sorption (heavy line) and desorption isotherms (light line) for CM (solid line) and DCM (dashed line). Inset- comparison plots of CM vs. DCM for sorption and desorption.

which was indicative of the presence of mesopores (Gregg and Sing 1982). Sorption and desorption isotherms were not coincidental, and thus sorption was a hysteretic process.

Sorption/desorption isotherms represent the amount sorbed as a mathematical function of sorbate pressure or concentration. Comparison plots equate the functions of two sorbents and permit comment about their relative sorptive characteristics. Specifically, comparison plot shape indicates differences in sorption mechanisms while slope relates the amount sorbed (Gregg and Sing 1982). Comparison plots of N_2 gas sorption and desorption for CM and DCM (inset in Figure 6) were linear (r^2 = 0.998 for both sorption and desorption). Thus, removal of waxes apparently did not affect the way in which N_2 sorbed to or desorbed from the cuticle. However, sorption decreased about 30 % (slope = 0.7) when waxes were extracted.

Rheological properties of the cuticle were affected by hydration and removal of waxes, while surfactant treatment produced no effect in addition to that of hydration (Figure 7 and Tables II and III). Cuticular response to hydration was measured in several ways. First, linear expansion of the cuticle during the initial hydration period was about 2 to 3 % of total initial length (Table II). The average time required was 3 h (data not shown). Second, cuticular elastic extension increased about six-fold following hydration (Table III). Plastic extension was not affected by hydration. Third, fracture point, or amount of stress required to break the cuticle, for dry cuticles was twice that of hydrated cuticles. Note that total extension before fracturing of the CM was the same (about 3 %) for dry and hydrated cuticles (Figure 7).

Augmenting buffer solution with 1.59 (data not shown) and 15.9 mmol kg^{-1} TX-100 had no effect in addition to that of hydration (Table III). This was consistent with and perhaps related to the observation that surfactant did not increase the maximum water content of the cuticle (Table II).

The effects of hydration and dewaxing of the cuticle were in some ways similar. Removal of waxes nearly doubled elasticity and halved the fracture point (Table III). Also, the effects of hydration and wax removal on elasticity and fracturing were apparently independent and additive to one another. The effect of the dewaxing process was further examined to determine whether high temperature or

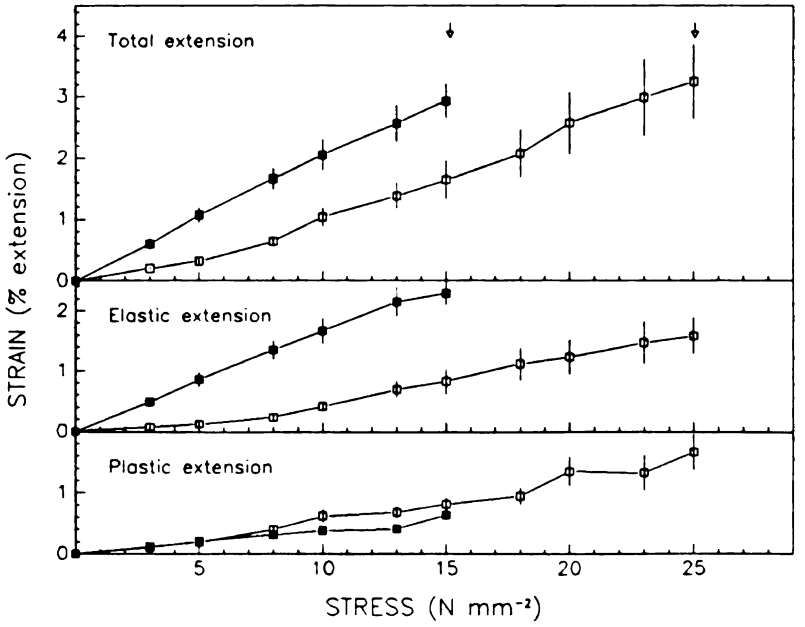


Figure 7. Stress-strain diagrams for hydrated (▪) and dry (□) CM. Stress is the force applied per cross-sectional area of the cuticle. Strain is the percent extension (total = elastic + plastic). Arrows represent average fracture point. Bar equals SE for 5 replicates.

Table II. *Water content and linear expansion of water equilibrated tomato fruit cuticles.*

Cuticle	Treatment	Water content (w/w)	Linear expansion (%)
CM	Buffer	0.47	2.6 ± 0.4
CM	TX-100	0.53	3.1 ± 0.3
DCM	Buffer	0.52	2.4 ± 0.3
DCM	TX-100	0.56	3.6 ± 0.5

Data for linear expansion are the means ± SE of five replicates. TX-100 solution consisted of 15.9 mmol kg^{-1} surfactant in buffer.

Table III. *Rheological properties of tomato fruit cuticles.*

		Extension (%)			
Cuticle	Treatment	Total	Elastic	Plastic	Fracture point (g)
CM	Dry	0.49 ± 0.05	0.20 ± 0.06	0.29 ± 0.05	30.0 ± 5.1
CM	Buffer	1.60 ± 0.19	1.29 ± 0.17	0.31 ± 0.05	15.2 ± 1.6
CM	TX-100	1.69 ± 0.21	1.36 ± 0.09	0.34 ± 0.03	14.8 ± 1.9
DCM	Dry	0.80 ± 0.07	0.36 ± 0.08	0.44 ± 0.06	16.0 ± 3.2
DCM	Buffer	2.58 ± 0.44	2.16 ± 0.37	0.42 ± 0.09	9.4 ± 1.1
DCM	TX-100	2.09 ± 0.04	1.75 ± 0.11	0.34 ± 0.07	8.9 ± 2.0

Extension data are the means (± SE) for five replicates for 5 g (0.049 N) vertical force applied for 5 min at 22°C. Buffer solution consisted of 20 mM citrate (pH 3.2). TX-100 solution consisted of 15.9 mmol kg^{-1} surfactant in buffer solution.

solvent extraction affected cuticular rheology. To this end, cuticles were either kept at the temperature used for wax extraction (50°C) for ten d or repeatedly extracted with solvent (1:1 v/v chloroform:methanol) at 22°C. Solvent, but not heat, treatment affected the rheological properties of the cuticle (data not shown).

Compliance (strain/stress) is an index that allows comparison of the extensibility of various materials. Cuticular compliances for 5 g mass were 0.040 and 0.072 $cm^2 N^{-1}$ for the dry CM and DCM, respectively, and 0.258 and 0.432 $cm^2 N^{-1}$ for hydrated CM and DCM, respectively. In comparison, compliances for polymers typically ranged between 0.2 and 2.0 $cm^2 N^{-1}$. For example, the compliance of low density polyethylene is 0.22 $cm^2 N^{-1}$ (Ferry 1980).

Surfactant sorption

The sorption isotherm for TX-100 was characterized by two plateaus (Figure 8). The first plateau was approached at concentrations of around 0.1 %, the second plateau at about 0.8 %. Based on shape, this isotherm can be classified as Type L4 (Giles et al. 1960).

In spite of the complexity of the sorption isotherms, the comparison plot for CM and DCM (Figure 8 inset) was nearly linear, suggesting that the process of sorption of TX-100 was not mechanistically affected by the presence of waxes. Cuticular waxes reduced sorption of TX-100. The slope of the comparison plot of CM vs. DCM (1.06) suggests that the DCM sorbed about 6 % more surfactant at all concentrations (Figure 8 inset). In contrast, isolated wax sorbed about twice as much TX-100 as did CM or DCM at the lowest three concentrations (0.0159, 0.159, and 1.59 mmol kg^{-1}, Figure 9). Also, unlike the two plateau sorption isotherms of CM and DCM, the four points of the sorption isotherm for isolated wax (Figure 9 inset) suggest a simple Langmuirian isotherm (Type L1, Giles et al. 1960). The maximum amount of surfactant sorbed by CM, DCM, or isolated wax was about the same (200 mmol kg^{-1}).

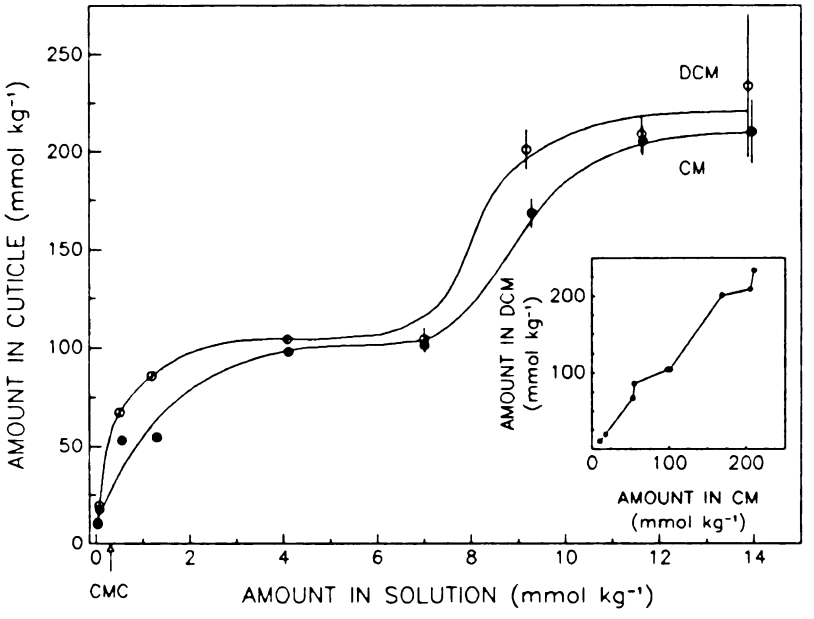


Figure 8. TX-100 sorption isotherms for CM (●) and DCM (○) at 25°C. Bar equals SE for 10 replicates. Absence of bar indicates that SE was less than the diameter of the symbol. Inset-comparison plot of CM vs. DCM.

PARTITION COEFFICIENT

Figure 9. TX-100
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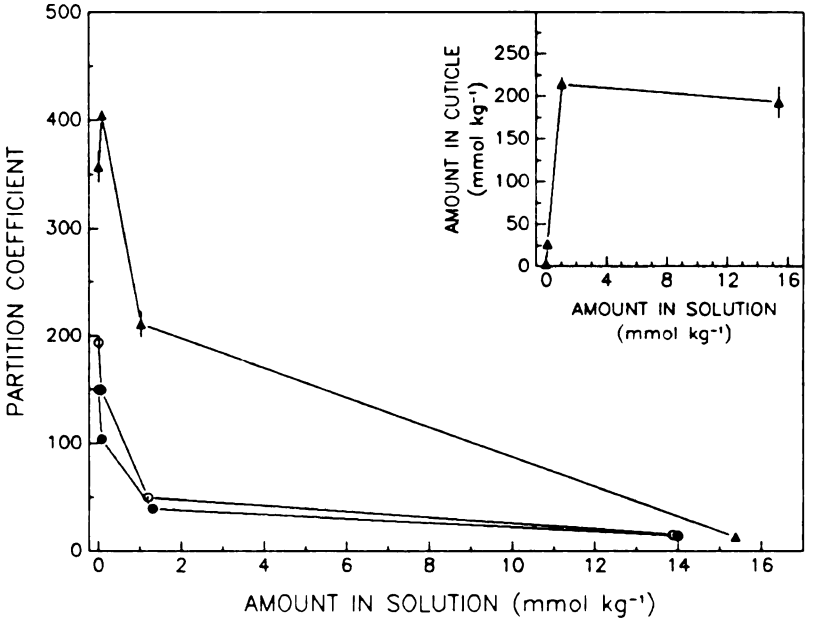

Figure 9. TX-100 partition coefficients for CM (●), DCM (○), and isolated wax (▲). Bar equals SE for ten (CM and DCM) or five (isolated wax) replicates. Absence of bar indicates that SE was less than the diameter of the symbol. Inset-TX-100 sorption isotherm for isolated wax.

Table IV. *Langmuir constants calculated from tomato fruit cuticle sorption isotherms of TX-100 and TX-45.*

	Langmuir constants			
	TX-100		TX-45	
Cuticle	b	$A_{sorb\ max}$ (mmol kg^{-1})	b	$A_{sorb\ max}$ (mmol kg^{-1})
CM	1.60	110	0.34	227
DCM	3.21	110	1.05	430

TX-100 constants were calculated for the lowest five surfactant concentrations (0.0795, 0.159, 0.795, 1.59, and 4.77 mmol kg^{-1}). TX-45 constants were calculated from data of Shafer and Bukovac 1987. Correlation coefficients (r^2) for the corresponding Langmuir plots were greater than 0.98.

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Affinity constants (b) of DCM were more twice those of CM for both TX-100 and TX-45 (Table IV). Maximum amount of TX-45 sorbed ($A_{sorb\ max}$) by DCM was about twice that of CM, whereas the $A_{sorb\ max}$ for TX-100 was the same for both.

Cuticular surface areas calculated for various molecular probes are listed in Table V. In general, surface area was not affected by the removal of waxes with the calculated surface areas ranging from 31 to 109 $m^2\ g^{-1}$.

Discussion

The N_2 sorption by the cuticle is characterized by a nearly linear isotherm (Figure 6). Typically, rigid materials such as metals have N_2 adsorption isotherms that become concave to the abscissa as P/P_o approaches 0.3 (Gregg and Sing 1982). This is an indication that the number of sites available for adsorption is limited and that a monolayer of N_2 is forming. However, isotherms for flexible materials such as rubbers tend to be linear. For these materials, the N_2 molecules are not simply adsorbing to the surface and forming a monolayer as pressure increases, but are partitioning into the polymer matrix (Stannett et al. 1979). In this case, the term "sorption" is used because N_2 association with the surface (adsorption) can not be readily distinguished from that with the interior of the polymer (absorption). The non-rigidity of the cuticle also may cause low pressure hysteresis. Previously, low pressure hysteresis was attributed to a sorption-induced irreversible deformation of the sorbent (Bailey et al. 1971).

Cuticular sorption of compounds from solution usually increases upon the extraction of waxes from the matrix (Bukovac et al. 1990). In the case of N_2 sorption, however, the DCM sorbs less than the CM. This suggests that waxes provide additional sites for N_2 sorption. A model that explains this is one in which waxes act as a filler in the cuticular matrix. When the desiccated cuticles are analyzed for N_2 sorption, waxes may not make full contact with the matrix, providing additional sorption sites. A similar concept of incomplete "wetting" by a polymer filling is believed to increase sorption of a

Table V. *Surface area of tomato fruit cuticles as determined by several molecular probes using Langmuir analysis.*

	Surface area (m^2 g^{-1})	
Molecular probe	CM	DCM
TX-100	31	31
TX-45	57	109
Ethylene glycol	80	90
Methylene blue	34	36

TX-100, TX-45, and methylene blue sorption experiments were performed at 25°C; ethylene glycol experiment was performed at 22°C. Data for surface area as determined by TX-45 sorption was taken from Shafer and Bukovac 1987. Surface area determination by methylene blue sorption was taken from Morse, 1971.

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polymer sorbent with fillers (Stannett et al. 1979). When the cuticle swells during hydration, the waxes make more complete contact with the matrix thus blocking sorption sites.

The response of the cuticle to stress with time (Figure 2), is similar to that of a "leathery" polymer (Meares 1965). Alternatively, the strain response as a functions of time and force may be classified as viscoelastic in nature (Ferry 1980). This classification is based on the following. First, total extensibility comprises both elastic (reversible) and plastic (irreversible) components (Figure 2). Second, the time response of extension is a linear function of the logarithm of time (Figure 2, inset). Third, both plasticity and elasticity are linear functions of weight (Figure 7). Kutschera and Schopfer (1986) used a similar device and concluded that maize coleoptiles were also viscoelastic. Coleoptile extensibility is due primarily to plastic deformation and factors that affect growth also affect plasticity. Extensibility of the cuticle, in contrast, is largely due to elastic deformation, and extension is affected by factors that affect elasticity.

The rheology studies provide two important observations. First, water affects the mechanical properties of the cuticle by (1) inducing extension of the cuticle (Table II), (2) increasing cuticular elasticity (Table III), and (3) making the cuticle more susceptible to fracturing. These features are common in cases where solvents plasticize or cause swelling in polymers (Meares 1965; Fels and Li 1974). Further, water plasticization of the cuticle also may be responsible for the reduced rate of sorption of surfactant by dry cuticles (Section IV). Second, waxes reduce cuticular elasticity and susceptibility to fracturing (Table III). These observations further support the concept that waxes act as polymer fillers as suggested in the discussion of N_2 sorption (Meares 1965). As a filler, waxes reduce the mobility of the matrix, thus effectively acting as a crosslinking agent that provides rigidity to an otherwise flexible matrix (Zlotnik-Mazori and Stark 1988).

The TX-100 sorption isotherm at low concentrations for this system is typical for non-ionic surfactants (Clunie and Ingram 1983). Here partitioning below the CMC is approximately constant and the amount which sorbs reaches a local maximum around the CMC (Shafer and Bukovac 1987; Figure 9). However, at solution concentrations above the CMC (> 7.9 mmol kg^{-1} or 0.05 % w/v) a second

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sorption plateau appeared. There may be several explanations for this observation, including: (1) multi-layer formation, (2) re-orientation of the sorbed molecules to maximize the efficiency of the available sorption space, (3) sorption-induced changes in the cuticular structure which causes an increase in the number of sites available for sorption.

The third explanation suggests a means by which surfactants may affect cuticular permeability. Specifically, if the surfactant alters the cuticle such that more sites become available for sorption, it may open up the cuticle for the permeation of other molecules. This may occur in several ways. First, the surfactant may act as a humectant and thus allow greater interaction between water and cuticle leading to water plasticization of the cuticle. Second, the surfactant itself may plasticize the cuticle. If so, then initial extension or response to mechanical stress may be altered. However, the results of the rheology experiments indicate that surfactants do not affect cuticular rheology (Tables II and III), and therefore suggest that surfactants do not affect properties such as swelling or polymer chain mobility.

This conclusion is tentative since the experimental apparatus used for measuring mechanical properties of the CM may not be sufficiently sensitive to detect small but potentially significant changes in the polymer matrix. Also, the procedure used in these experiments required the complete immersion of the cuticle in solution. Surfactant effects as a humectant may not be apparent in this system since all cuticles were held in solution. In practice, foliar sprays on the surface of the leaf quickly dry and thus the outer morphological surface of the cuticle may lose water to the environment. In contrast, a deposit on the cuticle containing a surfactant acting as a humectant, may keep the cuticle hydrated and thus potentially more permeable than cuticles without surfactant deposits.

The interpretation of the second plateau of the sorption isotherm is unclear. This plateau may be due to surfactant properties more than cuticular properties. Several items about the concentrations at which the second plateau was observed are noteworthy. Typically, surfactant isotherms are not carried out beyond several times the CMC (e.g., Clunie and Ingram 1983; Rosen 1989). In this study, however, the isotherm was prepared with concentrations that were nearly 50 times the CMC. At this high concentration, unusual events may be occurring in solution, including the formation of large

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aggregates of surfactant that associate with the cuticular surface. The existence of such aggregates or other changes in solution properties is supported by the observation of the increased viscosity (Appendix II) and changes in NMR spectra (Han et al. 1989) of TX-100 solution around the concentration associated with the second plateau (15.9 mmol kg^{-1}).

The question of surfactant sorption mechanisms highlights one of the problems encountered in interpreting sorption data. Sorption by materials such as metals is easier to understand because interactions are confined to events occurring at the surface or in pores. In these cases of simple adsorption, the saturation of the surface is assumed to result from an association of a molecule with every available site on the surface, forming a monolayer of molecules. Consequently, the number of molecules that are required to saturate the surface can be used to calculate the surface area, provided that the area occupied by each molecule is known.

When a material such as a polymer is saturated, however, sorbate-sorbent interactions are not as easy to visualize. In polymer systems, partitioning into the matrix occurs. The number of molecules required to saturate the polymer is a function of number of molecules required to both form a monolayer on the surface and fill all interior sites within the polymer. This will be true as long as the molecules are able to penetrate the polymer. In the case of cuticular sorption, molecules used as surface area probes (Table V) are either known to penetrate the cuticle (methylene blue, Morse 1971; TX-100, Petracek and Bukovac 1989) or can be assumed to penetrate the cuticle based on their size (TX-45 and ethylene glycol). The consequence of absorption is an overestimation of the surface area, since for both surface and interior associations are involved. Chiou et al. (1990) suggested the use of the term "apparent surface area" to distinguish surface areas calculated from sorption data of partitioning events from those of surface events or "free surface area". Free surface area would be calculated from the data of N_2 sorption in which partitioning usually does not occur. However, the linear sorption isotherm of N_2 suggests that partitioning does in fact occur for N_2 as well, thus making the comparison of surface to interior events difficult. Still, surface areas calculated by the various

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probing molecules are similar. This may be because the cuticle has some finite volume available for sorbing molecules and that volume is not affected greatly by the presence of waxes.

The question of the role of waxes in surfactant sorption arises particularly from the observation that TX-100 sorption is greater for DCM than CM, but greater still for the isolated waxes themselves (Figure 9). This apparent contradiction may be clarified if the physical rather than chemical properties impart the sorptive characteristics of waxes. Cuticular waxes consist largely of hydrophobic compounds such as long chain alkanes and alcohols. The cutin matrix is slightly more polar due to the presence of hydroxyl and occasional unesterified acid groups (Kolattukudy 1981; Baker et al. 1982). Surfactant hydrophile association with the cuticle should be greater with the more polar matrix than with the more hydrophobic waxes. However, cuticular waxes are somewhat crystalline in nature and this crystallinity may present a greater barrier to surfactant sorption than polarity differences. As discussed above, waxes may act as an impenetratable cutin matrix filler, and as such, they may block sorption sites. When waxes are extracted by solvent, their crystalline nature may be lost due to homogenization of the various wax constituents. The reformed waxes are amorphous and thus are more likely to be penetrated by a sorbate such as a surfactant. In this case, waxes in their isolated form may physically more accommodating to the surfactant molecules than the polymer matrix.

Acknowledgments

This paper is based on work supported, in part, by grants C.W.U. 3607-20300-004-01S and C.A.N. 58-5114-7-1002 from the Agricultural Research Service, United States Department of Agriculture. We thank Dr. Gary Willingham, Rohm and Haas, for the gift of Triton X-100. We also thank Dr. Hans Kende for the use of the extensiometer.

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SECTION III: CUTICULAR TRANSPORT PROPERTIES: 2. SORPTION AND DESORPTION OF AN OCTYLPHENOXY SURFACTANT

Abstract

Sorption and desorption of the nonionic surfactant Triton X-100 (TX-100) were examined for cuticles enzymatically isolated from mature tomato (*Lycopersicon esculentum* Mill. *cv.* Pik Red) fruit. Cuticular sorption of TX-100 is a hysteretic process as illustrated by the nonsingularity of the sorption/desorption isotherms. Hysteresis was evident in two fractions of sorbed surfactant. One fraction could be extracted by citrate buffer solution (about 85 to 90 % of the total amount sorbed), but was more difficult to desorb than predicted by two phase extraction theory. The other fraction could not be extracted even after extensive desorption by buffer solution, but could be desorbed by less polar solvents or exchanged with surfactants of similar structure. Hysteresis suggested that a gradient of site strengths exists in the cuticle. Whether this gradient is due to binding affinity or location of the site could not be determined, but solvent polarity is obviously critical for desorption of the surfactant. In general, the presence of cuticular waxes did not markedly affect surfactant sorption or desorption. Solution pH did not affect sorption or desorption except in extreme alkaline conditions (pH 13) under which sorption was significantly enhanced.

Introduction

Surfactants are amphipathic compounds that are often included in spray formulations to enhance the performance of foliar applied chemicals (Foy and Smith 1969). Surfactants increase the interaction of polar and non-polar phases. At low concentrations, surfactants adsorb to and reduce the free

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energies of surfaces or interfaces, thus increasing the wetting of hydrophobic surfaces such as the cuticular membrane (CM) of plants. At high concentrations, surfactants form aggregates (micelles) which emulsify and thus improve the solubility and dispersal of hydrophobic compounds in aqueous solution (Attwood and Florence 1983; Rosen 1989). Both properties are important for efficient spray application. Further, recent studies suggest that surfactants may also increase the permeability of the CM (Riederer and Schönherr 1990; Knoche, personal communication).

The CM is a lipoidal polymer that protects aerial parts of terrestrial plants from desiccation and pathogen invasion (Martin and Juniper 1970; Cutler et al. 1982) and serves as the primary barrier to the penetration of foliar applied chemicals (Bukovac et al. 1981). Consequently, factors which alter CM transport properties may have a tremendous impact both agronomically and ecologically. Still, recent reviews on foliar uptake of herbicides (Kirkwood 1987) and CM sorption (Bukovac et al. 1990) and permeation (Schönherr and Riederer 1989) suggest that the processes of CM transport are not well understood.

One strategy for studying surfactant effects on CM permeability is to examine the individual interactive processes of permeation. Hence, cuticular permeation may be examined through the study of sorption, diffusion, and desorption. Sorption studies (Shafer and Bukovac 1987) established that TX-100 was readily sorbed to the cuticle and that sorption approached an apparent local maximum near the critical micelle concentration (CMC). This response may be related to a limitation in the number of monomers available for sorption (Clunie and Ingram 1983; Rosen 1989). Further study established a second local maximum at much higher concentrations. While the precise mechanism for this response was not determined, it was suggested that sorption may be limited by the amount of surfactant available for sorption and/or the cuticular sorption capacity (Section II). In this study, we have characterized the sorption and desorption of TX-100 by isolated tomato fruit cuticles and determined how several factors that affect these processes.

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Plant material

Locally grown, pesticide-free mature tomato (*Lycopersicon esculentum* Mill. cv. Pik Red) fruit were selected free of visible defects. Fruits were sectioned and sections were incubated at room temperature in several changes of enzyme solution consisting of cellulase (0.2 % w/v; Sigma), pectinase (4 % w/v; ICN Nutritional Biochemicals), and NaN_3 (1 mM) in 50 mM sodium citrate buffer solution at pH 4.0 (Orgell 1955; Shafer and Bukovac 1987). The cuticles were rinsed extensively with flowing distilled water and any remaining cellular debris was removed manually. The cuticles were then air dried and stored in sealed jars at room temperature. Cuticles isolated in this manner will be referred to as cuticular membranes (CM). Waxes were batch extracted from isolated CM with chloroform:methanol (1:1 v/v) at 50°C and these cuticles will be referred to as DCM. Unless specified, the term isolated cuticles will refer to both CM and DCM.

Chemicals

Unless stated otherwise, buffer solution consisted of 20 mM citrate titrated with NaOH to pH 3.2. NaN_3 (1 mM) was included to inhibit bacterial and fungal growth. Citrate was included in solutions of pH beyond the citrate buffering range in order to maintain similar conditions.

TX-100 (α-[4-(1,1,3,3,-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-ethanediyl); Rohm and Haas), an ethoxylated octylphenoxy (OP) surfactant (Figure 1), is a mixture of ethoxymers with a mean number (n) of 9.5 ethylene oxide (EO) groups per molecule and follows a Poisson distribution (average MW is 628). The CMC is 0.302 $mmol \cdot kg^{-1}$ or 0.019 % at 20°C (Rohm and Haas 1988). Sorption and desorption studies were performed with ring-labeled TX-100 ([U-^{14}C]OP + 9.5 EO; 28.1 $MBq \cdot g^{-1}$) using scintillation spectrometry. TLC and radio-TLC (silica gel and 95:5 v/v water saturated methyl ethyl ketone:methanol) established an identical distribution of labeled and unlabeled surfactant molecules. Nonlabeled TX-100 was used to adjust concentrations in the radiolabel studies when

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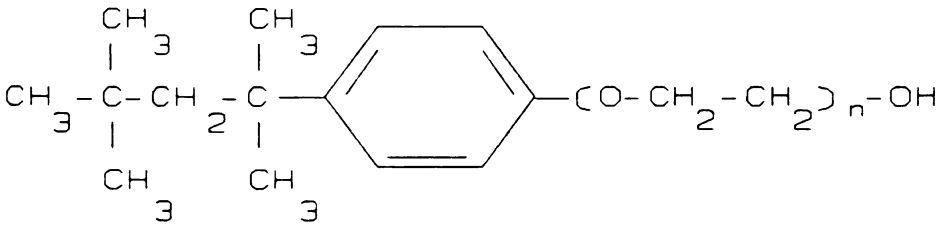

Figure 1. General structure of the octylphenoxy polyoxyethylene surfactants.

Surfactant sorption/desorption

Sorption: Five mg of isolated CM or DCM (approx. 2 x 10 mm strips) were weighed in 5 mL glass vials and dosed with 1.5 mL of surfactant solution. Vials without cuticles (control) were also prepared to detect and correct for surfactant sorption to the glass. Vials were sealed with Teflon-lined caps and shaken horizontally in a water bath at 25.0 ± 0.5°C. Sorption was followed by assaying the sorbate solution (100 μl) and determining radioactivity by liquid scintillation spectrometry (LKB-Wallac-LSC model 1211). Scintillation cocktail consisted of either 100 $g \cdot L^{-1}$ naphthalene and 5 $g \cdot L^{-1}$ diphenyloxazole (PPO) in 10 mL 1,4-dioxane (time course and isotherm experiments only) or 10 mL Safety-Solve (Research Products International Corp.). The amount sorbed was calculated by the difference method (Appendix I).

The effect of pH and the depolymerzing agent BF_3 on sorption were examined by pretreating CM with buffer solution (pH 3 or 13), methanol, or 12 % BF_3 in methanol for 48 h before sorption.

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After pretreatment, CM were extensively rinsed with the buffer solution. Initial sorbate dosing solution consisted of 1.59 mmol $\cdot$ kg^{-1} (0.1 % w/v) TX-100 in buffer at 22°C.

Stepwise desorption: After sorption equilibrium was established, the dosing solution was removed with an automatic pipette equipped with a flexible tip. Particular care was taken to remove all free standing solution. Desorption was initiated (time = 0) on addition of desorbing buffer solution (1.5 mL) or other desorbing solvent. Desorption was followed by radioassay of the desorbing solution and amount remaining sorbed was calculated by difference. At equilibrium, desorbing solution was exchanged for fresh desorbing solution and the sequence was repeated.

Extended desorption: Following the final stepwise desorption sequence, isolated cuticles were transferred to and packed in glass capillary tubes (3 mm i.d.). Each tube was packed with replicates of the same treatment separated by glass wool. Buffer solution was flowed through each tube for 30 days at a rate of about 1 L $\cdot$ d^{-1}. The desorbed isolated cuticles were then oxidized at 900°C in an OX#400 biological oxidizer (R. J. Harvey Instrument Corporation) and the radiolabeled carbon dioxide was trapped in 20 mL of 1:2 v/v Carbo-Sorb II (Packard) : toluene-based scintillant (3a20, Research Products International Corporation) and radioassayed. Surfactant desorbed by either the stepwise or extended desorption procedure was termed "buffer extractable"; the remaining fraction retained by the CM was termed "buffer non-extractable."

Initial experiments were performed to establish the time required for equilibration of the surfactant-isolated cuticle system. For sorption and stepwise desorptions, solutions were periodically sampled over a prolonged equilibration period (greater than 300 d). Equilibrium was reached when the amount of surfactant in solution remained constant. Time required for equilibration in the extended desorption system was determined by oxidizing cuticles after 1, 2, 5, and 30 d of desorption. More than 95 % of the buffer extractable fraction remaining in the cuticle after four stepwise desorptions was removed in the first 24 h of extended desorption. The remaining buffer extractable fraction desorbed within the next four days. Additional time was given for sorption, stepwise desorptions, and extended desorptions, to assure full equilibration (Hartley and Graham-Bryce 1980).

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Several preliminary experiments were also performed to test the limitation of the desorption technique. Of primary concern was that free standing solution, which may not be adequately removed from the isolated cuticle, might contain high levels of the sorbate that may be quickly released into the desorbing solution. The "non-sorbed" material, i.e. the surfactant in the adhering solution, would mask the desorption event, and thus the amount of material which actually desorbed would be overestimated. This is potentially a greater problem for the first stepwise desorption because of the high activity of any adhering sorbate. This concern was addressed by preparing mass balances for both calculated and directly measured surfactant levels in the isolated cuticle and solution. At each step of the process, the amount of surfactant in the isolated cuticle was calculated by difference and measured directly. For direct measurement, selected isolated cuticles were blotted to remove free standing solution, oxidized, and radioassayed. Three desorption techniques were evaluated: (1) decanting of solution, (2) transferring the isolated cuticles to new vials, and (3) blotting and transferring the isolated cuticles to new vials. The amount of surfactant in the oxidized isolated cuticles varied less than five percent among desorption techniques for all steps of the process. Since calculated and directly measured values were in closest agreement for the decanting technique (within 5 %), this technique was adopted for all experiments.

Final desorption: A series of experiments was performed to assess the desorption characteristics of the buffer non-extractable fraction. Isolated cuticles were equilibrated with 1.59 $mmol \cdot kg^{-1}$ radiolabeled TX-100 and subjected to four stepwise desorptions and an extended desorption as described above. Isolated cuticles were placed in vials and subjected to an additional four stepwise desorptions in 1.5 mL of (1) surfactant solution (1.59 $mmol \cdot kg^{-1}$, the molar equivalent of 0.1 % TX-100), (2) buffer solution of pH ranging from 0.2 to 13.2, or (3) various solvents (see Table IV). In a fourth series of treatments, the effect of buffer additives (e.g., urea and NaCl) as well as of temperature, sonication, vacuum, and the depolymerizing agent BF_3 were examined. Following the last stepwise desorption step, the isolated cuticles were oxidized and the trapped $^{14}CO_2$ was radioassayed.

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Models of sorption/desorption:

Freundlich model: The relationship between sorption and desorption isotherms was evaluated by fitting the isotherm data to the Freundlich equation:

$$(1)\quad A_{cut} = k \cdot A_{soln}^{1/n}$$

where A_{cut} and A_{soln} are the concentrations of surfactant A in the cuticle and solution, respectively, and k and n are arbitrary constants (Adamson 1982).

Extraction model: The extent of desorption was predicted from the sorption partition coefficient and an equation adapted from two phase extraction theory:

$$(2)\quad \ln A_{cut} = \ln A_o + x \cdot \ln \left[\frac{Wt_{cut} \cdot K}{Wt_{soln} + Wt_{cut} \cdot K} \right]$$

where A_o is the initial concentration, x is the number of stepwise desorptions, and Wt_{cut} and Wt_{soln} are the weights of cuticle and solution, respectively (Skoog and West 1979).

Results

Time course

Equilibrium was attained within 240 h for sorption and 36 h for stepwise desorption (Figure 2). Time required to reach equilibrium was similar for CM and DCM. The amount of TX-100 remaining in the cuticle after extended desorption was about 10 to 15 % of the total amount sorbed.

Sorption/desorption isotherms

Isotherms for sorption and the first stepwise desorption were not coincidental (Figure 3). For all concentrations, the amount of surfactant remaining in both CM and DCM after desorption was

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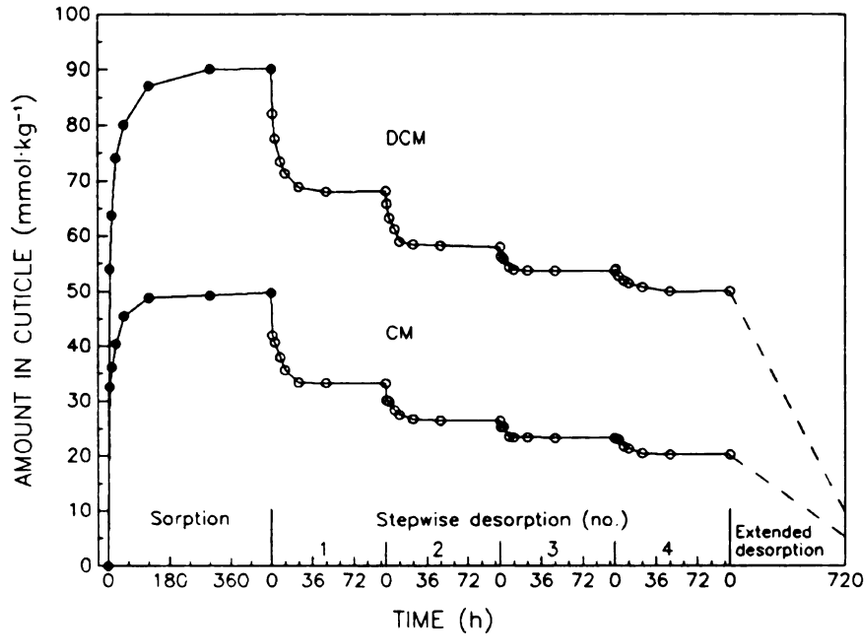

Figure 2. Time courses for TX-100 sorption (●), four stepwise desorptions (○), and extended desorption (- - -) for isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles. Initial sorption solution consisted of 1.59 mmol · kg^{-1} (0.1 % w/v) surfactant in buffer. Buffer was used for stepwise and extended desorption solutions. Sorption and desorption performed at 25°C.

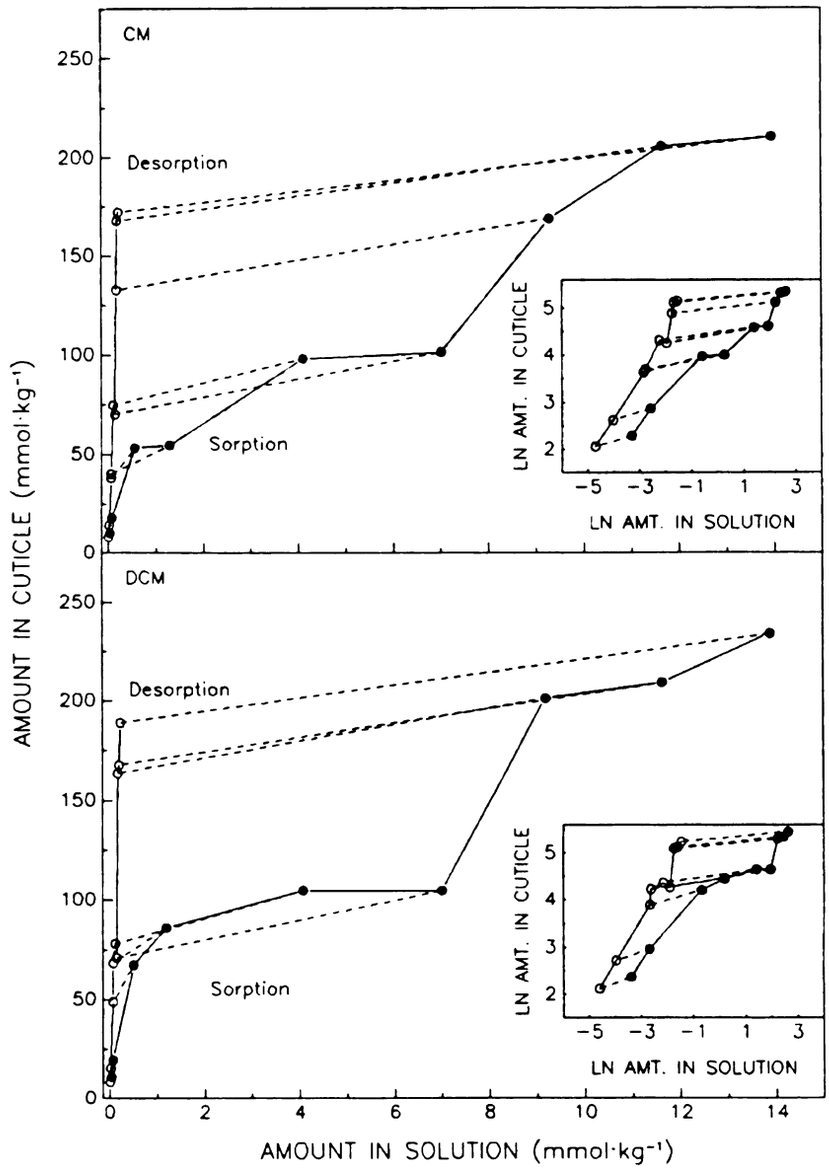

Figure 3. TX-100 sorption (●) and desorption (○) isotherms for isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles at 25°C. Initial concentrations of TX-100 (MW = 628, Rohm and Haas 1988) used for the sorption isotherm experiment were 0.005, 0.01, 0.05, 0.1, 0.3, 0.5, 0.67, 0.83, and 1.0 % (w/v) corresponding to 0.0795, 0.159, 0.795, 1.59, 4.77, 7.95, 10.6, 13.2, and 15.9 mmol kg^{-1}, respectively. Dashed lines connect respective sorption and desorption points. Insets are isotherms plotted on a logarithmic scale.

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several times greater than expected based on the sorption isotherm. Thus, the cuticle exhibits hysteresis in the sorption/desorption of TX-100. Isotherms plotted on a log-log scale (Figure 3 insets) more clearly illustrates the extent of hysteresis at all concentrations. Subsequent stepwise desorptions gave a similar trend (Figure 4).

The log-log plots of TX-100 sorption by isolated cuticles depict the linearized form of the Freundlich equation (Figures 3 and 4). The Freundlich constants were calculated for isotherms for sorption, each stepwise desorption, and desorption for each initial sorbate concentration (Table I). The Freundlich constant n, an index of isotherm linearity, was equal to 1 for linear isotherms such as those for the individual desorption steps. For curvilinear isotherms such as those of sorption and the desorption corresponding to each sorption concentration, n was greater than 1. Constants for corresponding CM and DCM sorption and desorption isotherms were similar.

The relationship between stepwise desorption number and the amount of TX-100 remaining in the cuticle after a series of stepwise desorptions (Figure 5) showed that the actual amount desorbed lagged behind the values predicted from the sorption partition coefficient (eqn 2). Further, the actual amount desorbed lagged behind the predicted value even if the data are adjusted for the buffer non-extractable fraction (about 15 % of the amount sorbed) by subtracting from the amount sorbed (data not shown).

As predicted by the equation for two phase extractions (Eqn 2), the number of stepwise desorptions (x) was linearly related to the logarithm of the amount sorbed ($\ln A_{cut}$) ($\ln A_{cut} = 2.28 - 0.76 \cdot x$; $r^2 = 0.96$). However, close inspection of this plot suggested that the relationship was curvilinear (upper curve, upper inset of Figure 5). Desorption data from this system gives a slightly better fit when the logarithm of number of extractions is plotted against the amount sorbed (lower inset: $A_{cut} = 7.74 - 1.40 \cdot \ln x$; $r^2 = 0.99$).

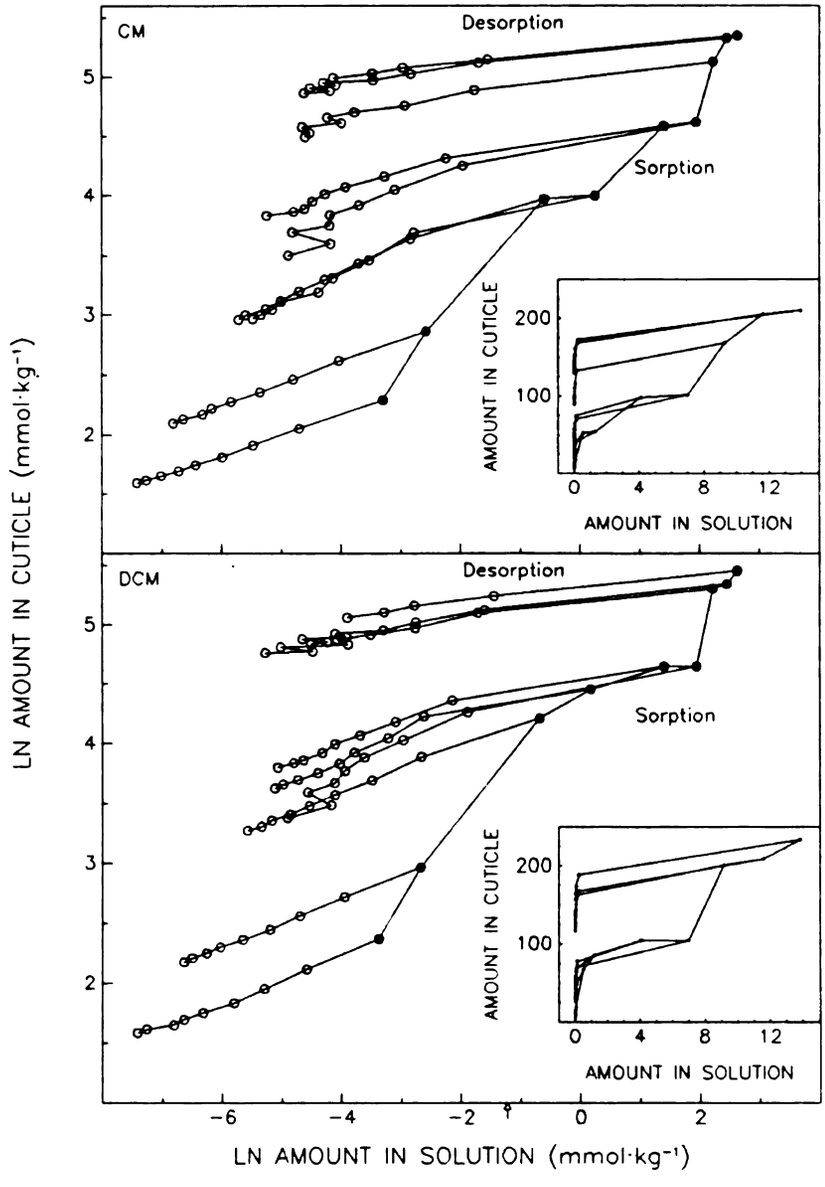

Figure 4. TX-100 sorption (●) isotherm and respective isotherms for eight stepwise desorptions (○) for isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles at 25°C. Arrow indicates CMC. Insets are isotherms plotted on an arithmetic scale.

Table I. *Freundlich constants for TX-100 sorption by and desorption from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Freundlich constants (Amount sorbed = k · Amount in solution$^{1/n}$) were calculated from sorption/desorption isotherm data (Figure 3). Desorption constants were calculated for curves describing isotherms for (1) each desorption step and (2) initial sorption concentration.

	Freundlich constants			
	CM		DCM	
	k	n	k	n
Sorption	55	2.0	66	2.2
Desorption step				
Des. 1	660	1.0	700	1.0
Des. 2	2900	0.9	2800	0.9
Des. 3	7100	0.8	6600	0.8
Des. 4	11000	0.8	9000	0.8
Initial sorption concn ($mmol \cdot kg^{-1}$)				
0.080	17	5.8	20	5.1
0.159	28	5.5	33	5.0
0.795	63	4.9	79	5.1
1.59	57	5.3	91	6.0
4.77	88	8.6	93	7.4
7.95	82	6.5	83	5.5
10.6	145	11.5	175	13.3
13.2	179	15.7	180	14.1
15.9	184	19.3	202	16.9

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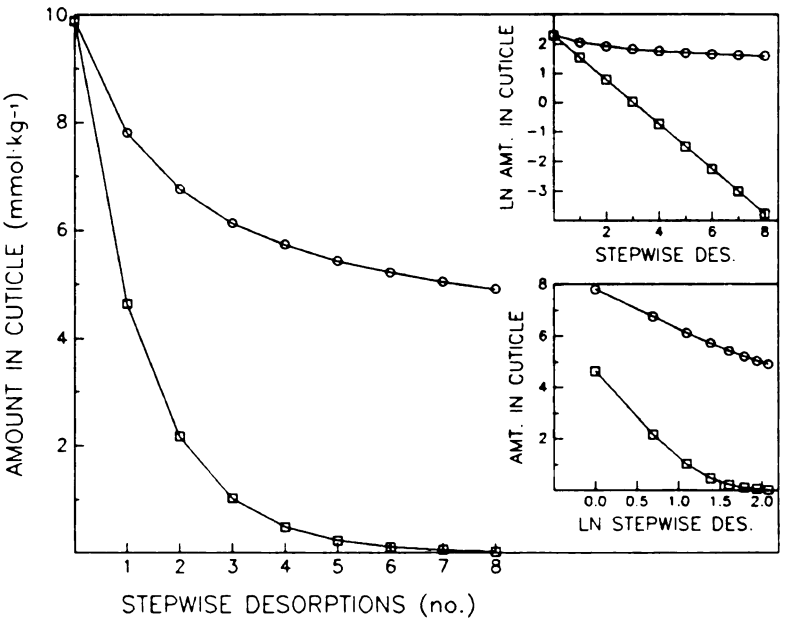

Figure 5. Graphical representation of predicted and actual data illustrating the relationship between stepwise desorption number and the amount of TX-100 remaining in the isolated tomato fruit CM. Actual values (O) were obtained from stepwise desorption of TX-100 in which the initial sorption solution consisted of 0.0795 mmol · kg^{-1} (0.05 % w/v) surfactant (Figure 3). Theoretical values (□) were predicted from the sorption partition coefficient based on two phase extraction theory.

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Effect of solvent on sorption and desorption

In general, pH did not affect sorption (Table II) or desorption (Figure 6) of TX-100 by the cuticle. However, sorption more than doubled from a strongly alkaline sorbate solution or when the CM was pretreated at pH 13. Sorption also more than doubled by pretreating the CM with 12 % BF_3 in methanol. However, pretreatment with methanol had no effect.

Desorption of TX-100 was reduced by NaCl, but increased by urea (Figure 6). Responses of CM and DCM to NaCl were the same. Enhanced desorption due to urea was greater for DCM. Further study showed that urea-enhanced desorption was slow. For urea, the time required to reach half-equilibrium ($t_{1/2}$) was 12 h compared with an average $t_{1/2}$ of 45 min for the other aqueous solution treatments.

Methanol was most effective in desorbing TX-100 from the cuticle (Figure 6). The effect of methanol was not affected by the initial sorbing concentration or the presence of cuticular waxes. Additionally, the rate of desorption in methanol was very rapid ($t_{1/2}$ was about 10 min). Continuous exposure of cuticles to fresh methanol in a flow through system over a five-day period extracted all but 0.05 % of the sorbed surfactant (data not shown).

Desorption of the buffer non-extractable fraction

Surfactants with similar ethoxy moieties were the most effective in exchanging the sorbed TX-100 (Table III). The exchange capacity of surfactants with similar EO chain lengths was unaffected by the hydrophobe. Additional studies showed that continuous exposure to fresh unlabeled TX-100 (1.59 $mmol \cdot kg^{-1}$) in a flow-through system over a five-day period removed all but 0.4 % of total amount of the radiolabeled surfactant sorbed.

As with stepwise desorption, pH did not affect desorption of the buffer non-extractable fraction, except under strongly alkaline (pH 13) conditions (Table IV). The effectiveness of solvents was related to their polarity, with acetone and methanol being most effective. Non-polar solvents (hexane and

Table II. *The effect of pH, BF_3, and CH_3OH on sorption of TX-100 by isolated tomato fruit CM.*

Pretreatment time: 48 h. Initial sorbate dosing solution consisted of 1.59 mmol·kg^{-1} (0.1 % w/v) TX-100 in buffer at 22°C. Amount in cuticle is the mean (± SE) of five replicates.

Pretreatment solution	Sorbate solution	Amount in cuticle
pH	*pH*	*mmol·kg^{-1}*
3	3	49.2 ± 0.9
3	6	50.3 ± 0.3
3	9	50.7 ± 1.8
3	13	127.6 ± 0.5
13	3	107.0 ± 1.4
13	13	137.9 ± 2.1
12 % BF_3 in CH_3OH	3	129.2 ± 0.7
CH_3OH	3	49.3 ± 1.4
CH_3OH	13	117.6 ± 2.3

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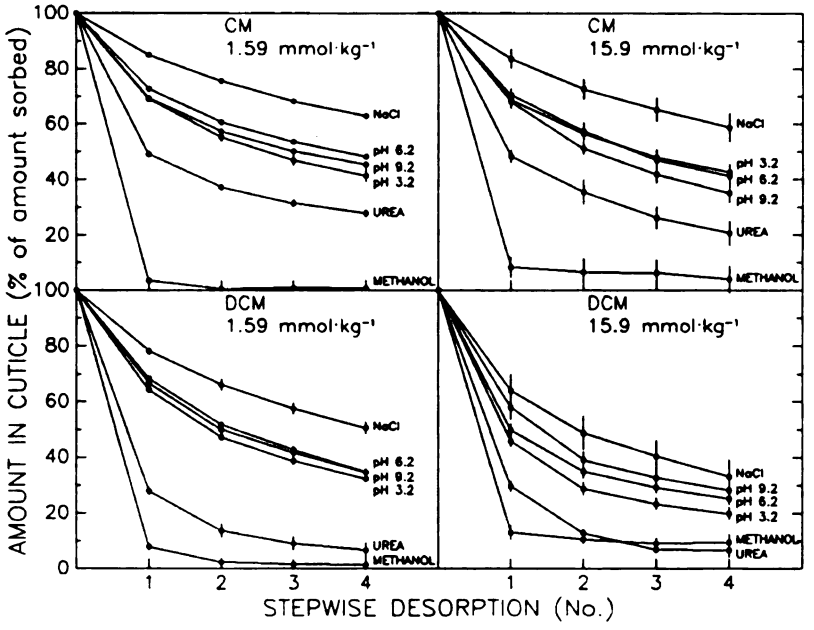

Figure 6. Effect of pH, NaCl, urea, and methanol on the desorption of TX-100 from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles. Initial TX-100 sorbate concentrations are listed. Concentrations for NaCl and urea were 1.0 and 5.0 mM, respectively. Values represent the mean (± SE) of five replicates.

Table III. *Exchange of the buffer non-extractable fraction of TX-100 from isolated tomato fruit cuticles (CM) by various surfactants.*

Cuticles were equilibrated with 1.59 mmol · kg^{-1} (0.1 % w/v) [^{14}C]TX-100 at 22 °C, extensively desorbed with buffer solution, and subjected to four stepwise desorptions in 1.5 mL of 1.59 mmol · kg^{-1} of the surfactants listed (see materials and methods). Cuticles were oxidized to determine the amount of radioactivity remaining in the cuticle. Amount in cuticle (mean ± SE, n = 5) is the percent of the amount initially sorbed remaining in the cuticle after the fourth surfactant exchange.

Surfactant	Ethylene oxide	Hydrophobe	Amount in cuticle
	no. per molecule		*% of amount sorbed*
Buffer			11.7 ± 1.0
TX-35	3	Octylphenyl	10.5 ± 0.4
TX-45	5	Octylphenyl	7.1 ± 0.3
TX-100	9.5	Octylphenyl	4.6 ± 1.3
TX-165	16	Octylphenyl	5.9 ± 0.2
TX-405	40	Octylphenyl	8.1 ± 0.4
CO-630	10	Nonylphenyl	4.2 ± 0.1
LA-C_9	10	Nonyl	5.4 ± 0.4

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Table IV. *Desorption of the buffer non-extractable fraction of TX-100 from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles by various solvents and selected treatments.*

Cuticles were equilibrated with 1.59 mmol·kg^{-1} (0.1 % w/v) [^{14}C]TX-100 at 22°C, extensively desorbed with buffer solution, and subjected to four stepwise desorptions by 1.5 mL of the solvents and buffer treatments listed (see materials and methods). Cuticles were oxidized to determine the amount of radioactivity remaining in the cuticle. Amount in cuticle (mean ± SE, n = 5, N.D. is not determined) is the percent of the amount initially sorbed remaining in the cuticle after the fourth stepwise desorption. Dielectric constants are listed for 25°C (Weast and Astle 1981 except DMSO, Windholz 1983).

		Amount in cuticle	
Solvent		CM	DCM
	pH	*% of amount sorbed*	
Buffer	0.2	11.5 ± 0.6	11.7 ± 0.8
Buffer	3.2	12.4 ± 0.7	12.0 ± 1.2
Buffer	6.2	12.1 ± 0.7	13.0 ± 0.2
Buffer	9.2	11.4 ± 0.4	12.0 ± 0.1
Buffer	13.2	7.6 ± 0.2	7.1 ± 0.5
	Dielectric constant		
Hexane	1.9	4.4 ± 0.2	10.7 ± 0.6
Chloroform	4.8	2.6 ± 0.1	7.0 ± 0.8
Ethyl acetate	6.0	2.3 ± 0.2	2.6 ± 0.2
Acetone	20.7	2.1 ± 0.1	2.0 ± 0.1
Methanol	32.0	0.9 ± 0.1	2.6 ± 1.3
DMSO	45.0	2.7 ± 0.2	2.8 ± 0.3
Water	81.0	11.7 ± 0.6	12.5 ± 1.1
	Treatment		
Buffer	5 M urea	12.7 ± 1.2	12.7 ± 0.8
Buffer	1 M NaCl	13.0 ± 0.4	12.3 ± 0.6
Buffer	1 M NH_4Cl	12.8 ± 0.5	13.4 ± 0.4
Methanol	12 % BF_3 in methanol	0.8 ± 0.1	2.1 ± 0.9
Buffer	45°C	13.5 ± 0.5	13.0 ± 0.4
Buffer	75°C	12.5 ± 0.4	12.9 ± 0.4
Buffer	Sonication (1 h)	11.7 ± 0.3	N.D.
Buffer	Vacuum (2.7 Pa; 1 h)	12.1 ± 0.7	N.D.

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chloroform) were effective for CM, but not DCM. NH_4Cl, NaCl, and urea in buffer, as well as high temperatures, sonication, and vacuum did not promote desorption.

Discussion

Sorption/desorption hysteresis

Sorption/desorption isotherms represent relationships between the amount of sorbate in the solution and the sorbent at equilibrium and constant temperature. These relationships are influenced by the affinities and capacities of the two phases (sorbent and solvent) for the sorbate and are characteristic of the components of a system (Giles et al. 1960; Kipling 1965). When sorption is completely reversible, sorption and desorption isotherms are coincidental or singular.

One prominent feature of TX-100 sorption and desorption isotherms for the isolated tomato fruit cuticle is that the isotherms are nonsingular (Figures 3 and 4). Isolated cuticular sorption of TX-100 is not completely irreversible and the cuticle exhibits hysteresis. Hysteresis has been previously documented with various textiles and the sorption of other ethoxylate surfactants (Gordon and Shebs 1968; Waag 1968). Further, with the exception of 2,4-dichlorophenoxyacetic acid (Morse 1971), tomato fruit cuticles exhibited hysteresis for sorption of methylene blue (Morse 1971), benzyladenine (BA), naphthaleneacetic acid (NAA), gibberellic acid (GA_3), and related Triton X surfactants (Appendix V, Table XI and Figures 22 and 24), as well as N_2 (Section II).

Two models can be visualized to explain these data. The first is for sorbents which have a fixed number of sites available for sorption on the surface (adsorption). As the sorbate level increases, proportionally less sorbate adsorbs due to competition for sites. In some cases, multi-layers of sorbate may form on the surface once the first layer is filled. For completely reversible processes, the number of sites that are filled or molecules that are in a monolayer is concentration dependent. However, the amount sorbed may depend on whether an equilibrium level of sorbate was attained by increasing (sorption) or decreasing (desorption) the sorbate level. An example of such a history-dependent process

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is the sorption of gases by rigid porous materials. One theory used to explain adsorption hysteresis is the "ink bottle" theory, a model based on the observation that an ink bottle is easier to fill than to empty. The model suggests that sorption in pores is controlled by pressure-dependent effective radii. Since these radii favor pore filling over emptying, desorption often lags behind sorption at a given pressure (Adamson 1982).

The second model is for sorbents of which the sorbate can penetrate the matrix (absorption). As the sorbate concentration increases, the proportion of sorbate which sorbs remains constant. In this case sorption is limited by the affinities of the two phases for the sorbate and not by the number of sorption sites. Flexible polymers (e.g., rubbers) are example sorbents of this type (Rogers 1985). In theory, sorption and desorption are simply processes of sorbate partitioning to and from the sorbent. If sorption is completely reversible, the sorption and desorption partition coefficients are equal. In practice, sorption is often hysteretic. Unfortunately, sorption hysteresis of polymers cannot be explained by the ink-bottle theory and others like it because polymers lack well-defined pores and rigid structures. Comparably satisfying theories are needed for explaining sorption hysteresis for polymeric sorbents.

We focused our attention on the second model since the CM often behaves as a constant partitioning polymer (Bukovac et al. 1990). Several hypotheses have attempted to explain sorption hysteresis for polymeric sorbents. Two features are common. First, they require that some polymer property changes as sorbent levels increase. Second, they emphasize that the polymer is both flexible enough to accommodate increasing sorbate and is sufficiently rigid to sustain irreversible sorption-induced conformational changes (Bailey et al. 1971; Hiemenz 1984). With this in mind, hysteresis may be explained by a concentration dependence of the binding sites per sorbate molecule (Kipling 1965), the effect of the sorbate to arrangement of the polymer chains (Giles et al. 1974), or the sorbate-sorbent free energy of interaction (Bryan 1987). For example, while the overall free energy of water binding to a protein may be constant, binding forces of individual molecules may increase as the sorbate concentration increases. This may be due to the forcing of some sorbate molecules into tighter

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As mentioned above, the hysteretic nature of isolated cuticular sorption of TX-100 is characterized by (1) a buffer extractable fraction that does not desorb as predicted by sorption partitioning (Figures 2, 3, and 4) and (2) a buffer non-extractable fraction that does not desorb even after extensive desorption. One view of these two fractions is that they result from TX-100 binding to sites that are distinctly "reversible" or "resistant" (Di Toro and Horzempa 1982). This hypothesis is further supported by the linear relationship found between buffer non-extractable fraction and the amount sorbed (Section IV). This hypothesis fails to account for the cuticular sorption/desorption data because the irreversible fraction consists of more than the buffer non-extractable fraction. A simple way to illustrate this is to correct the desorption isotherms by subtracting the non-extractable fraction (about 10 to 20 % of the total amount sorbed) from the desorption isotherms in Figure 3. If sorption hysteresis were due only to this fraction, the corrected desorption curves should become coincidental with the sorption isotherm. Subtraction of this fraction accounts for some, but not all of the difference between the sorption and desorption isotherms (not shown). Clearly, the buffer extractable fraction contributes to sorption hysteresis.

An alternative hypothesis suggests that the failure to desorb may be explained by a sorbent that has a gradation of site affinity. With time, more remote sites with increasing affinities become filled (Steinberg et al. 1987). Although no single site may be classified as irreversible, it is possible to imagine a gradation of sites that range from low to very high affinity. As desorption proceeds, low affinity sites empty, while high affinity sites remain occupied. Molecules sorbed to sites of very high affinity may be effectively irreversibly sorbed.

Freundlich's equation is often used as a model for desorption. While the fit of the Freundlich equation is reduced by the second plateau in our TX-100 sorption isotherm ($r^2 \geq 0.96$), the constants allow comparisons of various isotherm shapes. Isotherms that are convex to the x axis, such as the cuticular sorption isotherms for TX-100, n is greater than one. Isotherms for each desorption step are

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nearly linear (n is about 1), indicating that extraction by buffer solutions with surfactant concentrations below the CMC is strictly a partitioning event that is presumably not limited by sorbate or sites. The values of n for isotherms for each concentration are all greater than one, and are much greater than the n of the sorption isotherm. The degree of reversibility of sorption can be quantified by comparing the ratios of n for sorption against n for desorption with smaller ratios indicating greater reversibility (Di Toro and Horzempa 1982). By Freundlich analysis, sorption of the TX-100 at higher concentrations is less reversible than for lower concentrations. This was also the case for CM and DCM of tomato and pepper fruits (Appendix IV, Figure 15). The apparent increase in affinity for the high concentrations is difficult to understand. However, this may be used as an argument against multi-layer formation on the surface at high concentration. Presumably multi-layers of surfactant should be more readily accessible than the absorbed or surface absorbed material.

Regardless of the mechanism of hysteresis, several aspects of sorption hysteresis are of practical interest. First, a fraction of sorbate that can not be extracted by buffer solution cannot diffuse through the cuticle. This fraction is effectively immobilized as if it were chemically bonded with the cuticle. From this perspective, interpretation of the diffusion time lag in transport studies is complicated by immobilization of the penetrant. Immobilization may effectively reduce the driving force thus causing an underestimation of the diffusion coefficient (Fenelon 1974; Crank 1975). Therefore, one strategy for improving the uptake of foliar applied chemicals may be to minimize or remobilize the immobilized fraction. Another strategy may be to improve the desorbability of the buffer-extractable fraction.

Second, cuticular sorption hysteresis may be an important consideration with respect to nutritional and environmental concerns. The cuticle, as the outer barrier of plant organs, may contain a high dose of pesticide that has not diffused into the plant. Repeated washings may remove the surface residues, but desorption studies suggest that a fraction of the absorbed sorbate may persist. We note that buffer non-extractable fractions were found for all sorbates tested including BA, NAA, GA_3, and the Triton X surfactants TX-35, TX-102, TX-165, and TX-405 (Appendix V, Figures 23 and 24). The desorptive properties of the cuticle may be important with respect to environmental partitioning in that

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cutinaceous material is resistant to degradation and persists for long periods in the environment. Also, a re-examination of the partitioning between the cuticle and the environment may be necessary to account for hysteresis.

Solvent effects on sorption and desorption

The increase in sorption at high pH (Table II) may have resulted from (1) increased hydrogen bonding between surfactant and cuticle due to removal of weakly acidic hydrogens (Morrison and Boyd 1979) or (2) creation of new or the strengthening of existing sorption sites through depolymerization of the matrix (Holloway 1982). If alkalinization affected sorption only through the deprotonation of weakly acidic moieties, then the efffect of pretreatment of the cuticles with base would not persist in acidic conditions. However, alkaline pretreatment of CM increased surfactant sorption under acidic conditions (Table II). A similar enhancement of sorption was obtained for CM pretreated with the depolymerizing agent BF_3 (12 % in methanol). These results suggest that the alkaline effect on sorption is probably due to depolymerization.

Surfactant desorption was decreased by NaCl and increased by urea. One interpretation of the effects of buffer solution additives on desorption (Figure 6) may be related to their effect on water structure. Salts such as NaCl are known as "water structure makers", i.e. they increase the interaction among water molecules. Increasing the affinity of water for itself decreases its interaction with more non-polar molecules like the surfactant. Urea, on the other hand, is a "water structure breaker". As such, urea reduces the interactions between water molecules and thereby increases its interaction with the surfactant (Rosen 1989). We observed that the rate of urea enhancement of desorption is slow. This may be due to low rate of urea penetration of the cuticle (Yamada et al. 1965).

If desorption is considered a partitioning process, then the most effective extracting solvents should have the best solvency characteristics as determined by Flory-Huggins theory of polymer solubility (Cohen Stuart et al. 1984). The degree of solvent-sorbate interaction is influenced by many factors, most important of which is the solvent polarity relative to sorbate polarity. Although TX-100 is water

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We thank Dr.

soluble, solvents that are less polar than water may be expected to be more effective than water because of the nonpolar nature of the hydrophobe. Indeed, methanol, which is slightly nonpolar, is a very effective solvent in that it desorbed nearly all of the sorbed surfactant in the first stepwise desorption (Figure 6).

The effectiveness of methanol may be further enhanced if it induces swelling in the cuticle (Freeman and Cheung 1981). The $t_{1/2}$ for surfactant desorption by methanol is about 10 min compared with a $t_{1/2}$ of about 45 min for buffer solution. Since the $t_{1/2}$ of a solvent is inversely related to the diffusion coefficient (Crank 1975), methanol increases the diffusion coefficient of TX-100 for the cuticle. The importance of solvent polarity is also apparent for desorbing the buffer non-extractable fraction (Table IV). Solvents that are slightly polar are most effective. Part of the effectiveness of the nonpolar solvents is that it may induce swelling of the polymer thus increase the accessibility of the physically "trapped" molecules.

The exchangability of certain surfactants with the buffer non-extractable surfactant is somewhat surprising in that it suggests a site specificity (Table III). A potential scenario of surfactant sorption is that at least some of molecules sorb to the cuticle and migrate to a high affinity regions. These molecules can be removed only when they are displaced by molecules of similar structure. This model suggests that cuticular properties such as polarity may be probed by a series of molecules of different sizes and polarities.

Acknowledgments

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SECTION

Abstract

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SECTION IV: CUTICULAR TRANSPORT PROPERTIES: 3. EFFECT OF TEMPERATURE ON SORPTION AND DESORPTION OF AN OCTYLPHENOXY SURFACTANT

Abstract

Triton X-100 (TX-100, OP+9.5 EO) sorption by and desorption from cuticular membranes (CM) isolated from tomato (*Lycopersicon esculentum* Mill. *cv.* Pik Red) fruit were examined as functions of temperature and sorbate concentration. The rate of TX-100 sorption was limited by diffusion and thus can be described by Fick's Law of diffusion. Sorption, below the critical micelle concentration (CMC), and desorption kinetics fit first order processes based on the relationship between driving force and rate. Rates of sorption and desorption generally increased slightly with temperature, (activation energies < 15 $kJ \cdot mol^{-1}$). CM/buffer and octanol/buffer partition coefficients for TX-100 below the CMC increased with temperature. Enthalpy changes associated with transfer for CM/buffer and octanol/buffer were about 25 and 5 $kJ \cdot mmol^{-1}$, respectively. Temperature effect on TX-100 partitioning can be related to dehydration of the polyoxyethylene chain with increasing temperature. Desorption was less temperature-dependent than sorption. Cuticular waxes reduced the extent of sorption of TX-100, but not the rates of sorption and desorption or extent of desorption. The magnitude of the buffer non-extractable fraction of TX-100 in the CM was a linear function of the amount sorbed. The lack of complete reversibility of sorption/desorption suggested that sorbate interaction with the cuticle was a complex process that may be related to sorption-induced changes in the cuticle.

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Introduction

The cuticle is a non-living, hydrophobic membrane that covers the aerial parts of terrestrial plants. The cuticle restricts excessive water loss and pathogen invasion (Martin and Juniper 1970; Cutler et al. 1984) and limits penetration of foliar applied chemicals (Bukovac et al. 1981). While cuticle permeability has been examined frequently (for a recent review see Schönherr and Riederer 1989), the process of permeation is not well understood.

Surfactants are used in foliar spray formulations to increase the efficacy of the active ingredient (a.i.). In addition to improving the dispersal of a hydrophobic a.i. in the spray solution and increasing the wetting of the cuticle, surfactants may also alter cuticle permeability (Foy and Smith 1969; Seaman 1990). Recent studies indicate that some surfactants, including the ethoxylated octylphenoxy surfactants, increase the permeability of isolated cuticular membranes (CM) to water (Riederer and Schönherr 1990) and 1-naphthaleneacetic acid (NAA, Knoche personal communication). However, little is known about the mechanisms by which surfactants interact with the cuticle.

One approach to the study of intermolecular interactions is to examine the kinetics and thermodynamics of sorption and desorption. While surfactants represent an inherently complex mixture, this approach has been used with some success in determining their role in detergency (Fava and Eyring 1956; Shaeiwitz et al. 1981). From one perspective, surfactant/cuticle interactions and cuticle permeation in general can be viewed as the summation of several transport processes. The overall process requires that the penetrant sorb to, diffuse through, and desorb from the cuticle.

First, sorption of TX-100 to isolated tomato fruit cuticles is characterized by a complex sorption isotherm (Shafer and Bukovac 1987a, and Section II). While cuticular sorption isotherms for 2,4-dichlorophenoxyacetic acid (2,4-D, Morse 1971), NAA (Shafer et al. 1988), and benzyladenine (BA, Shafer personal communication) are linear over a wide concentration range, the sorption isotherm of TX-100 is characterized by three phases. The isotherm is near linear at concentrations below the CMC (0.019 %), reaches a local plateau near the CMC, and increases sharply and reaches a second plateau

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at concentrations around 1.0 % (w/v). These isotherms suggest that sorption is limited by either the number of sites on the sorbent or amount of sorbate molecules available for sorption (Section II).

Second, the desorption isotherm of the TX-100 for isolated tomato fruit cuticles is not coincidental with the sorption isotherm. The lack of complete reversibility of sorption suggests that the association is not simple partitioning between the two phases, but may result from changes induced in the cuticular membrane during sorption (Section III).

Third, TX-100 permeates isolated cuticles (Petracek and Bukovac 1989; Schönherr and Riederer 1989; Appendix VI). Thus, the surfactant interacts with the cuticle both at the surface and within the matrix. Both cuticular sorption (Shafer and Bukovac 1987) and permeation (Petracek and Bukovac 1989) of TX-100 are significantly reduced on removal of soluble cuticular lipids.

In this section, we report on further examinations of sorption and desorption characteristics of isolated tomato fruit cuticles. The objective was to determine temperature and concentration effects on the rate and extent of TX-100 sorption and desorption by isolated tomato fruit cuticles in order to gain insight into the interaction between surfactant and cuticle.

Materials and methods

Plant material

Locally grown, pesticide-free mature tomato (*Lycopersicon esculentum* Mill. cv. Pik Red) fruit were selected free of visible defects. Fruits were sectioned and sections were incubated at room temperature in several changes of enzyme solution consisting of cellulase (0.2 % w/v; Sigma), pectinase (4 % w/v; ICN Nutritional Biochemicals), and NaN_3 (1 mM) in 50 mM sodium citrate buffer solution at pH 4.0 (Orgell 1955; Shafer and Bukovac 1987). The cuticles were rinsed extensively with flowing distilled water and any remaining cellular debris was removed manually. The cuticles were air dried and stored in sealed jars at room temperature. Cuticles isolated in this manner will be referred to as cuticular membranes (CM). Waxes were batch extracted from isolated CM with chloroform:methanol

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(1:1 v/v) at 50°C and these cuticles will be referred to as DCM. Unless specified, the term isolated cuticles will refer to both CM and DCM.

Chemicals

Buffer solution: Buffer solution consisted of 20 mM citrate titrated with NaOH to pH 3.2 with NaN_3 (1 mM) included to inhibit bacterial and fungal growth.

Surfactant: TX-100 (α-[4-(1,1,3,3,-tetramethylbutyl)phenyl]-ω-hydroxypoly(oxy-1,2-ethanediyl); Rohm and Haas) is an ethoxylated octylphenoxy (OP+nEO) surfactant with an average of 9.5 ethylene oxide (EO) groups per molecule. TX-100 is a mixture of molecules whose number of EO units follows a Poisson distribution (average MW = 628). Ring-labelled TX-100 ([U-^{14}C]OP + 9.5 EO; specific activity, 28.1 MBq · g^{-1}) was used to follow sorption and desorption. Labeled and nonlabeled surfactant co-chromatographed on TLC and radio-TLC (silica gel and 95:5 water saturated methyl ethyl ketone:methanol). Four surfactant concentrations were used in these experiments: 0.0159, 0.159, 1.59, and 15.9 mmol · kg^{-1} corresponding to 0.001, 0.01, 0.1, and 1 % w/v surfactant solution, respectively. These concentrations were chosen because they represented characteristic points on the TX-100/isolated cuticle sorption isotherm. Two concentrations, 0.0159, 0.159 mmol · kg^{-1}, are below the CMC of TX-100 (0.302 mmol · kg^{-1} or 0.019 %, w/v Rohm and Haas 1988) and represent the near linear phase of the isotherm. The first and second plateaus of the isotherm are represented by 1.59, and 15.9 mmol · kg^{-1}, respectively.

Sorption/desorption kinetics and thermodynamics

Sorption and desorption: Five mg of sectioned cuticles (approx. 2 x 10 mm strips) were weighed in 5 mL glass vials and equilibrated with surfactant solution. Sorption was followed over time by radioassay of aliquots (100 μL) in 10 mL scintillation cocktail (Safety-Solve: Research Products International Corp) by liquid scintillation spectrometry (Packard Tri-Carb 1500 Liquid Scintillation Analyzer). Samples were counted to a 2 σ error of 1.0 % and corrected for background. The amount

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sorbed was calculated based on the difference between the amount of surfactant in vials with and without isolated cuticles. Stepwise desorptions were performed by successively decanting the solution after equilibration from the vials and replacing with fresh buffer. Similar to sorption, desorption was followed by radioassay and the amount remaining in the cuticle was calculated by difference (Appendix I). Extended desorption was performed by packing columns with isolated cuticles and subjecting them to a continuous flow (about 1 $L \cdot day^{-1}$) of fresh buffer solution for thirty days. The extensively desorbed cuticles were oxidized at 900 °C in an OX400 biological oxidizer (R. J. Harvey Instrument Corporation). Radiolabeled carbon dioxide from the oxidized tissue was trapped in 20 mL of 1:2 v/v Carbo-Sorb II (Packard) : toluene-based scintillant (3a20, Research Products International Corporation) and radioassayed.

Kinetics: Two concerns in performing sorption kinetics experiments were addressed in preliminary studies. First, sorption may be limited by the time required to hydrate the dry (dehydrated) cuticle rather than by sorption *per se*. Hydration rate is slow as evidenced by the observation that dry cuticles float on the surface of the buffer solution for several hours. To minimize this problem, cuticles were prehydrated in 1.5 mL buffer solution for 48 h prior to initiating the sorption experiment. Second, sorption may be rate limiting by inadequate mixing of the sorbate solution and by formation of boundary layers. A preliminary study established that rates of sorption and desorption were maximized by rapidly shaking the vials placed at a 45° angle with short, abrupt strokes.

Temperature effects on surfactant sorption were examined by measuring the rate of sorption by prehydrated cuticles at four concentrations of TX-100 (0.0159, 0.159, 1.59, and 15.9 $mmol \cdot kg^{-1}$) and four temperatures (5, 15, 22, and 35 °C). Temperature effects on surfactant desorption were established by first equilibrating the cuticles in TX-100 at four concentrations of surfactant at 22 °C, and then desorbing (stepwise) the cuticles at the above four temperatures. All experiments were performed in controlled temperature rooms maintained within ± 0.5 °C. Solutions and vials containing weighed cuticles were equilibrated at their appropriate temperature prior to the start of the experiment. At zero time, 1.5 mL

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of sorbate solution were added to the vials. Initial rates of sorption and desorption were followed by assaying the solutions (100 μl) at 10, 20, and 30 min.

Since sorption and desorption are mass transfer processes, their respective rates can be quantified by analysis used for reaction kinetics. The process of transferring sorbate A from one phase to another can be described by a simple two-phase partitioning event in which neither phase is site limited. The initial sorption rate or rate of depletion of the sorbate from solution ($-dA_o/dt$) were calculated from a regression line through four time points (0, 10, 20, and 30 min) on a plot of time vs. amount in solution. The initial desorption rate or rate of depletion of the sorbate from the cuticle was calculated from a regression line of the plot of time vs. amount in the cuticle. Both rates can be expressed in terms of the rate equation:

$$(1) \quad -\frac{dA_o}{dt} = k \cdot A_o^{\,n}$$

where k is the rate constant and n is the order of reaction or number of molecules involved in each event. Thus, the slope of a plot of ln A_o vs. ln ($-dA_o/dt$) gives the order of reaction. If the order of reaction is known, then Eqn (1) can be used to calculate rate constants for all concentrations. The activation energy (E_a) can then be estimated from the rate constants by equation 2:

$$(2) \quad \ln k = -\frac{E_a}{R \cdot T} + \ln C$$

where C is the Arrhenius constant, R is the gas constant, and T is the temperature (Shoemaker et al. 1981; Laidler 1987).

Alternatively, sorption and desorption can be analyzed as processes whose rates are limited by diffusion. The time course of a process can be expressed in terms of time$^{1/2}$ and M_t/M_∞ where M_t/M_∞ is the ratio amount in cuticle (sorption) or solution (desorption) to the equilibrated amounts at time *t*. For processes that are diffusion controlled and obey Fick's laws of diffusion, a plot of time$^{1/2}$ vs. M_t/M_∞

is approximately linear through M_t/M_∞ equals 0.5 or the time required to attain half of the equilibrium level ($t_{1/2}$). In this case the diffusion coefficient can be determined by equation 3:

$$(3)\quad D = \frac{0.049 \cdot l^2}{t_{1/2}}$$

where l is the thickness of the sorbent (Crank 1975; Rogers 1985; Cussler 1988).

Thermodynamics: The effects of temperature on sorption and desorption were evaluated in the same experiment. For this determination, kinetic experiments were carried out to equilibrium. Both sorption and desorption were expressed as partition coefficients ($K_{cuticle/buffer}$, $K_{c/b}$) or the ratio of concentrations of surfactant in the cuticle to that in buffer solution. Changes in free energy (ΔG) of transfer can be calculated for sorption and desorption by equations 4 and 5, respectively:

$$(4)\quad \Delta G = - R \cdot T \cdot \ln K_{c/b}$$

$$(5)\quad \Delta G = R \cdot T \cdot \ln K_{c/b} .$$

Since desorption proceeds in the opposite direction of sorption, the sign in equation 5 is positive. Also, both equations imply that concentration is proportional to activity. This assumption, which is not true for surfactant concentrations above the CMC, will be addressed in the discussion. Changes in enthalpy (ΔH) and entropy (ΔS) of transfer are related to ΔG and temperature as shown in equation 7:

$$(7)\quad \Delta G = \Delta H - T \Delta S .$$

Values for ΔH and ΔS were estimated by linear regression of the relationship between T and ΔG (Peters 1975; Riederer and Schönherr 1986).

Octanol/buffer solution partitioning: Five mL buffer solution containing radiolabeled surfactant (0.0159, 0.159, 1.59, and 15.9 mmol $\cdot$ kg^{-1}) was partitioned against 5 mL 1-octanol at 5, 15, 22, and 35°C. Solutions were vortexed for 10 s in a 20 mL plastic test tube and allowed to separate for 6 h. One mL

samples were taken from the bottom (buffer) phase by inserting a syringe needle through the test tube wall and the top (octanol) phase with a pipette. This procedure accounted for more than 95 % of the total surfactant in all cases. The partition coefficient ($K_{octanol/buffer}$, $K_{o/b}$) was calculated as the ratio of surfactant concentration in octanol to that in the buffer solution. The thermodynamic constants (ΔG, ΔH, and ΔS) for the transfer of surfactant from buffer to octanol were calculated as described above.

Results

Kinetics

The rate of sorption of TX-100, expressed as square root of time ($t^{1/2}$) vs. the fraction of the equilibrated sorption level (M_t/M_∞), was significantly greater for prehydrated than non-prehydrated CM (Figure 1). Sorption, which is controlled by simple diffusion, is linear through M_t/M_∞ equals 0.5 or $t_{1/2}$ (Crank 1975; Rogers 1985). The time course of TX-100 sorption to prehydrated CM was linear, indicating that sorption of TX-100 by CM was diffusion-controlled. In contrast, the sorption time course for the non-prehydrated CM was non-linear suggesting that the sorption was controlled, in part, by the rate of hydration.

The linearized form of the rate equation (eqn. 1) illustrated in Figure 2 for sorption and four stepwise desorptions of TX-100 by CM at 22°C confirms that the initial rates of sorption and desorption ($-dA_o/dt$) were dependent on their respective driving forces (A_o). In general, the slopes of the rate equation curves are similar for sorption and desorption and thus the orders of reaction and the rate constants are similar for both processes. This suggests that the mechanisms of TX-100 sorption and desorption by CM are similar. However, closer inspection of these curves indicates several differences.

First, the slope of the sorption rate curve decreased with increasing concentration. The slopes for sorbate concentrations below and above the CMC are 1.02 and 0.72, respectively (Figure 2). Similar changes in the rate curves were noted for all temperatures and for both CM and DCM (Appendix IV, Figures 17 and 18). Second, curves for the rate equations for stepwise desorptions were nearly linear

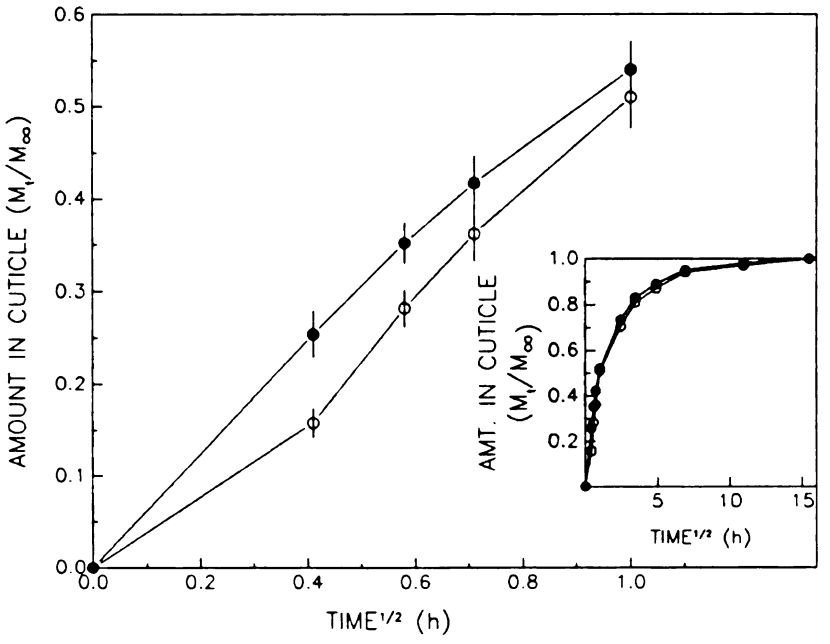

Figure 1. Effect of prehydration on the rate of isolated tomato fruit cuticle (CM) sorption of TX-100 (1.59 mmol·kg^{-1}). Sorption rates for prehydrated CM (●) and non-prehydrated CM (○) are expressed in terms of fraction sorbed vs. time$^{1/2}$. Inset depicts an extended time course of sorption.

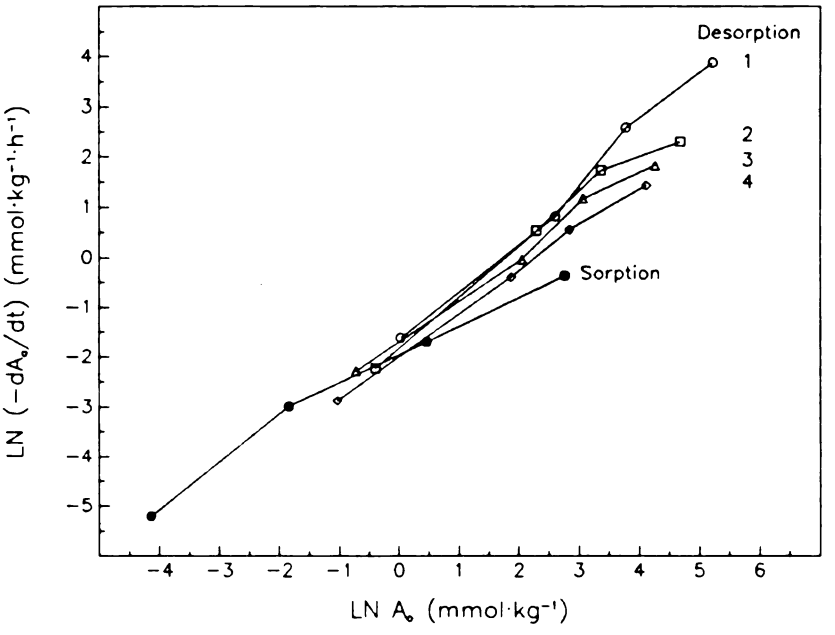

Figure 2. Graphic representation of rate equations ($\ln -dA_0/dt = n \cdot \ln A_0 + \ln k$) for the sorption (●) and stepwise desorptions (no. 1, □; no. 2, ▵; no. 3, ◇; no. 4, ▽) of TX-100 by isolated tomato fruit cuticle (CM) at 22°C. The four points on each rate curve represent initial sorbate solution concentrations of 0.0159, 0.159, 1.59, and 15.9 $mmol \cdot kg^{-1}$.

and the slopes equal to one. Thus, desorption is a first-order process (Figure 2). For the series of stepwise desorptions, the rate equation curves shift towards the abscissa for each successive step. This shift corresponds to a concomitant reduction in rate constants for each desorption step. A similar decrease in desorption rate for successive stepwise desorptions was observed for BA (Appendix V, Table VII).

Rate constants were calculated for sorption and desorption by eqn. 1. Both processes were assumed to be first order for all initial sorbate concentrations (Table I). The validity of this assumption will be discussed later. The rates of sorption increased with temperature except for CM at the highest concentration. The Arrhenius equation (eqn. 2) was used to quantify the temperature effect on the initial rate of sorption and desorption. Sorption activation energies were relatively low ($< 15\ kJ \cdot mol^{-1}$) corresponding to about 25 % increase in rate constant for every 10°C increase (Appendix IV). Rates of desorption were less temperature sensitive than were rates of sorption (activation energies < 10 $kJ \cdot mol^{-1}$). For the highest initial sorbate concentration of 15.9 $mmol \cdot kg^{-1}$, the rate constants for sorption and desorption decreased with an increase in temperature.

Thermodynamics

Surfactants strongly favored the cuticle over the buffer solution at all temperatures and concentrations (Tables II and III). The decrease in $K_{c/b}$ and ΔG values with increasing concentration corresponds to a decrease in rate of sorption with an increase in concentration. With the exception of the highest concentration (15.9 $mmol \cdot kg^{-1}$), sorption increased with an increase in temperature. For the lower three concentrations (0.0159, 0.159, and 1.59 $mmol \cdot kg^{-1}$), the $K_{c/b}$ increased about 50 % for every 10°C increase (Table II). The increase in partitioning with temperature translated into positive ΔH contribution of about 25 $kJ \cdot mol^{-1}$ (Table IV). Contributions from ΔS were large and positive. While the positive contribution of enthalpy contributed adversely to surfactant partitioning into the cuticle, the entropy component apparently drove the process. At the highest concentration (15.9

Table I. *Kinetic rate constants (k) for TX-100 sorption to and desorption from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Rate constants were calculated from the initial sorption or desorption rates which assumed first order processes. Stepwise desorption (Des) rate constants were determined for cuticles equilibrated at 22°C. All values are the means (± SE) of eight replicates.

		Rate constant			
		Initial sorbate solution concentration ($mmol \cdot kg^{-1}$)			
Process	Temp	0.0159	0.159	1.59	15.9
	°C		h^{-1}		
			CM		
Sorption	5	0.26 ± 0.03	0.22 ± 0.02	0.07 ± 0.01	0.06 ± 0.01
	15	0.32 ± 0.05	0.29 ± 0.04	0.10 ± 0.02	0.05 ± 0.02
	22	0.34 ± 0.04	0.31 ± 0.04	0.11 ± 0.02	0.04 ± 0.01
	35	0.41 ± 0.04	0.38 ± 0.06	0.13 ± 0.02	0.04 ± 0.01
Des 1	5	0.16 ± 0.02	0.16 ± 0.01	0.30 ± 0.02	0.38 ± 0.12
	15	0.19 ± 0.02	0.19 ± 0.01	0.35 ± 0.03	0.31 ± 0.04
	22	0.20 ± 0.03	0.17 ± 0.01	0.30 ± 0.01	0.26 ± 0.09
	35	0.25 ± 0.02	0.20 ± 0.01	0.30 ± 0.02	0.24 ± 0.07
Des 2	5	0.15 ± 0.01	0.14 ± 0.01	0.13 ± 0.01	0.18 ± 0.10
	15	0.27 ± 0.01	0.18 ± 0.01	0.20 ± 0.02	0.11 ± 0.08
	22	0.16 ± 0.01	0.17 ± 0.01	0.20 ± 0.01	0.09 ± 0.04
	35	0.29 ± 0.02	0.21 ± 0.01	0.25 ± 0.02	0.12 ± 0.07
Des 3	5	0.12 ± 0.02	0.10 ± 0.01	0.10 ± 0.01	0.12 ± 2.52
	15	0.19 ± 0.01	0.15 ± 0.01	0.16 ± 0.02	0.10 ± 0.07
	22	0.21 ± 0.01	0.12 ± 0.01	0.15 ± 0.02	0.09 ± 0.08
	35	0.29 ± 0.02	0.16 ± 0.02	0.19 ± 0.02	0.14 ± 0.02
Des 4	5	0.15 ± 0.03	0.08 ± 0.01	0.09 ± 0.01	0.13 ± 1.33
	15	0.22 ± 0.01	0.13 ± 0.01	0.16 ± 0.02	0.16 ± 1.61
	22	0.16 ± 0.02	0.10 ± 0.01	0.10 ± 0.01	0.12 ± 1.51
	35	0.28 ± 0.02	0.14 ± 0.01	0.18 ± 0.03	0.25 ± 0.05

Continued...

Table I (continued)

		DCM			
Sorption	5	0.29 ± 0.04	0.25 ± 0.01	0.10 ± 0.01	0.04 ± 0.01
	15	0.35 ± 0.04	0.29 ± 0.02	0.13 ± 0.02	0.05 ± 0.02
	22	0.41 ± 0.04	0.33 ± 0.04	0.14 ± 0.02	0.07 ± 0.01
	35	0.46 ± 0.05	0.37 ± 0.03	0.18 ± 0.03	0.08 ± 0.02
Des 1	5	0.14 ± 0.01	0.13 ± 0.01	0.26 ± 0.02	0.28 ± 0.07
	15	0.13 ± 0.01	0.16 ± 0.01	0.29 ± 0.01	0.25 ± 0.07
	22	0.13 ± 0.02	0.18 ± 0.01	0.27 ± 0.01	0.20 ± 0.09
	35	0.14 ± 0.02	0.19 ± 0.02	0.29 ± 0.01	0.21 ± 0.11
Des 2	5	0.16 ± 0.01	0.15 ± 0.01	0.15 ± 0.01	0.12 ± 0.06
	15	0.22 ± 0.01	0.18 ± 0.01	0.19 ± 0.01	0.09 ± 0.03
	22	0.16 ± 0.01	0.18 ± 0.01	0.21 ± 0.01	0.10 ± 0.09
	35	0.25 ± 0.01	0.24 ± 0.02	0.23 ± 0.01	0.28 ± 0.10
Des 3	5	0.13 ± 0.01	0.11 ± 0.01	0.13 ± 0.01	0.05 ± 0.18
	15	0.20 ± 0.02	0.15 ± 0.01	0.14 ± 0.01	0.07 ± 0.11
	22	0.20 ± 0.01	0.12 ± 0.00	0.14 ± 0.01	0.09 ± 0.10
	35	0.25 ± 0.01	0.18 ± 0.02	0.19 ± 0.01	0.19 ± 0.03
Des 4	5	0.18 ± 0.02	0.08 ± 0.01	0.11 ± 0.01	0.06 ± 0.82
	15	0.21 ± 0.01	0.13 ± 0.01	0.13 ± 0.01	0.17 ± 0.18
	22	0.16 ± 0.01	0.10 ± 0.01	0.10 ± 0.02	0.10 ± 0.04
	35	0.24 ± 0.01	0.18 ± 0.03	0.17 ± 0.02	0.24 ± 0.09

Table II. *Effect of temperature and concentration on sorption of TX-100 by isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Sorption partition coefficients for cuticle/buffer solution ($K_{c/b}$) are the means (± SE) of ten replicates. Free energy change due to the transfer of surfactant from buffer solution to cuticle (ΔG) was calculated by the equation $\Delta G = - R \cdot T \cdot \ln K_{c/b}$. Values for ΔG are listed in parentheses as $kJ \cdot mmol^{-1}$.

	Partition coefficient			
	Initial sorbate solution concentration ($mmol \cdot kg^{-1}$)			
Temp	0.0159	0.159	1.59	15.9
°C	CM			
5	50.5 ± 2.9 (-9.4)	36.1 ± 2.0 (-8.3)	20.8 ± 1.4 (-7.0)	15.4 ± 1.0 (-4.3)
15	110.9 ± 6.0 (-11.7)	84.1 ± 2.6 (-10.6)	26.1 ± 1.0 (-7.8)	7.4 ± 0.7 (-2.7)
22	149.8 ± 2.5 (-12.3)	103.8 ± 2.5 (-11.4)	39.2 ± 1.0 (-9.0)	14.0 ± 0.3 (-4.4)
35	169.3 ± 5.5 (-13.6)	164.8 ± 7.9 (-13.1)	40.3 ± 0.5 (-9.5)	5.0 ± 0.5 (-1.9)
	DCM			
5	91.0 ± 4.5 (-10.4)	70.6 ± 2.2 (-9.8)	25.0 ± 1.6 (-7.4)	8.9 ± 0.4 (-3.0)
15	143.7 ± 0.9 (-11.9)	113.4 ± 2.3 (-11.3)	35.5 ± 1.2 (-8.5)	9.9 ± 0.4 (-3.4)
22	193.7 ± 6.3 (-12.9)	149.7 ± 4.9 (-12.3)	49.7 ± 1.2 (-9.6)	15.1 ± 0.5 (-4.6)
35	216.1 ± 1.2 (-13.8)	188.8 ± 1.6 (-13.4)	51.3 ± 1.0 (-10.4)	9.1 ± 0.8 (-3.4)

Table III. *Effect of temperature and concentration on desorption of TX-100 from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Cuticles were equilibrated with 0.0159, 0.159, 1.59, or 15.9 mmol · kg^{-1} TX-100 at 22°C. Values for desorption partition coefficients for cuticle/buffer solution ($K_{c/b}$) are the means (± SE) of ten replicates. Free energy change due to the transfer of surfactant from cuticle to buffer solution (ΔG) was calculated by the equation $\Delta G = R \cdot T \cdot \ln K_{c/b}$. Values for ΔG are listed in parentheses as kJ · $mmol^{-1}$.

		Partition coefficient			
		Initial sorbate solution concentration (mmol · kg^{-1})			
Process	Temp	0.0159	0.159	1.59	15.9
	°C	CM			
Des 1	5	298 ± 10 (13.2)	474 ± 10 (14.2)	347 ± 14 (13.5)	113 ± 18 (10.9)
	15	278 ± 4 (13.5)	429 ± 7 (14.5)	350 ± 6 (14.0)	157 ± 20 (12.1)
	22	288 ± 5 (13.9)	461 ± 7 (15.1)	370 ± 9 (14.5)	187 ± 28 (12.9)
	35	273 ± 5 (14.4)	472 ± 8 (15.8)	384 ± 10 (15.2)	252 ± 26 (14.1)
Des 2	5	496 ± 8 (14.3)	894 ± 36 (15.7)	830 ± 37 (15.5)	295 ± 75 (13.1)
	15	386 ± 8 (14.3)	727 ± 23 (15.8)	705 ± 25 (15.7)	438 ± 76 (14.6)
	22	438 ± 7 (14.9)	778 ± 13 (16.4)	658 ± 24 (15.9)	413 ± 74 (14.8)
	35	361 ± 6 (15.1)	733 ± 24 (16.9)	666 ± 30 (16.7)	541 ± 73 (16.1)
Des 3	5	724 ± 37 (15.2)	1340 ± 46 (16.6)	1245 ± 90 (16.5)	540 ± 182 (14.5)
	15	507 ± 46 (14.9)	1070 ± 58 (16.7)	1021 ± 42 (16.6)	705 ± 166 (15.7)
	22	566 ± 24 (15.6)	1199 ± 40 (17.4)	974 ± 51 (16.9)	653 ± 105 (15.9)
	35	445 ± 24 (15.6)	1147 ± 40 (18.0)	995 ± 65 (17.7)	886 ± 117 (17.4)
Des 4	5	876 ± 98 (15.7)	1670 ± 155 (17.2)	1485 ± 223 (16.9)	411 ± 260 (13.9)
	15	566 ± 64 (15.2)	1319 ± 134 (17.2)	1423 ± 191 (17.4)	874 ± 229 (16.2)
	22	715 ± 37 (16.1)	1795 ± 106 (18.4)	1201 ± 100 (17.4)	686 ± 139 (16.0)
	35	536 ± 53 (16.1)	1505 ± 126 (18.7)	1150 ± 122 (18.0)	1252 ± 396 (18.3)

Continued...

Table III (continued)

		DCM			
Des 1	5	300 ± 12 (13.2)	442 ± 6 (14.1)	392 ± 12 (13.8)	132 ± 18 (11.3)
	15	316 ± 5 (13.8)	431 ± 7 (14.5)	396 ± 10 (14.3)	187 ± 32 (12.5)
	22	335 ± 6 (14.3)	488 ± 8 (15.2)	443 ± 12 (15.0)	264 ± 30 (13.7)
	35	356 ± 7 (15.0)	487 ± 10 (15.7)	459 ± 14 (15.7)	266 ± 40 (14.3)
Des 2	5	471 ± 34 (14.4)	769 ± 49 (15.4)	723 ± 94 (15.2)	344 ± 84 (13.5)
	15	416 ± 8 (14.4)	699 ± 22 (15.7)	710 ± 22 (15.7)	373 ± 88 (14.2)
	22	469 ± 9 (15.1)	773 ± 24 (16.3)	770 ± 29 (16.3)	565 ± 59 (15.6)
	35	431 ± 8 (15.5)	726 ± 43 (16.9)	771 ± 37 (17.0)	495 ± 62 (15.9)
Des 3	5	570 ± 88 (14.7)	1051 ± 75 (16.1)	1053 ± 171 (16.1)	544 ± 205 (14.6)
	15	540 ± 22 (15.1)	1036 ± 48 (16.6)	1116 ± 50 (16.8)	595 ± 195 (15.3)
	22	582 ± 29 (15.6)	1129 ± 44 (17.3)	1219 ± 90 (17.5)	975 ± 231 (16.9)
	35	558 ± 21 (16.2)	1000 ± 78 (17.7)	1065 ± 64 (17.9)	738 ± 281 (16.9)
Des 4	5	603 ± 74 (14.8)	1406 ± 131 (16.8)	1398 ± 272 (16.7)	783 ± 398 (15.4)
	15	614 ± 56 (15.4)	1392 ± 97 (17.3)	1420 ± 132 (17.4)	629 ± 409 (15.4)
	22	682 ± 37 (16.0)	1524 ± 116 (18.0)	1668 ± 268 (18.2)	919 ± 331 (16.8)
	35	604 ± 46 (16.4)	1283 ± 138 (18.3)	1290 ± 86 (18.3)	938 ± 366 (17.5)

Table IV. *Thermodynamic constants for the sorption and desorption of TX-100 from isolated (CM) and dewaxed isolated (DCM) tomato cuticles.*

Changes in enthalpy (ΔH) and entropy (ΔS) due to sorption and stepwise desorption (Des) were graphically determined from the equation $\Delta G = \Delta H - (\Delta S \cdot T)$.

	Initial sorbate solution concentration ($mmol \cdot kg^{-1}$)							
	0.0159	0.159	1.59	15.9	0.0159	0.159	1.59	15.9
	CM				DCM			
Process	ΔH							
	$kJ \cdot mol^{-1}$							
Sorption	28.3	35.3	17.1	-21.8	20.5	23.0	17.1	19.1
Des 1	1.7	-0.5	-2.6	-18.8	-4.2	-2.9	-4.2	-16.9
Des 2	6.4	3.8	5.0	-13.1	1.3	0.7	-2.0	-9.9
Des 3	10.1	2.6	4.9	-10.8	0.0	0.8	-0.4	-8.8
Des 4	9.5	0.6	6.6	-23.2	-0.5	1.8	1.4	-6.5
	ΔS							
	$J \cdot K^{-1} \cdot mol^{-1}$							
Sorption	134	155	85	-57	112	119	90	26
Des 1	-41	-53	-58	-107	-62	-61	-65	-102
Des 2	-28	-42	-38	-95	-46	-53	-62	-85
Des 3	-18	-50	-41	-91	-53	-55	-56	-85
Des 4	-21	-59	-37	-135	-55	-54	-56	-78

mmol · kg^{-1}) partitioning was consistently affected by temperature. Thus, ΔH for the process at high surfactant concentrations was probably small.

As with sorption, $K_{c/b}$ for desorption were also expressed as the ratio of surfactant concentration in the cuticle to that in buffer solution (Table III). If sorption were a completely reversible process, sorption and desorption partition coefficients for any given concentration should be identical. However, the partition coefficients for desorption were greater than for sorption and increased with each stepwise desorption. This phenomenon is a direct result of sorption hysteresis (Section III). Similar to sorption, partitioning of TX-100 into the solution during desorption also increased with temperature. Changes in free energy for desorption have the opposite sign of that of sorption, reflecting the transfer of surfactant from cuticle to buffer solution. Calculated changes in enthalpy (ΔH) also reflect this change in direction. For desorption, ΔH calculated for the transfer of surfactant from cuticle to solution were near zero. The highest concentration (15.9 mmol · kg^{-1}) was an exception where the ΔH was negative and relatively large (about -15 kJ · mol^{-1}).

Temperature has a greater effect on sorption than on desorption (Figure 3). The anomalous (inverted) temperature response observed for sorption and desorption for the highest initial sorbate concentration (15.9 mmol · kg^{-1}) is also apparent.

The amount of surfactant that could not be desorbed from the cuticle through extensive buffer extraction tended to decrease with temperature (Table V). In general, the amount of buffer non-extractable surfactant was nearly constant across initial sorbate solution concentrations for any given temperature when expressed as the percent of the total amount sorbed.

Octanol/buffer partitioning

Similar to cuticular sorption studies, the surfactant favored the octanol phase over the buffer phase (Table VI). However, partition coefficients for the cuticle (Table II) were generally much greater than for octanol ($K_{o/b}$ range: 3 to 6 vs. $K_{o/c}$ range: 5 to > 200). Although the amount of TX-100 partitioning into the octanol phase increased with temperature at all concentrations, the temperature

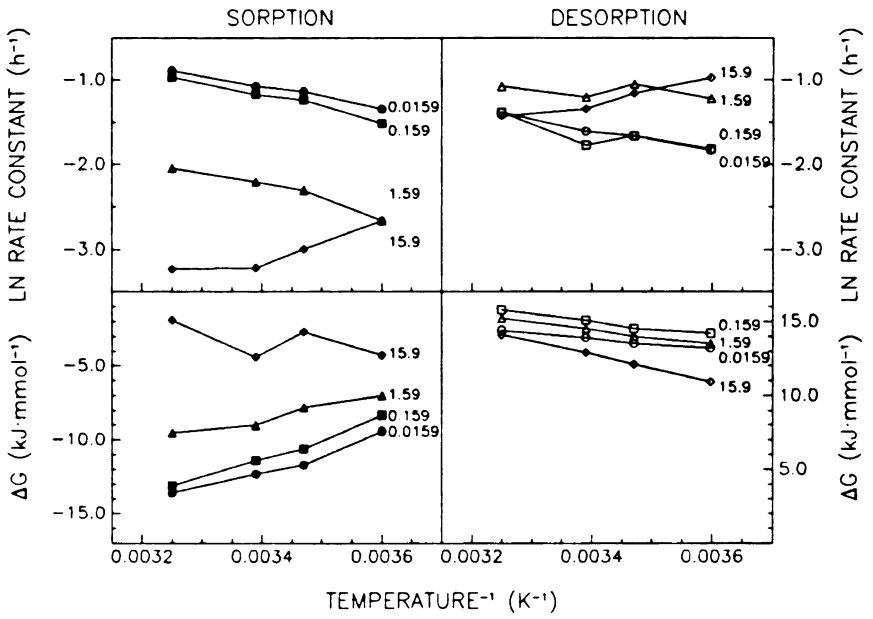

Figure 3 Effect of temperature and concentration on sorption (left) and the first stepwise desorption (right) of TX-100 from isolated tomato fruit cuticles (CM). The sorption and desorption rate constants (k) and free energies of transfer (ΔG) are presented in the upper and lower plots, respectively. Values listed are the initial sorbate concentrations.

Table V. *Effect of temperature and initial surfactant sorption concentration on the TX-100 buffer non-extractable fraction isolated (CM) and dewaxed isolated (DCM) tomato cuticles.*

Isolated tomato fruit cuticles, which were equilibrated with [14C]TX-100 at 22°C, were extensively desorbed with buffer at the temperatures listed. The cuticles were oxidized and the collected oxidation product was radioassayed to determine the amount of surfactant remaining in the cuticle. Amount remaining in the cuticle is the mean (± SE) of ten replicates. Values in parentheses are the amounts remaining in mmol · kg^{-1}.

	Initial sorbate solution concentration (mmol · kg^{-1})			
Temp	0.0159	0.159	1.59	15.9
°C	*% of amount sorbed*			
	CM			
5	37.2 ± 1.3 (0.465)	26.6 ± 1.4 (4.43)	22.8 ± 0.9 (12.1)	22.2 ± 1.6 (18.7)
15	20.3 ± 0.8 (0.249)	18.5 ± 0.6 (3.03)	14.3 ± 0.6 (7.5)	11.6 ± 1.0 (10.1)
22	16.6 ± 0.6 (0.204)	16.0 ± 0.5 (2.58)	12.9 ± 0.8 (6.5)	13.8 ± 0.9 (12.3)
35	17.1 ± 0.6 (0.205)	14.7 ± 0.5 (2.46)	13.9 ± 0.6 (7.1)	10.9 ± 0.9 (9.5)
	DCM			
5	31.1 ± 1.4 (0.452)	23.5 ± 1.0 (4.21)	18.9 ± 0.8 (12.6)	22.2 ± 1.7 (20.1)
15	16.4 ± 0.4 (0.241)	17.0 ± 0.5 (3.15)	14.5 ± 0.2 (9.5)	17.1 ± 0.7 (15.2)
22	13.8 ± 0.5 (0.204)	14.6 ± 0.6 (2.69)	14.0 ± 0.3 (9.2)	14.7 ± 1.1 (15.0)
35	14.1 ± 0.4 (0.208)	14.9 ± 1.1 (2.67)	13.8 ± 0.4 (8.9)	14.2 ± 1.3 (13.2)

Table VI. *Effect of concentration and temperature on TX-100 octanol/citrate buffer solution partition coefficients.*

Partition coefficients for octanol/citrate buffer solution ($K_{o/b}$) are the means (± SE) of five replicates. Free energy change due to the transfer of surfactant from buffer solution to octanol (ΔG) was calculated by the equation $\Delta G = -R \cdot T \cdot \ln K_{o/b}$. Values for ΔG are listed in parentheses as $kJ \cdot mmol^{-1}$. Changes in enthalpy (ΔH) and entropy (ΔS) due to transfer were graphically determined from the equation $\Delta G = \Delta H - (\Delta S \cdot T)$.

	Partition coefficient			
	Initial sorbate concentration solution ($mmol \cdot kg^{-1}$)			
Temp	0.0159	0.159	1.59	15.9
°C				
5	3.32 ± 0.07 (-2.77)	3.33 ± 0.06 (-2.78)	4.81 ± 0.09 (-3.63)	2.96 ± 0.07 (-2.51)
15	3.83 ± 0.09 (-3.22)	3.62 ± 0.11 (-3.08)	5.35 ± 0.04 (-4.02)	4.54 ± 0.07 (-3.62)
22	4.18 ± 0.12 (-3.51)	3.98 ± 0.09 (-3.39)	5.53 ± 0.04 (-4.19)	5.34 ± 0.16 (-4.11)
35	4.19 ± 0.10 (-3.67)	4.14 ± 0.12 (-3.64)	5.55 ± 0.26 (-4.39)	5.92 ± 0.09 (-4.55)
	ΔH			
	$kJ \cdot mol^{-1}$			
	5.6	5.4	3.3	16.2
	ΔS			
	$J \cdot K^{-1} \cdot mol^{-1}$			
	30.4	29.4	25.3	68.2

sensitivity of the process was less than for the cuticle (Table IV). The ΔH of transfer of TX-100 from buffer solution to octanol was positive and was particularly large for 15.9 $mmol \cdot kg^{-1}$ (16 $kJ \cdot mol^{-1}$). Similar to cuticular partitioning, octanol partitioning was driven by a large, positive ΔS contribution.

Discussion

Kinetic and thermodynamic studies are often used to characterize intermolecular interactions. The study of transport mechanisms such as sorption, desorption, and diffusion in multi-component systems is complicated by numerous interactions. Study of surfactant-cuticle interaction is further confounded by the complexity of the components of the system. Consequently, some of these complicating factors must be considered:

(1) **Surfactant.** The surfactant TX-100 is not a pure compound, but a mixture of molecules that vary in length of the ethyoxylate chain. Thus, the size and polarity of surfactant molecules vary slightly, albeit in a regular fashion (Greenwald and Brown 1954).

Surfactant micellization complicates the question of driving force. Below the CMC, only the monomeric form of the surfactant is present while above the CMC, both monomer and micelle forms are present. For solutions with surfactant concentrations above the CMC, the monomer concentration is constant and equal to the CMC. In theory, only the surfactant monomer is sorbed. Thus, the driving force for surfactant sorption should be the concentration at the CMC and remain constant as the concentration increases (Clunie and Ingram 1983; Rosen 1989).

Unfortunately, the properties of surfactants at high concentrations are not fully understood. As the concentration increases above the CMC, the surfactant may associate with the surface as micelles or planar sheets (Fava and Eyring 1956; Rosen 1989). From a practical perspective, the properties of high concentration surfactant solutions may be very important since foliar spray droplets quickly evaporate and thus concentrate the surfactant in solution.

Properties of ethoxylate surfactants such as TX-100 are further complicated by the sensitivity of the polyoxyethylene chain to changes in temperature. Increasing temperature presumably causes the

polyoxyethylene chain to dehydrate thus making the surfactant more hydrophobic in nature. Consequently, surfactant sorption to hydrophobic surfaces increases with temperature, reducing the CMC (Keh et al. 1989; Rosen 1989).

(2) **Cuticle.** Polymers such as the cuticle both adsorb and absorb the sorbate. If absorption predominates over adsorption, interactive events which occur at the surface of the polymer may be masked by absorption. This is particularly unfortunate in the study of surfactant-cuticle interaction since surface events are of great interest. Absorption is evident from the penetration of the TX-100 through the cuticle (Stevens and Bukovac 1987; Petracek and Bukovac 1989).

Additionally, the cuticle may undergo temperature induced phase changes (Schreiber and Schönherr 1990). These phase changes may significantly alter the physical properties of the cuticle.

(3) **Surfactant-cuticle interactions.** Cuticular sorption of the surfactant is irreversible or hysteretic (Section III). The cause of hysteresis is not well understood and the resulting effects, such as the concentration dependence of various processes, are not known. However, analysis of the thermodynamic properties assumes the process is reversible. Calculation of thermodynamic constants from partition coefficients of systems not completely reversible may be inappropriate.

Thus, strict interpretation of the kinetics and thermodynamics of cuticular sorption and desorption of TX-100 is complicated. Still, we can consider the data from these studies both in terms of general transport phenomenon as well as the theoretical aspects of intermolecular interaction.

To this end, we can consider cuticular sorption/desorption of the surfactant as a series of transport processes (Table VII). The hypothesis that diffusion limits the rate of cuticular transport is supported by previous data on the rates of micellization and demicellization (Rosen 1989), TX-100 diffusion in solution (Weinheimer et al. 1981), and adsorption to, desorption from, and diffusion in polymers (Crank and Park 1968). From these discussions, we anticipate that all processes are relatively rapid with respect to diffusion in the polymer. This hypothesis is further supported by studies showing that cuticular permeation by TX-100 was a function of cuticular thickness (Appendix VI).

Table VII *Summary of processes involved in cuticular sorption and desorption of a surfactant.*

Cuticular transport may be visualized in the following series of steps:

$$A_{micelle} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_{monomer} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A_{monomer} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A_{adsorb} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A_{absorb}$$

Rate constant	Process	Rate
k_1	Demicellization	Rapid
k_{-1}	Micellization	Rapid
k_2 and k_{-2}	Mass flow and diffusion in solution	Rapid with adequate mixing
k_3	Adsorption	Rapid
k_{-3}	Desorption	Rapid
k_4 and k_{-4}	Diffusion in cuticle	Slow

In sorption/desorption experiments, the sorption by and release of the surfactant from the cuticle are measured, thus, all processes listed in Table VII are being measured. The surface events of adsorption and desorption are probably not measurable either kinetically because they are probably not rate limiting or thermodynamically because the capacity of the matrix of the cuticle far exceeds that of the surface. Thus, sorption/desorption experiments address the rate of diffusion. If this assumption is correct, then our data can be used to address the effects of temperature and concentration on diffusion and permeation.

Since sorption/desorption are rate limited by diffusion, the rates of these processes can be used to calculate diffusion coefficients (eqn. 3). The diffusion coefficient for TX-100 (1.59 $mmol \cdot kg^{-1}$) is 1.36 x 10^{-15} $m^2 \cdot s^{-1}$ for an estimated $t_{1/2}$ of 1 h using a cuticle thickness of 10 μm (Section II). This is about 30 % greater than the value calculated by the time lag method for steady state diffusion (Petracek and Bukovac 1989). The diffusion coefficient for the first stepwise desorption ($t_{1/2}$=45 min) is 1.81 x 10^{-15} $m^2 \cdot s^{-1}$.

The permeance (P) of a polymer may be described simply in terms of the diffusion (D) and sorption partition (K) coefficients:

(7) $P = D \cdot K$

The activation energy of permeation (E_p) is then the sum of the activation energy of diffusion (E_d) and the change in enthalpy (ΔH) of sorption (Yasuda and Stannett 1975):

(9) $E_p = E_d + \Delta H$

Since diffusion coefficients can be calculated from the rate of sorption or desorption, and the partition coefficients can be determined experimentally by sorption and desorption experiments, permeance and activation energies of permeation can then be calculated. For example, an activation energy of permeation of 1.5 $mmol \cdot kg^{-1}$ TX-100 through the isolated tomato fruit CM is calculated to be 30 $kJ \cdot mol^{-1}$ (Appendix VI, Figure 27) and 14 $kJ \cdot mol^{-1}$ based on sorption data (Appendix IV, Table V).

One limitation of this approach is that not all interactions in the sorption/desorption system are necessarily involved in cuticular permeation. Also, factors that act as permeation barriers may not affect sorption/desorption processes as they would a diffusion system. For example, waxes, which clearly limit cuticular permeation, may not affect the sorption of the surfactant because more readily accessible sites are available on the cuticle.

Another limitation of this approach is that desorption data should yield permeances and activation energies comparable with those of sorption. However, hysteresis complicates the understanding of the process. Since the desorption partition coefficient increases with each desorption step, the calculated permeances also increase. This difficulty may be overcome if one can correct for the immobilized (Fenelon 1974) or resistant fraction (Di Toro and Horzempa 1982).

Our data on the effects of temperature and concentration on sorption/desorption may also be discussed in terms of kinetics and thermodynamics. In general, the rate and extent of sorption generally increases with temperature (Tables II and III). Kinetic data indicate that sorption is a first order process at concentrations below the CMC and that the process is less than first order for higher surfactant concentrations (Figure 2). Alternatively, the non-linearity of the curves for the rate equation may be related to non-linear increase in driving force with an increase in surfactant concentration. This phenomenon may be a characteristic of surfactant micellization and the inability of the micelle to sorb (cf. BA; Appendix V, Table VI).

The interpretation of the kinetic data depends on knowing the driving force or effective concentration. In a system with a simple sorbate such as BA, the driving force is assumed to be the concentration of BA in solution. This assumption is confirmed by the linearity of the sorption isotherm which suggests that concentration and activity of BA are constant over a wide concentration range. This assumption is reaffirmed by the linear curves for the sorption rate equation (Appendix V, Figure 21) and linear relationship between flux and concentration.

However, for TX-100, the interpretation is more difficult in that the apparent concentration may not be the driving force. This concern arises from the non-linearity of both the sorption isotherm above

the CMC (Section II) and the concentration-flux curve (Appendix VI, Figure 27). Both suggest that amount that can be sorbed is limited. If this limitation is a solution factor such as micellization, then a corrected driving force, one accurately reflecting the "true" driving force, should be used for the rate analysis. Unfortunately, the true driving force is not known. Certainly, if the true driving force is the CMC, then the rate of sorption should be greatest at the CMC. This is not the case, for the rate continues to increase as the concentration is increased above the CMC. We suggest that this increase in sorption rate may be related to the cause of the stepped sorption isotherm as well as to the increase in flux above the CMC. The relationship between surfactant driving force and concentration is extremely important to understanding the activity of surfactant in a foliar spray system, particularly when considering the high concentration encountered the during droplet drying phase.

One difficulty in interpreting thermodynamics data derived from sorption or desorption experiments is that several interactions occur simultaneously in the system. While the interaction of greatest interest is between the sorbate and the cuticle, other interactions between sorbate and solvent may have a greater influence on the process. This may well be the case for cuticular sorption of TX-100. As temperature increases, the ethoxylate surfactants become less water soluble. Consequently, micellization is favored and the CMC decreases (Keh et al. 1989). At the cloud point, the solution becomes turbid with water insoluble surfactant (Han et al. 1989). Both phenomena can be explained by the fact that the polyoxyethylene moiety is dehydrated as the temperature is increased. As a result, the surfactant molecule becomes less water soluble and interaction with hydrophobic molecules is increased (Rosen 1989).

The thermodynamics of ethoxylate surfactant sorption by silica has been reported (Gellan and Rochester 1985). Adsorption is an exothermic process ($\Delta H \approx -25$ kJ $\cdot$ mol^{-1}) and has been attributed to hydrogen bonding of the ethyoxylate chain to hydroxylated surface of silica. In contrast, sorption of ethoxylate surfactants to a hydrophobic graphon resulted in a positive change in enthalpy ($\Delta H \approx 15$ kJ $\cdot$ mol^{-1}). In this case, sorption was driven by a large entropy contribution attributed to the dehydration of the polyoxyethylene moiety (Corkill et al. 1964). The thermodynamics of sorption to the

cuticle is similar to that of graphon (Table IV). The positive ΔH is probably related to the breaking of water-surfactant hydrogen bonds. Concurrently, entropy increases due to the greater mobility of both water and the hydrophobe. This positive entropy contribution is sufficiently large to drive the sorption process.

The binding of TX-100 by the cuticle is of particular interest. The polyoxyethylene chain of the surfactant provides opportunity for hydrogen bonding. However, the cuticle is largely hydrophobic and has relatively few moieties for hydrogen bonding (Kolattukudy 1981; Holloway 1982). Previous studies showed that pH affected TX-100 sorption only when the solution was very alkaline (pH 13). The increase in sorption under these conditions was apparently due to depolymerization and could not be attributed to changes in hydrogen bonding. However, the thermodynamics experiment provides some evidence that the surfactant is not hydrogen bonded, based on the positive enthalpy of transfer. Based on previous models of sorption of nonionic surfactants (Clunie and Ingram 1983), we suggest that the cuticular sorption of TX-100 is through hydrophobic interaction.

In other studies of sorption by isolated cuticle, sorption either increased (2,4-D, Morse 1971; 4-nitrophenol, Riederer and Schönherr 1986; NAA, Shafer et al. 1988) or decreased (methylene blue, Morse 1971) with temperature. Interestingly, sorption isotherms for compounds of the first category are linear whereas those for compounds of the second category are asymptotic.

Both sorption and desorption increase with temperature. In a completely reversible process, the ΔH of transfer should carry the opposite sign for the reverse process. The reason for the positive enthalpy of sorption is probably related to the dehydration of the polyoxyethylene chain. As temperature increases, fewer water molecules are associated with the chain. Consequently, the molecule becomes less polar and less soluble in aqueous solution. However, the driving force for desorption is not the reverse of sorption. Instead, the molecule must first hydrate and then desorb. Thus, the mechanisms of the two systems are different.

Alternatively, sorption may require the dehydration of the cuticle, thus causing ΔH of transfer to be negative. During desorption, hydration of the cuticle may not drive the process sufficiently and

thus the desorption capability of the buffer solution does not meet the expectation predicted by sorption. Since hysteresis has been observed for many different compounds (Appendix V, Table XI and Figures 23 and 24), that hysteresis is probably caused by the cuticle rather than compound.

Acknowledgments

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CONCLUSIONS

Properties of enzymatically isolated tomato fruit cuticles were examined with an emphasis on: (1) physicochemical properties of the cuticle, (2) sorption and desorption isotherms of TX-100, and (3) the influence of temperature, concentration and various solvent treatments on sorption and desorption.

Sorption isotherms of nitrogen gas were linear. This suggested that N_2 partitions into the cuticle rather than simply adsorbing to the surface. Consequently, surface area and porosity could not be determined. Cuticular hydration expressed as plasticization is apparent from the initial swelling of the cuticle caused by water as well as increased elasticity and decreased fracture point of the cuticle in the presence of water. Cuticles from which waxes were extracted were more elastic and prone to fracturing suggesting that waxes act as a polymer filler restricting the movement of the cutin matrix.

The sorption isotherm for TX-100 is characterized by two sorption plateaus, one of which is near the CMC (about 0.019 %) and the other at a concentration several fold greater than the CMC (about 0.7 %). Subsequent kinetics studies suggested that the first plateau is due to a limitation in availability of the monomeric form of the surfactant molecule. The second plateau may be the result of reorientation of the surfactant molecules on the surface. Comparison of sorption and desorption isotherms clearly show that sorption is not completely reversible (hysteretic). Hysteresis can be expressed in terms of the fraction of surfactant that can be desorbed by buffer solution (buffer extractable) and the fraction that cannot be desorbed (buffer non-extractable). The buffer extractable fraction is not affected by buffer pH, but is greatly influenced by solvent additives that affect water structure. Desorption of the extractable fraction of TX-100 from the isolated cuticle generally increased under conditions in which either solvent-solvent interactions or solvent polarity were reduced. The buffer non-extractable fraction (about 10 to 15 % of the total amount sorbed) could be desorbed either

by exchanging the surfactant with surfactant molecules of similar structure or be desorbed by in solvents less polar than water.

Sorption of TX-100 is limited by the rate of hydration. The time course of sorption for prehydrated cuticles suggests that the process is controlled by Fick's law of diffusion. Diffusion coefficients calculated from the rates of sorption and desorption are in reasonably good agreement with those calculated from steady-state diffusion studies. The rates of sorption and desorption increased with temperature, but activation energies were low. The extent to which sorption occurred increased with temperature. This is characteristic of an entropically driven process. This probably occurs because the polyoxyethylene moiety becomes dehydrated with increasing temperature. Consequently, the surfactant becomes more hydrophobic, thus increasing its affinity for the hydrophobic cuticle. If the processes of sorption and desorption were completely reversible, desorption should increase with temperature. However, desorption is less temperature dependent than sorption and thus the thermodynamics are not completely reversible.

APPENDICES

Appendix I: Sorption and desorption data calculations

Many of the data presented in this dissertation were obtained from experiments in which radiolabeled surfactant sorbate was sorbed to and sequentially desorbed from isolated cuticles (Figure 1). Unless otherwise noted, the amounts of sorbate in the sorbent were calculated by difference. This section provides a brief explanation of these calculations.

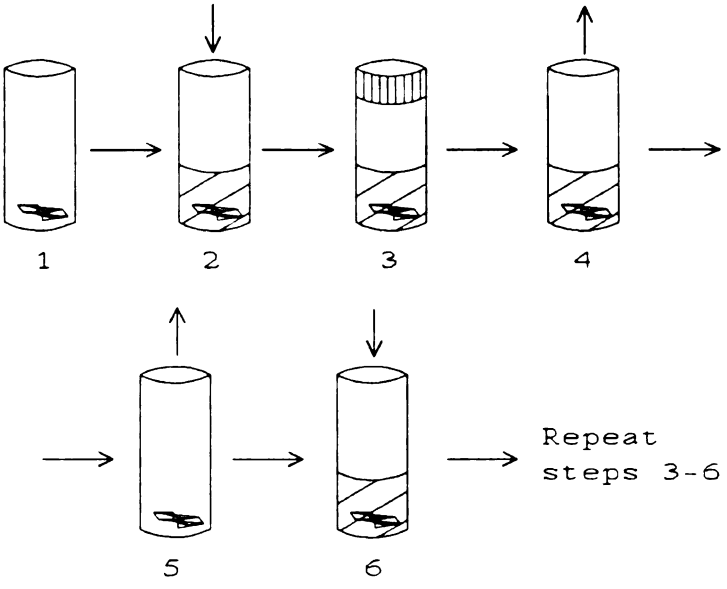


Figure 1. Sequence for sorption and stepwise desorption. (1) Weighing of isolated cuticles in sorption vessel. (2) Addition of sorption dosing solution. (3) Equilibration. (4) Sampling of solution. (5) Removal of solution. (6) Addition of desorption buffer solution. Steps (3) to (6) are repeated for sequential stepwise desorptions.

Correction for any sorbate sorption to the sorption vessel is made by conducting simultaneous sorption experiments in vessels in which the sorbent is present (sorbent) or absent (control). For these experiments, assume that sorbent and control vessels sorb the same amounts of material. The amount that is sorbed by the sorbent is then the difference in amounts present in the solution of the two vessels.

The total amount of sorbate remaining in control and sorbent solution ($control_{tot,\ sol}$ and $sorbent_{tot,\ sol}$, respectively) can be determined by assaying the sorbate solutions in both vessels:

$$(1)\quad control_{tot,\ sol} = \frac{control_{aliq,\ sol}\ control_{tot,\ vol}}{control_{aliq,\ vol}}$$

and:

$$(2)\quad sorbent_{tot,\ sol} = \frac{sorbent_{aliq,\ sol}\ sorbent_{tot,\ vol}}{sorbent_{aliq,\ vol}}$$

where $control_{aliq,\ sol}$ and $sorbent_{aliq,\ sol}$ are the amounts of sorbate in an aliquot solution, $control_{aliq,\ vol}$ and $sorbent_{aliq,\ vol}$ are the aliquot volumes, and $control_{tot,\ vol}$ and $sorbent_{tot,\ vol}$ are the total volumes of solution. Sorbate that has sorbed to the sorbent ($sorbent_{tot,\ sorb}$) is then calculated by difference:

$$(3)\quad sorbent_{tot,\ sorb} = control_{tot,\ sol} - sorbent_{tot,\ sol}\ .$$

For repeated samplings:

$$(4)\quad sorbent_{tot,\ sorb} = (control_{tot,\ sol} + \Sigma\ control_{prev,\ sol}) - (sorbent_{prev,\ sol} + \Sigma\ sorbent_{prev,\ sol})$$
$$= (control_{tot,\ sol} - sorbent_{prev,\ sol}) + (\Sigma\ control_{prev,\ sol} - \Sigma\ sorbent_{prev,\ sol})$$

where $\Sigma\ control_{prev,\ sol}$ and $\Sigma\ sorbate_{prev,\ sol}$ are the sums of sorbate taken in previous aliquot solutions.

During desorption a similar problem exists. In this case sorbate desorbs from the vessel. By again assuming that both control and sorbent vessels have sorbed the same amount of sorbate, we can determine how much sorbate is desorbing from either vessel and sorbent.

The amount of sorbate that remains sorbed to the sorbent after a desorption step ($sorbent_{tot,des}$) is determined by difference:

(5) $$sorbent_{tot,\ des} = sorbent_{tot,\ sorb} - (control_{tot,\ sol} - sorbent_{tot,\ sol}) \ .$$

For repeated samplings:

(6) $$sorbent_{tot,\ des} = sorbent_{tot,\ sorb} - (control_{tot,\ sol} - sorbent_{prev,\ sol}) + (\Sigma\ control_{prev,\ sol} - \Sigma\ sorbent_{prev,\ sol}) \ .$$

If stepwise desorptions are performed, $sorbent_{tot,\ sorb}$ determined from the previous desorption step, becomes $sorbent_{tot,\ des}$.

Additionally, note that the concentrations of (1) solution containing sorbent ($sorbent_{conc,\ sol}$) and (2) sorbate in the sorbent ($sorbent_{conc,\ sorb}$) are calculated as follows:

(7) $$sorbent_{conc,\ sorb} = \frac{sorbent_{tot,\ sorb}}{sorbent_{tot,\ wt}}$$

and:

(8) $$solvent_{conc,\ sol} = \frac{sorbent_{aliq,\ sol}}{sorbent_{aliq,\ vol}}$$

where $sorbent_{tot,\ wt}$ is the total weight of the sorbent. Partition coefficients can be calculated by dividing eqn (8) by eqn (7). By assuming that the hydrated cuticle has a specific gravity of unity, the units for the partition coefficient cancel.

The technique of repeated sampling and calculation by difference causes an accumulation of error. Consequently, results for these experiments should be verified by direct analysis of the sorbate in the sorbent. A complete mass balance of the system may be attained by oxidizing the sorbent at various stages of the sorption/desorption sequence.

Appendix II: Electron micrographs of isolated cuticles

Figure 2. Scanning electron micrographs of the outer morphological surface of isolated pepper *(Capsicum annuum)* fruit cuticles with (A and B) and without (C and D) waxes. Figures E and F are micrographs of the cell wall side of the cuticle with waxes. See Section II for materials and methods.

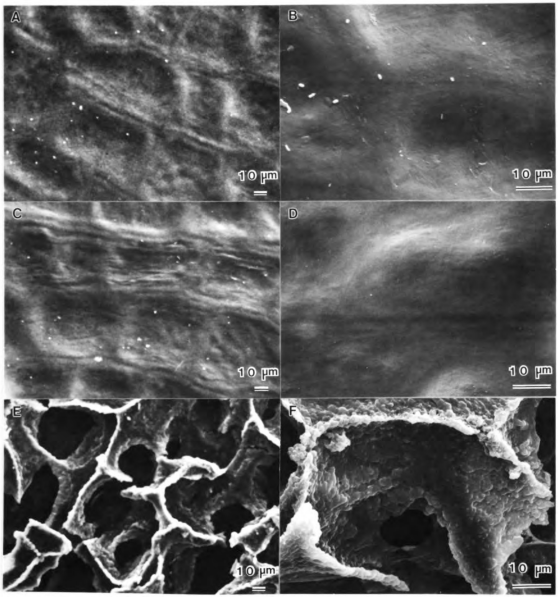

A
10 µm
B
10 µm
C
10 µm
D
10 µm
E
10 µm
F
10 µm

Figure 3. Scanning electron micrographs of isolated *Citrus aurantium* leaf cuticles. Figures A and B and figures C and D are micrographs of the outer morphological surface and cell wall side of the adaxial cuticles, respectively. Figures E and F and G and H are micrographs of the outer morphological surface and cell wall side of the abaxial cuticles, respectively.

A
100 µm
B
10 µm
C
100 µm
D
10 µm
E
100 µm
F
10 µm
G
100 µm
H
10 µm

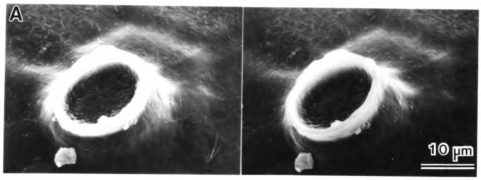
Figure 4. Stereopairs of tomato fruit cuticles (tilt equals 10° between micrographs). Figure A is a micrograph of a cross-sectional view of a freeze-fractured cuticle. Figure B is a micrograph of the outer morphological surface of the cuticle on a fresh tomato fruit. The specimens were excised and immediately examined by a scanning electron microscope equipped with a cold stage. Figure C is a micrograph of the outer morphological surface of a dewaxed isolated tomato fruit cuticle. Figure D is a micrograph of the outer morphological surface on an isolated tomato fruit cuticle.

A
10 µm
B
100 µm
C
100 µm
D
10 µm

Figure 5. Stereopairs of the cell wall-side of isolated tomato fruit cuticles (tilt equals 10° between micrographs). Figure C and D are micrographs of periclinal wall and a cuticular peg, respectively.

A
100 µm
B
10 µm
C
1 µm
D
1 µm

Figure 6. Stereopairs of isolated tomato fruit cuticles (tilt equals 10° between micrographs). Figure A is a micrograph of the base of a broken trichome. Figure B is a cross-sectional view of a freeze-fractured cuticle.


A
10 µm

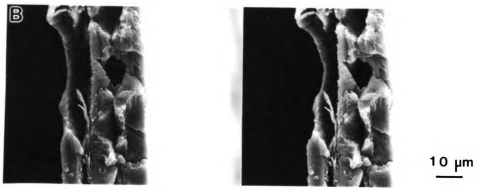

B
10 µm

Figure 7. Stereopairs of isolated pepper fruit cuticles (tilt equals 10° between micrographs). Figure A is a micrograph of a cross-sectional view of a freeze-fractured cuticle. Figure B is a micrograph of the outer morphological surface. Figures C and D are micrographs of the cell-wall side of the cuticle.

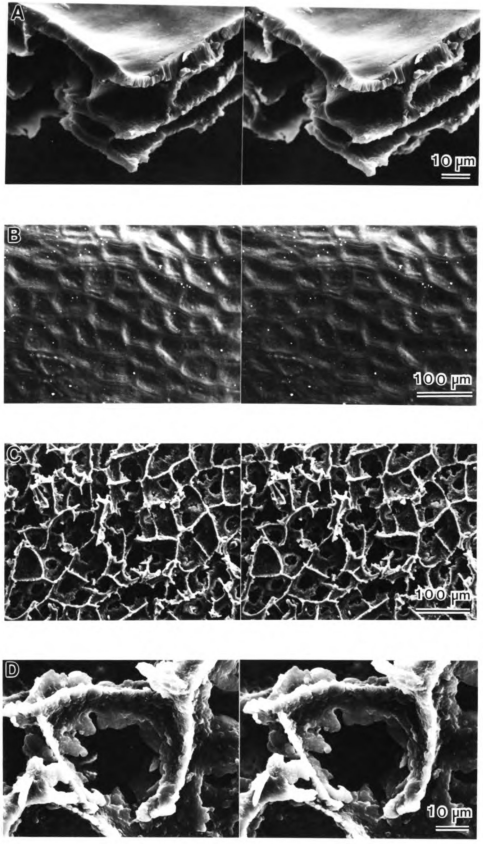
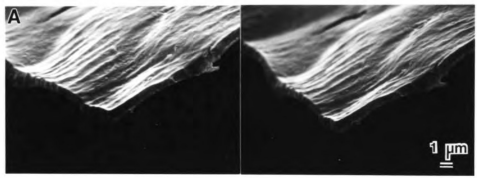
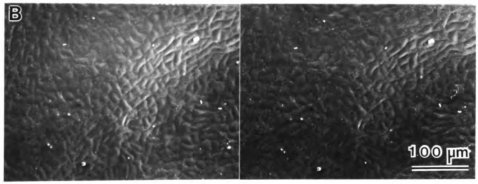
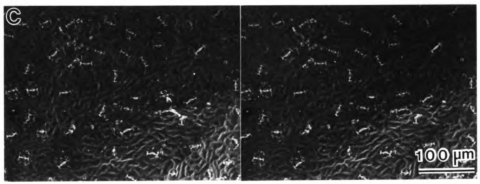
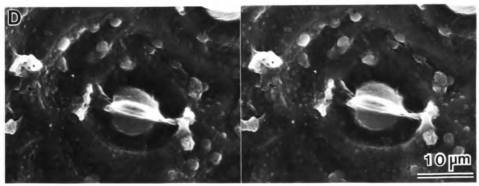

A
10 µm
B
100 µm
C
100 µm
D
10 µm

Figure 8. Stereopairs of isolated *Citrus aurantium* leaf cuticles (tilt equals 10° between micrographs). Figure A is a micrograph of a cross-section of a freeze-fractured adaxial cuticle. Figure B is a micrograph of the outer morphological surface of an adaxial cuticle. Figures C and D are micrographs of the outer morphological surface of an abaxial cuticle.


A
1 µm


B
100 µm


C
100 µm


D
10 µm

Appendix III: Physical properties of selected surfactants

Table I. *Properties of selected octylphenoxy polyethoxyl ethanol (Triton X series; TX) surfactants.*

Data taken from *Rohm and Haas Surfactants and Dispersants*: Handbook of Physical Properties, CS-16b, Rohm and Haas Company, 1988 except where noted.

Surfactant	Avg EO units[a]	MW	HLB[b]	Cloud point	Surface tension 0.1%	Surface tension 1.0%	CMC[c]	Aggr No.[d]	SA[e]
	no.			*°C*	*mN·m^{-1}*		*%*		*Å^2*
TX-35	3	338	7.8	insol.	29	-	0.004	-	38
TX-45	5	426	10.4	< 0	29	28	0.005	-	42
TX-100	9.5	628	13.5	65	31	30	0.019	114	48-54
TX-102	12.5	756	14.6	88	32	32	-	92	-
TX-165	16	910	15.8	>100	33	34	0.11	-	131
TX-405	40	1966	17.9	>100	48	41	0.17	28	88

[a] Average number of repeating ethylene oxide per molecule. [b] Hydrophile-lipophile balance. HLB = ((MW of EO / MW) · 100) / 5. [c] Critical micelle concentration. CMC for TX-35 and TX-45: Mukerjee and Mysels, 1971. Nat. Stand. Ref. Data Ser. Nat. Bur. Stand. 36. [d] Aggregation number: Keh et al, 1989. J. Colloid Interface Sci. 129:363-372. [e] Surface area.

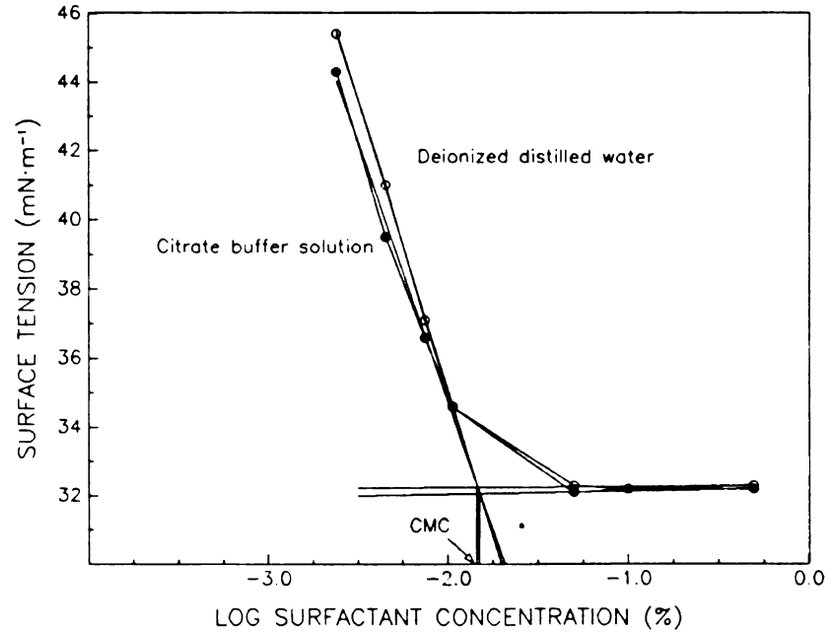


Figure 9. Surface tension of TX-100 in deionized distilled water (O) and in 20 mM citrate buffer solution at pH 3.2 (●). Surface tension was measured using a du Noüy ring surface tensiometer (Fisher Model 20 Surface Tensiometer, Fisher Scientific, Pittsburgh, PA) at 22°C.

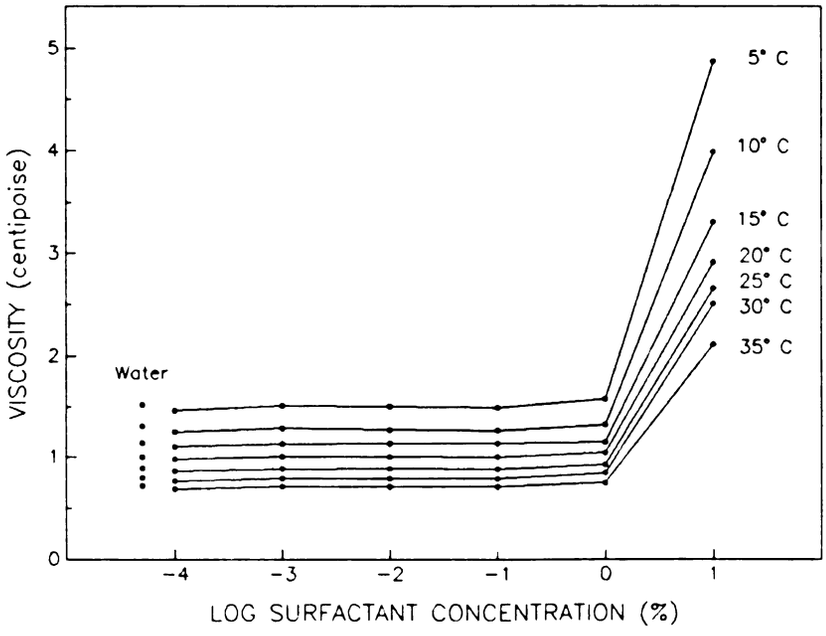


Figure 10. Effect of concentration and temperature on viscosity of TX-100 solutions. Viscosity was measured using a capillary viscometer (#100 Ostwald viscometer). Surfactant was prepared in 20 mM citrate buffer solution at pH 3.2.

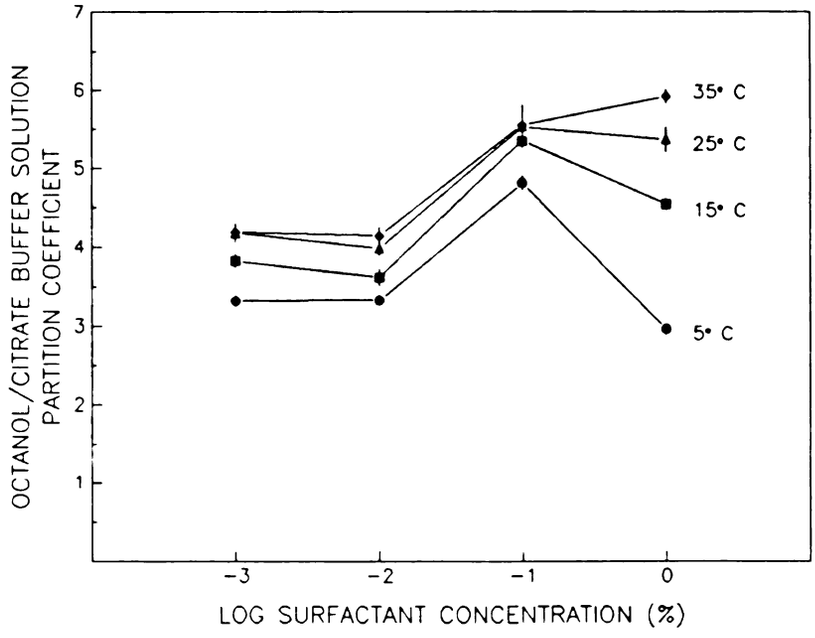


Figure 11. Effect of concentration and temperature on partition coefficient ($K_{o/b}$) of TX-100 for octanol and 20 mM citrate buffer solution (pH 3.2). See materials and methods in Section IV.

Appendix IV: Supplemental data for TX-100 sorption to and desorption from isolated cuticles

Supplemental data for Section II

Table II. *A comparison of water and surfactant buffer solution on contact angle droplets on isolated tomato fruit cuticles.*

Droplets (1 μl) were applied to the outer morphological surfaces with a syringe fitted with an automated dispenser on strips of isolated tomato fruit cuticular membranes. Contact angle of droplets on the inner morphological surface could not be determined. Optical determination of contact angle was based on droplet height and width (Mack, 1936. J. Phys. Chem. 40:159-167). Water was deionized and distilled. Surfactant solution consisted of 1.59 mmol·kg^{-1} (0.1%) TX-100 in 20 mM citrate buffer solution (pH 3.2) at 22°C. Values represent the mean (± SE) of ten replicates with ten droplets per replicate.

	Contact angle			
	No surfactant		Surfactant[a]	
Cuticle	Water	Buffer[b]	Water	Buffer
	degrees			
CM	76 ± 1[c]	78 ± 1	30 ± 1	32 ± 1
DCM	73 ± 1	71 ± 1	wetted	wetted

Table III. *Sorption of TX-100 (22°C) by waxes extracted from isolated tomato fruit cuticles.*

Equilibrium sorbate concentrations are the means (± SE) of 5 replicates. See materials and methods in Section II.

Initial sorbate concn in solution	Equilibrium sorbate concn in solution	Equilibrium sorbate concn in wax	Partition coefficient
$mmol \cdot kg^{-1}$	$mmol \cdot kg^{-1}$	$mmol \cdot kg^{-1}$	
0.0159	0.0083 ± 0.0002	2.91 ± 0.06	357 ± 14
0.159	0.088 ± 0.004	26.6 ± 0.4	404 ± 5
1.59	1.023 ± 0.03	214 ± 8	211 ± 12
15.9	15.39 ± 0.05	192 ± 19	13 ± 1

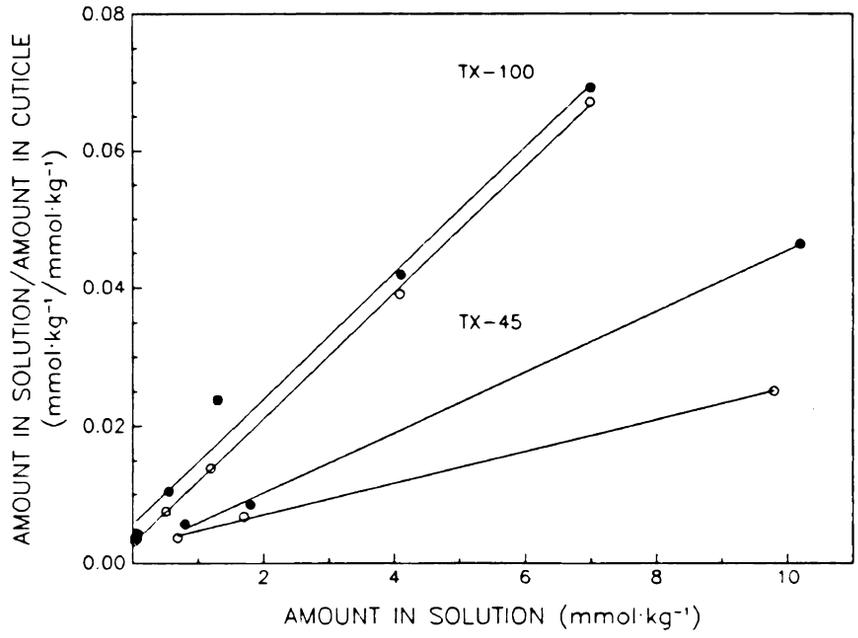


Figure 12. Langmuir plots of TX-100 (lowest five concentrations of Figure 5) and TX-45 (from Shafer and Bukovac, 1987. Plant Physiol. 85:965-970) for tomato fruit CM (●) and DCM (○) . See materials and methods in Section II.

Supplemental data for Section III

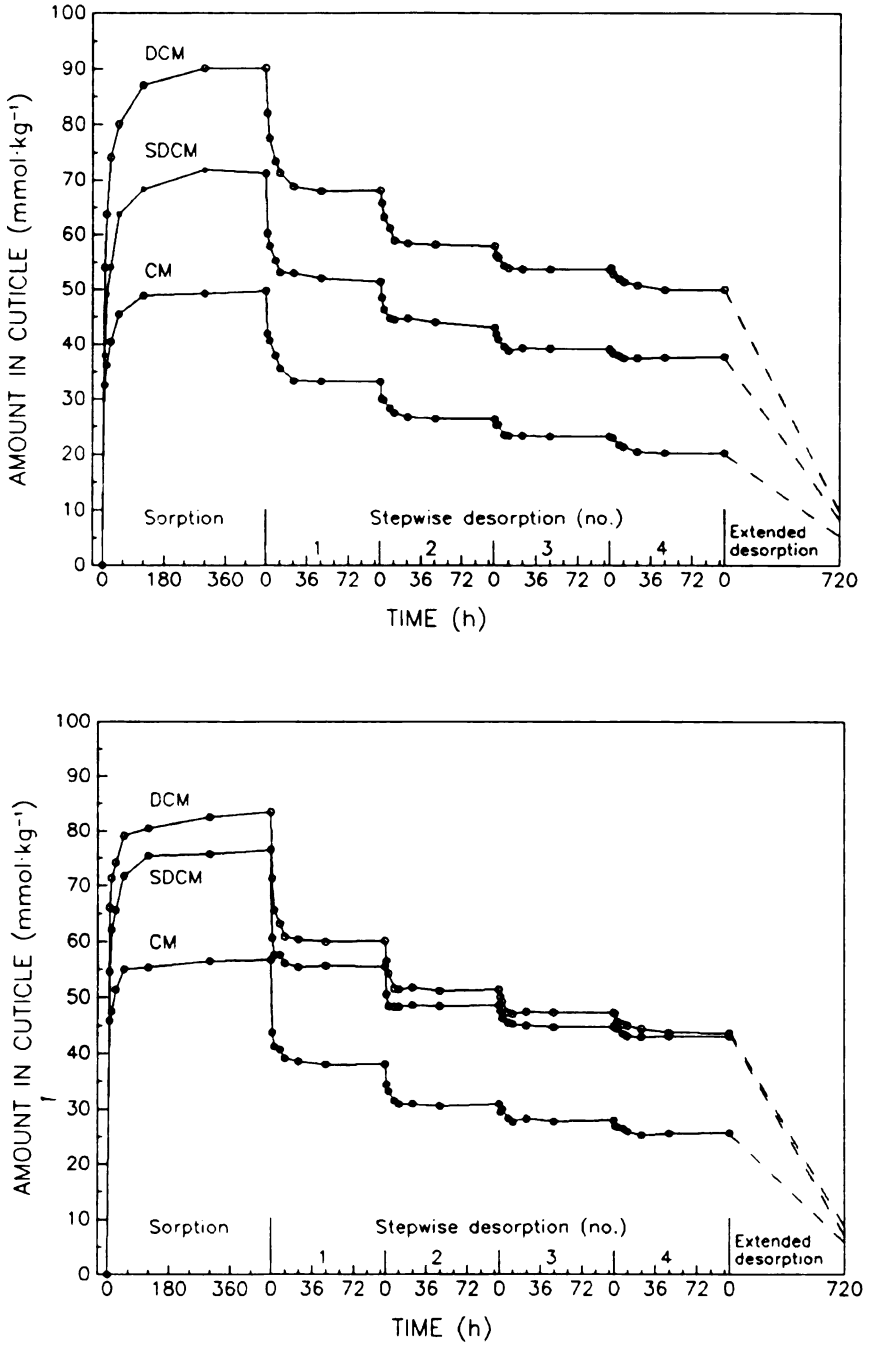


Figure 13. Time course for TX-100 sorption and desorption for isolated fruit cuticles of tomato (upper) and pepper (lower). Pepper fruit cuticles were not acidified. Surface dewaxed CM (SDCM) were stripped of epicuticular waxes with a cellulose acetate film. Dosing (sorption) solution consisted of 1.59 mmol·kg^{-1} (0.1% w/v) surfactant in 20 mM citrate buffer solution (1.5 mL, pH 3.2). Each stepwise desorption was against 1.5 mL citrate buffer solution at 22°C. Extended desorption was for 720 h. See materials and methods in Section III.

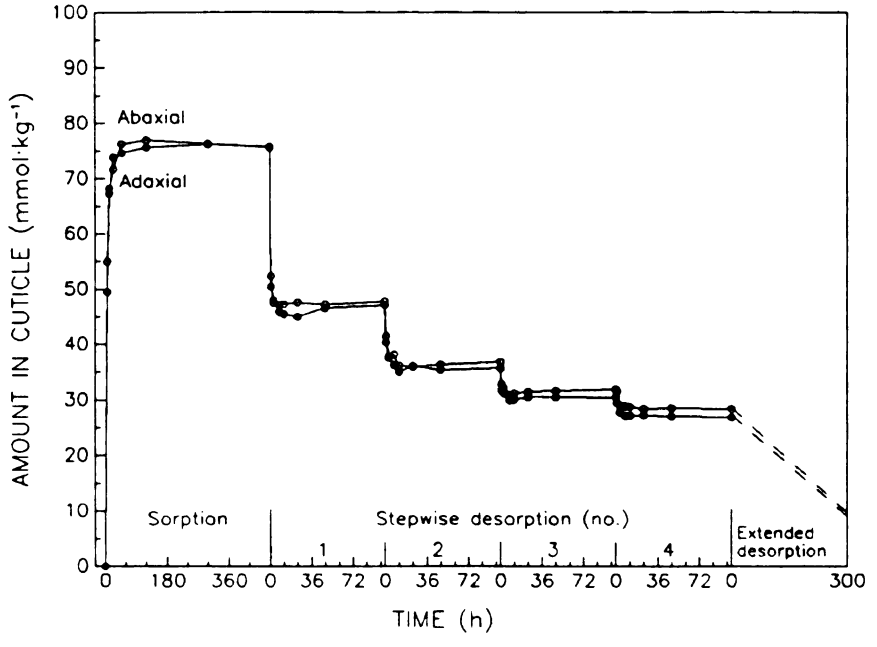


Figure 14. Time course of TX-100 sorption and desorption for isolated *Citrus aurantium* leaf cuticles (abaxial, ○; adaxial, ●). Dosing (sorption) solution consisted of 1.59 mmol · kg^{-1} (0.1% w/v) surfactant in 20 mM citrate buffer solution (1.5 mL, pH 3.2). Each stepwise desorption was against 1.5 mL citrate buffer solution at 22°C. Extended desorption was for 300 h. See materials and methods in Section III.

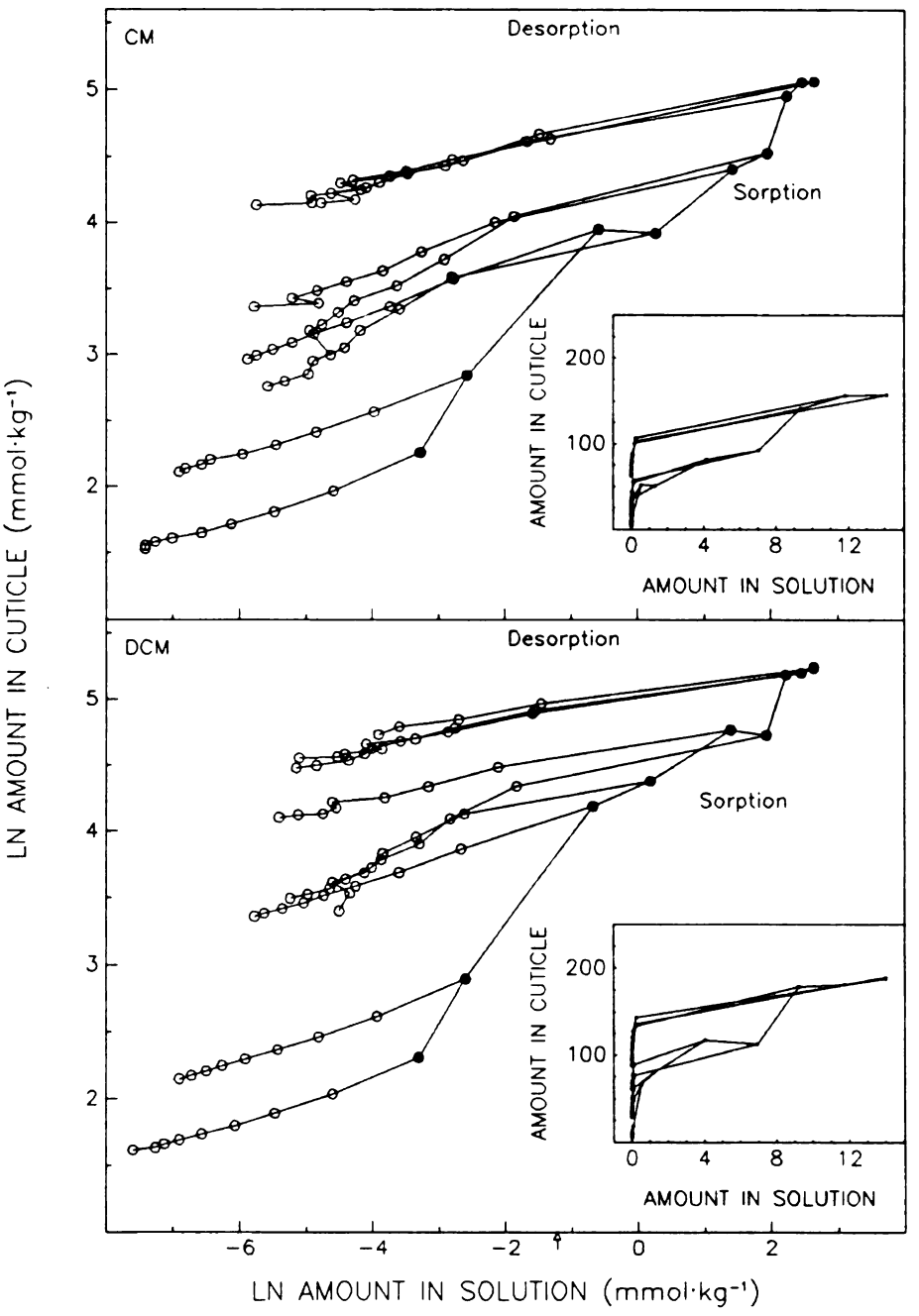


Figure 15. Sorption/desorption isotherms for TX-100 in the system of isolated pepper fruit cuticles (CM, upper; DCM, lower). Surfactant was prepared in 20 mM citrate buffer solution (pH 3.2) at 25°C. Arrow respresents CMC. Insets: arithmetic isotherms. See materials and methods in Section IV.

Table IV. *Freundlich constants for TX-100 sorption to and desorption from isolated (CM) and dewaxed isolated (DCM) pepper fruit cuticles.*

Constants for the Freundlich equation (Amount sorbed = k · Amount in solution$^{1/n}$) were calculated from sorption/desorption isotherm data (Figure 4). Desorption constants were calculated for curves describing isotherms for (1) each desorption step and (2) initial sorption concentration. See materials and methods in Section III.

	Freundlich constants			
	CM		DCM	
	k	n	k	n
Sorption	48	2.3	60	2.2
Desorption step				
Des. 1	332	1.2	555	1.1
Des. 2	916	1.1	1806	1.0
Des. 3	1714	1.1	2859	1.0
Des. 4	2684	1.1	4081	1.0
Initial sorption concn ($mmol \cdot kg^{-1}$)				
0.080	16	6.1	16	6.3
0.159	25	6.1	27	5.9
0.795	59	5.3	73	6.1
1.59	54	4.7	85	5.7
4.77	69	6.5	104	10.0
7.95	69	4.8	89	5.4
10.6	114	9.3	149	10.2
13.2	119	7.9	148	11.1
15.9	118	9.3	156	13.4

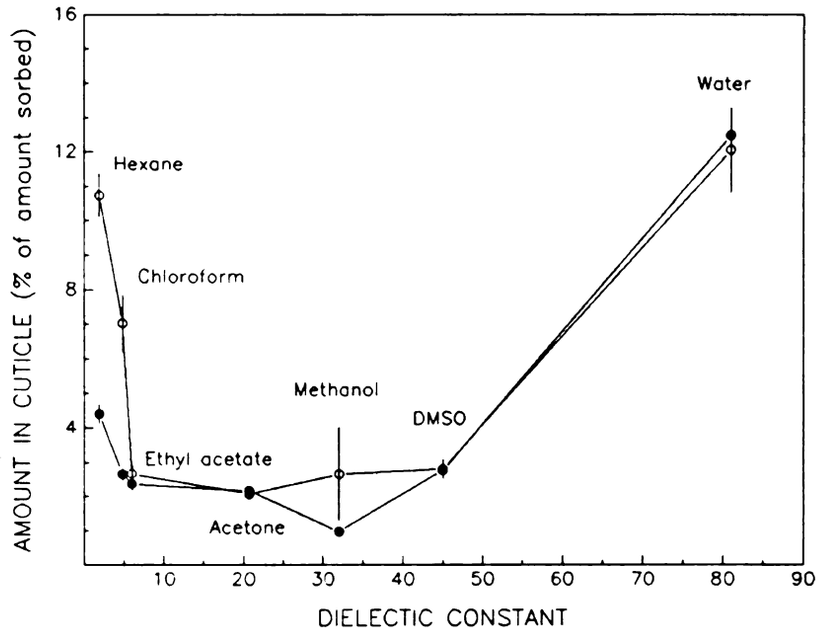


Figure 16. Effect of solvent polarity on the extraction of buffer non-extractable TX-100 from isolated tomato fruit cuticles (CM, ●; DCM, ○). Bar equals SE of five replicates. See materials and methods in Section III.

Supplemental data for Section IV

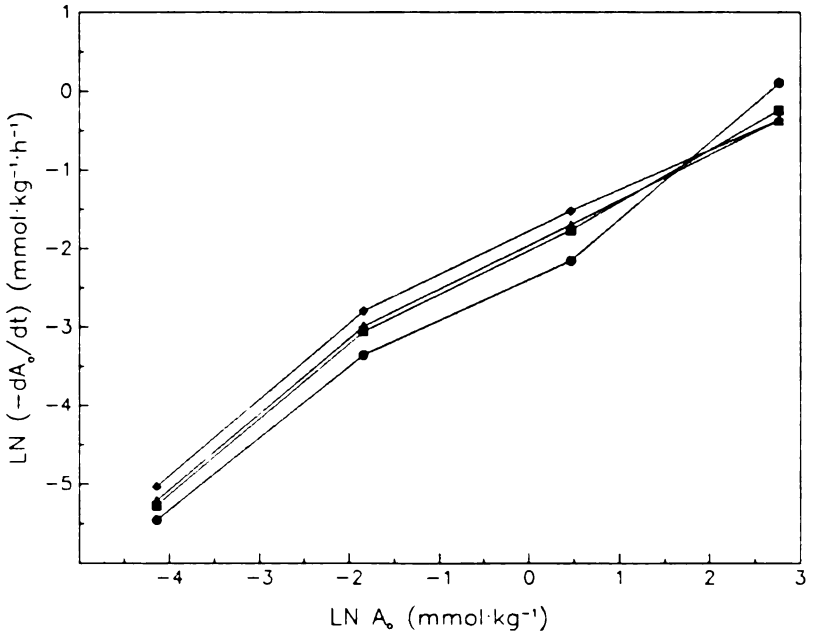


Figure 17. Effect of temperature on the rate of sorption of TX-100 by isolated tomato fruit cuticles (CM). Graph represents the rate equation $-dA_0/dt = n \cdot \ln A_0 + \ln k$ where $-dA_0/dt$ is the initial rate of loss of sorbate from solution, A_0 is the initial dosing (sorption) concentration, and n is the order of reaction. Initial dosing solution consisted of surfactant (0.0159, 0.159, 1.59, and 15.9 mmol · kg^{-1}) in 20 mM citrate buffer solution (1.5 mL, pH 3.2). Sorption was performed at four temperatures (5, ●; 15, ■; 22, ▲; and 35°C, ♦) See materials and methods in Section IV.

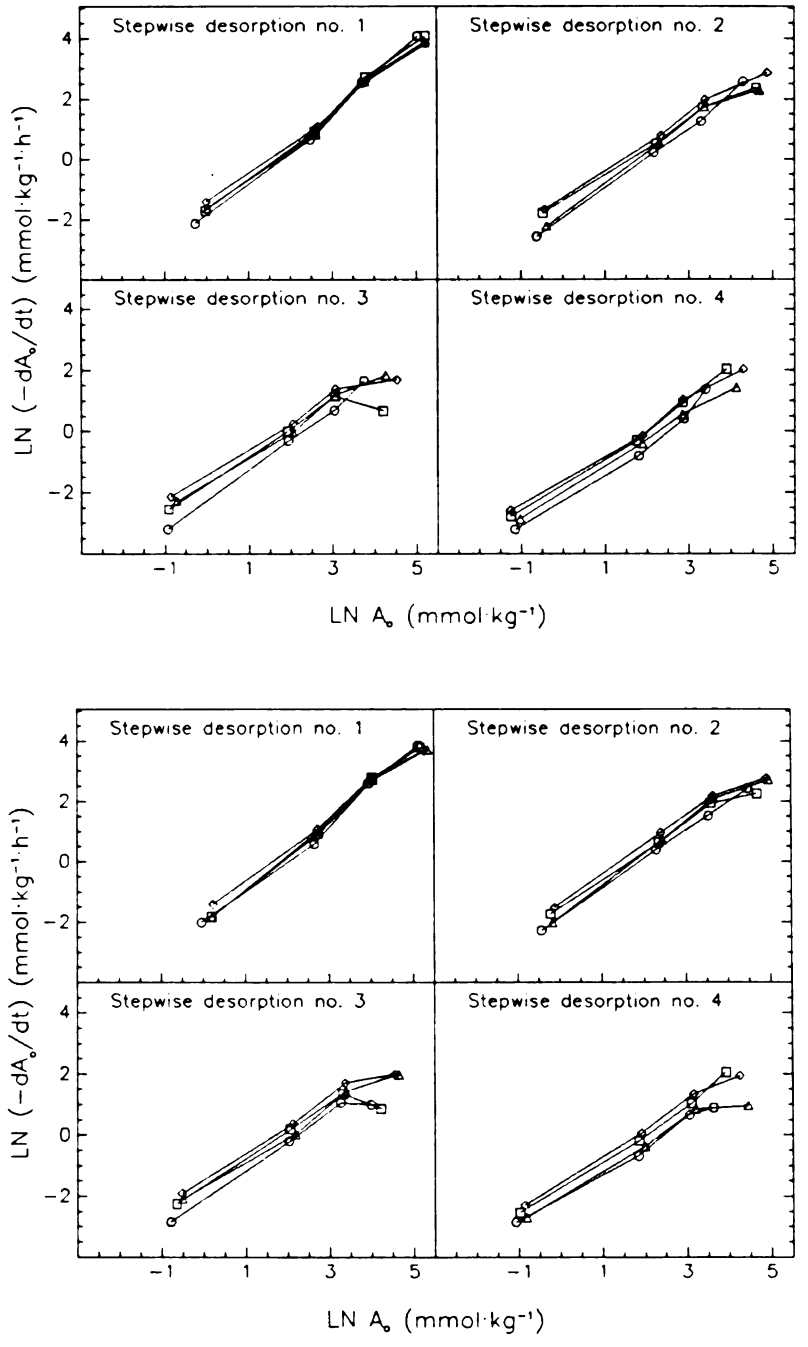


Figure 18. Effect of temperature and repeated desorptions on the initial rates of desorption (dA_o/dt) of TX-100 from isolated tomato fruit cuticles (upper, CM; lower, DCM). Initial dosing (sorption) solution consisted of surfactant (0.0159, 0.159, 1.59, and 15.9 mmol·kg^{-1}) in 20 mM citrate buffer solution (1.5 mL, pH 3.2) at 22°C. Stepwise desorption against buffer solution was performed at four temperatures (5, ○; 15, □; 22, △; and 35°C, ◇). See materials and methods in Section IV.

Table V. *Arrhenius constants for TX-100 sorption to and desorption from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Activation energies were calculated for sorption/desorption rate data by the Arrhenius equation: $\ln k = \ln C - [E_a / (R \cdot T)]$ where k is the rate constant, C is the pre-exponential factor, E_a is the activation energy, R is the gas constant, T is temperature. The Arrhenius equation gave a good fit for sorption (average $r^2 = 0.94$), but poorly for desorption (average $r^2 = 0.50$).

	Activation energy							
	CM				DCM			
	Initial sorbate solution concn ($mmol \cdot kg^{-1}$)							
	0.0159	0.159	1.59	15.9	0.0159	0.159	1.59	15.9
	$kJ \cdot mol^{-1}$							
Sorption	10.5	12.6	14.3	-6.2	11.2	9.5	13.6	17.3
Des. 1	9.9	4.6	-0.9	-12.9	6.5	9.7	2.0	-7.9
Des. 2	11.4	8.0	13.4	10.8	7.3	10.1	12.5	17.2
Des. 3	21.9	8.4	14.4	9.5	14.7	8.2	11.3	32.7
Des. 4	13.4	10.7	11.3	8.0	5.0	12.4	10.5	15.0
	Pre-exponential factor							
	h^{-1}							
Sorption	16.5	51.6	34.4	0.0	37.1	15.1	35.7	0.0
Des. 1	11.3	1.1	0.2	0.0	2.2	9.4	0.6	0.0
Des. 2	22.2	5.1	46.3	0.0	4.1	11.5	31.0	0.4
Des. 3	1482.4	4.2	52.1	4.0	78.6	4.0	14.6	6.0
Des. 4	46.5	8.6	12.3	3.8	4.2	1.5	18.5	45.0

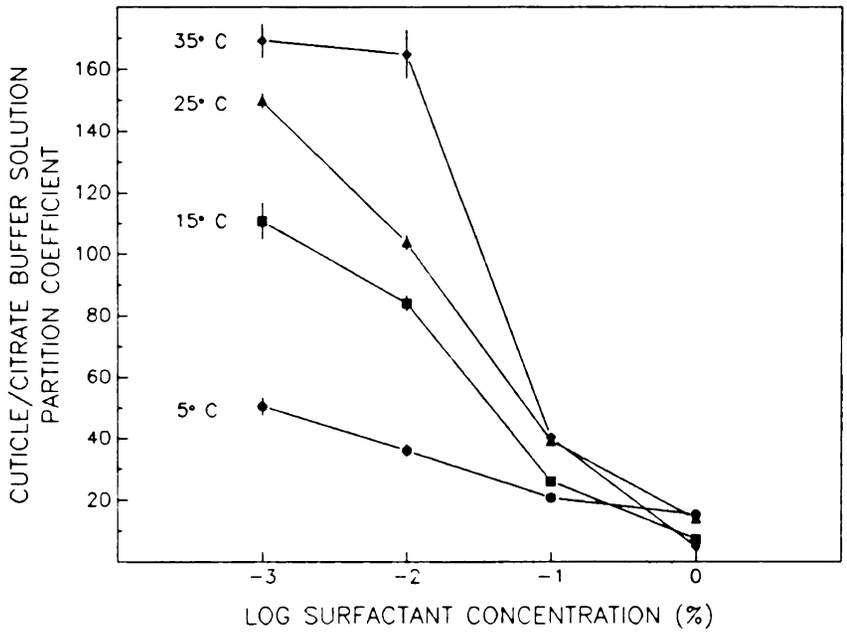


Figure 19. Effect of concentration and temperature on partition coefficient ($K_{c/b}$) of TX-100 for isolated tomato fruit cuticles (CM) and 20 mM citrate buffer solution at pH 3.2. See materials and methods in Section IV.

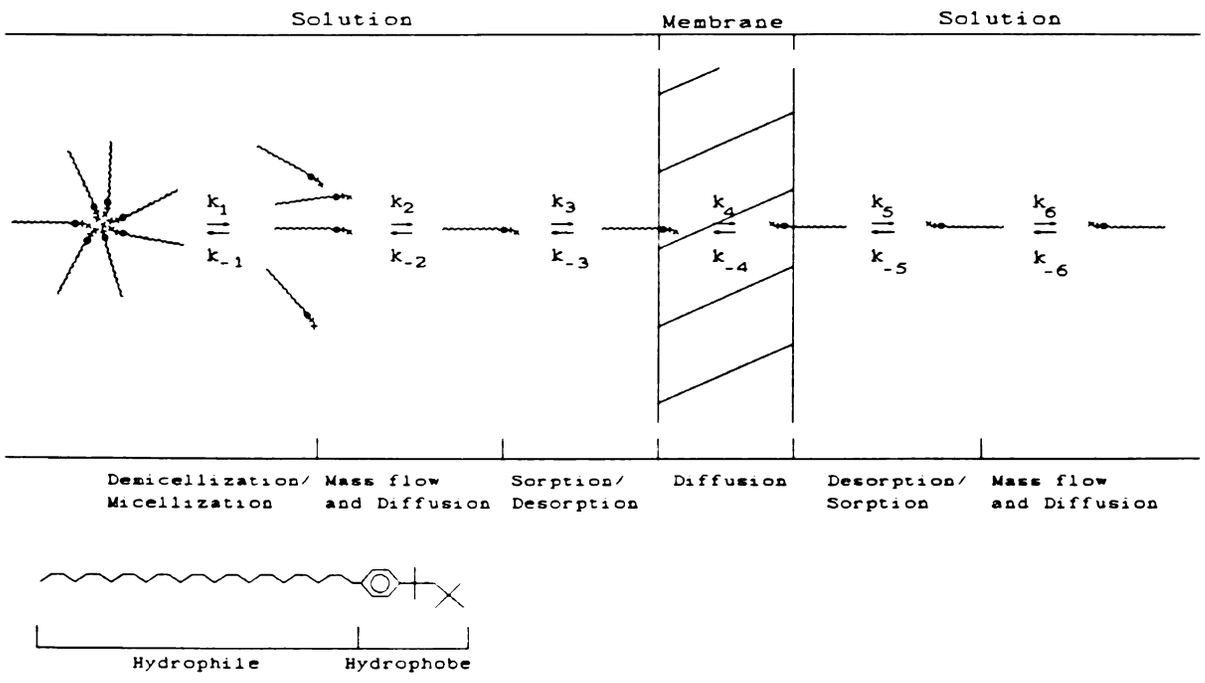
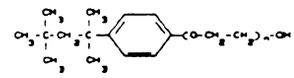
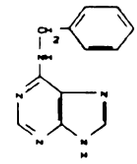
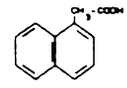
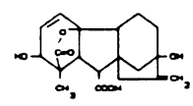


Figure 20. Model for mass transfer of surfactant through an isolated cuticular membrane. Rate constants: demicellization, k_1; micellization, k_{-1}; solution mass flow and diffusion, k_2, k_{-2}, k_6, and k_{-6}; sorption, k_3 and k_{-5}; desorption, k_{-3} and k_5; membrane diffusion, k_4 and k_{-4}.

Appendix V: Cuticular sorption and desorption of Triton surfactants, benzyladenine, naphthaleneacetic acid, and gibberellic acid

Table VI. *Names and structures of compounds used in sorption/desorption experiments.*

Common name	Structure			Chemical Abstracts name
Triton X surfactant (TX)		Surfactant	n[a]	α-[4-(1,1,3,3,-Tetramethylbutyl) phenyl]-ω-hydroxypoly (oxy-1,2-ethanediyl)
		TX-35	3	
		TX-45	5	
		TX-100	9.5	
		TX-102	12.5	
		TX-165	16	
		TX-405	40	
Benzyladenine (BA)				N-(phenylmethyl)-1H-Purin-6-amine
Naphthaleneacetic acid (NAA)				1-Naphthaleneacetic acid
Gibberellic acid (GA_3)				2,4a,7-Trihydroxy-1-methyl-8-methylenegibb-3-ene-1,10-dicarboxylic acid 1,4a-lactone

[a] Average number of ethylene oxide units per surfactant molecule.

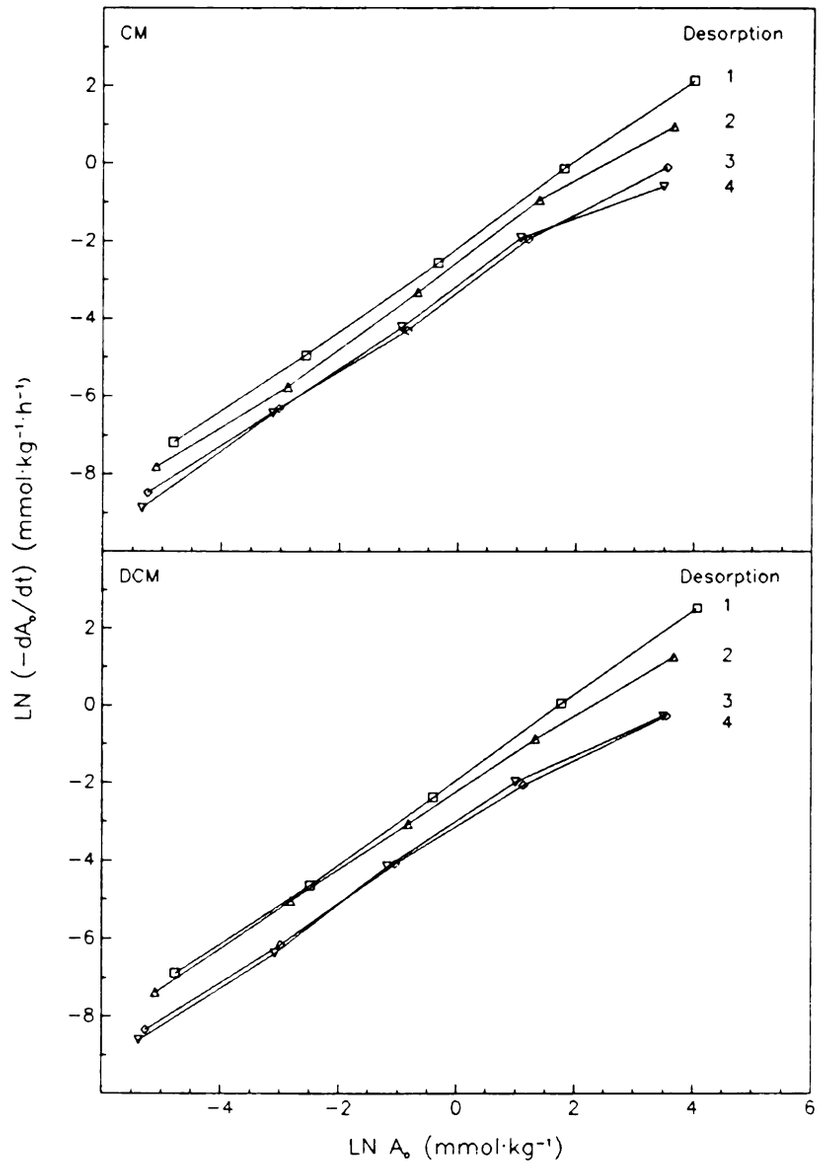


Figure 21. Effect of stepwise desorptions on the rate of desorption (dA_o/dt) of benzyladenine from isolated tomato fruit cuticles (upper, CM; lower, DCM). Desorption solution consisted of 20 mM citrate buffer (1.5 mL, pH 3.2) at 22°C. See materials and methods in Section IV.

Table VII. *Rate of benzyladenine desorption from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Rate constant (k) is calculated from the first order rate equation $d[A]_o/dt = k \cdot [A]_o$ where $d[A]_o/dt$ is the initial rate of desorption and $[A]_o$ is the initial sorbate concentration in the cuticle Values for rate constants represent the means (± SE) of five replicates. See materials and methods in Section IV.

	k				
	Initial sorbate solution concn ($mmol \cdot kg^{-1}$)				
Des.	0.0001	0.001	0.01	0.1	1
no.			h^{-1}		
			CM		
1	0.214 ± 0.011	0.201 ± 0.017	0.244 ± 0.013	0.343 ± 0.031	0.360 ± 0.040
2	0.069 ± 0.008	0.102 ± 0.010	0.074 ± 0.008	0.057 ± 0.013	0.068 ± 0.010
3	0.040 ± 0.008	0.038 ± 0.006	0.032 ± 0.009	0.044 ± 0.015	0.027 ± 0.012
4	0.029 ± 0.008	0.037 ± 0.011	0.039 ± 0.012	0.053 ± 0.014	0.017 ± 0.014
			DCM		
1	0.270 ± 0.005	0.257 ± 0.012	0.312 ± 0.010	0.413 ± 0.020	0.512 ± 0.043
2	0.106 ± 0.006	0.111 ± 0.010	0.111 ± 0.006	0.114 ± 0.009	0.092 ± 0.014
3	0.047 ± 0.008	0.043 ± 0.012	0.048 ± 0.008	0.042 ± 0.009	0.022 ± 0.010
4	0.040 ± 0.010	0.038 ± 0.012	0.052 ± 0.010	0.051 ± 0.016	0.023 ± 0.015

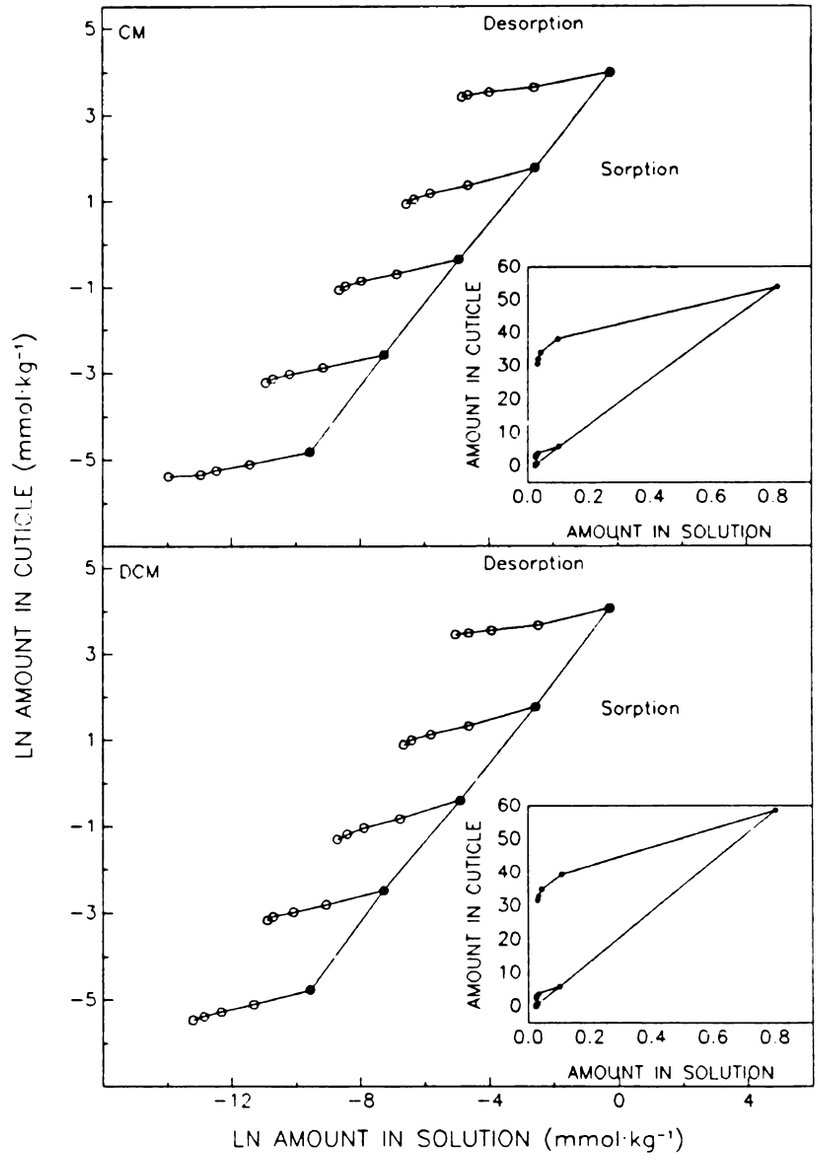


Figure 22. Sorption/desorption isotherms for benzyladenine in the system of isolated (CM) and dewaxed isolated (DCM) pepper fruit cuticles/buffer solution. Buffer solution consisted of 20 mM citrate (1.5 mL pH 3.2) at 25 and 22°C for sorption and desorption, respectively. Insets: arithmetic isotherms. See materials and methods in Section III.

Table VIII. *Freundlich constants for benzyladenine sorption to and desorption from isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Constants for the Freundlich equation (Amount sorbed = $k \cdot$ Amount in solution$^{1/n}$) were calculated from sorption/desorption isotherm data. Desorption constants were calculated for curves describing isotherms for (1) each desorption step and (2) initial sorption concentration. See materials and methods in Section III.

	Freundlich constants			
	CM		DCM	
	k	n	k	n
Sorption	68	1.07	69	1.07
Desorption step				
Des. 1	423	1.02	386	1.02
Des. 2	1529	0.98	1485	0.97
Des. 3	2708	0.97	2898	0.96
Des. 4	2980	0.98	4004	0.95
Initial sorption concn ($mmol \cdot kg^{-1}$)				
0.0001	0.04	6.5	0.05	5.2
0.001	0.30	5.5	0.31	5.5
0.01	1.93	5.1	2.21	4.2
0.1	10.56	4.8	9.80	4.9
1	48.76	10.7	48.70	11.7

Table IX. *Relationship between the initial benzyladenine sorption concentration and the amount not extractable with buffer in isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Tomato fruit cuticles were equilibrated with [^{14}C]BA and extensively desorbed with 20 mM citrate buffer solution (pH 3.2) at 22°C. The fraction not extracted by the buffer solution was determined by oxidation of the cuticle. Amount remaining in the cuticle is the mean (± SE) of 5 replicates. Values in parentheses are the amounts remaining in mmol·kg^{-1}. See materials and methods in Sections III and IV.

	Amount in cuticle	
Initial sorbate solution concn	CM	DCM
mmol·kg^{-1}	*% of amount sorbed*	
0.0001	25.1 ± 0.4 (0.00204)	22.6 ± 0.6 (0.00192)
0.001	25.8 ± 2.1 (0.0197)	21.1 ± 1.1 (0.0176)
0.01	27.0 ± 0.7 (0.191)	24.5 ± 0.3 (0.164)
0.1	21.4 ± 1.0 (1.26)	21.3 ± 1.9 (1.25)
1	16.6 ± 2.0 (8.94)	12.3 ± 1.9 (7.20)

Table X. *Rates of sorption and desorption of TX-100, gibberellic acid (GA_3), naphthyleneacetic acid (NAA), and benzyladenine (BA) by isolated cuticles.*

See materials and methods in Section IV for technique and calculations. Dosing solution consisted of 20 mM citrate buffer solution (1.5 mL, pH 3.2) with [^{14}C] compound. Experiments were conducted at 22°C except BA sorption (25°C). Initial concentrations of dosing solution were TX-35, TX-100, TX-102, TX-165, and TX-405, 1.59 mmol·kg^{-1}; BA, 1.0 μmol·kg^{-1}; GA_3, 7.98 μmol·kg^{-1}; NAA, 0.46 μmol·kg^{-1}. Cuticles were desorbed in stepwise series against buffer solution. Solutions were periodically radioassayed during initial stages of sorption and desorption, and amounts sorbed were determined by difference. Initial rates of sorption and desorption are expressed as the time required to reach one half the equilibrium amount sorbed ($t_{1/2}$). Sorption rates were determined for dehydrated cuticles. N.D. is not determined.

		$t_{1/2}$ (h)				
			Stepwise desorption number			
Cuticle	Compound	Sorption	1	2	3	4
Tomato CM	TX-100	1.2 ± 0.1	0.5 ± 0.1	0.7 ± 0.2	1.8 ± 0.4	1.1 ± 0.4
	GA_3	420 ± 60	5 ± 2	8 ± 3	10 ± 5	N.D.
	NAA	N.D.	0.6 ± 0.1	0.9 ± 0.2	0.5 ± 0.2	0.5 ± 0.2
	BA	15 ± 4	1.3 ± 0.3	3.1 ± 0.9	4.0 ± 1.0	3.2 ± 1.2
Tomato DCM	TX-100	1.4 ± 0.2	0.6 ± 0.1	0.6 ± 0.1	0.7 ± 0.4	0.8 ± 0.2
	BA	13 ± 2	1.1 ± 0.2	1.3 ± 0.3	3.0 ± 0.9	3.2 ± 1.2
Pepper CM	TX-100	2.3 ± 0.4	1.3 ± 0.5	1.3 ± 0.4	2.2 ± 0.7	4.5 ± 2.1
	GA_3	740 ± 70	6 ± 2	8 ± 4	10 ± 4	N.D.
Pepper DCM	TX-100	2.4 ± 0.4	2.1 ± 0.6	5.8 ± 2.4	1.9 ± 0.6	4.3 ± 1.2
Citrus CM	GA_3	460 ± 120	7 ± 3	10 ± 5	12 ± 7	N.D.

Table XI. *Partition coefficients for sorption and desorption of Triton X surfactants (OP+nEO), gibberellic acid (GA_3), and naphthyleneacetic acid (NAA) by isolated cuticles.*

See materials and methods in Section III for technique and calculations. Amendments are listed in Appendix Table IX. At sorption and desorption equilibria, solutions were radioassayed and partition coefficients were determined by difference. Partition coefficients are the mean (± SE) of 5 replicates for BA and NAA; 10 replicates for Triton surfactants and GA_3. N.D. is not determined.

		Partition coefficient				
			Stepwise desorption number			
Cuticle	Compound	Sorption	1	2	3	4
Tomato CM	TX-35	766 ± 22	1653 ± 30	2069 ± 37	2379 ± 40	2507 ± 63
	TX-100	39 ± 1	370 ± 9	658 ± 24	995 ± 65	1201 ± 100
	TX-102	22 ± 1	206 ± 16	375 ± 38	520 ± 63	467 ± 63
	TX-165	16 ± 1	161 ± 18	522 ± 89	917 ± 188	1242 ± 189
	TX-405	5 ± 1	49 ± 11	401 ± 95	809 ± 283	947 ± 340
	GA_3	18 ± 3	555 ± 71	2267 ± 205	2597 ± 493	N.D.
	NAA	196 ± 3	338 ± 7	413 ± 14	550 ± 23	965 ± 37
	BA	113 ± 1	536 ± 7	1299 ± 10	1958 ± 23	2257 ± 130
Tomato DCM	TX-35	940 ± 17	2008 ± 30	2496 ± 59	2807 ± 106	3082 ± 112
	TX-100	49 ± 1	443 ± 12	770 ± 29	1219 ± 90	1668 ± 268
	TX-102	27 ± 1	228 ± 23	437 ± 67	570 ± 110	652 ± 144
	TX-165	17 ± 2	133 ± 10	329 ± 57	532 ± 123	605 ± 168
	TX-405	5 ± 1	64 ± 11	535 ± 108	1046 ± 250	1251 ± 333
	BA	126 ± 2	519 ± 12	1220 ± 20	2084 ± 96	2301 ± 122
Pepper CM	TX-100	38 ± 1	592 ± 21	2151 ±151	4300 ± 405	6072 ± 328
	GA_3	20 ± 3	481 ± 95	2119 ± 654	2753 ± 878	N.D.
	NAA	211 ± 4	299 ± 9	402 ± 25	585 ± 42	920 ± 80
Pepper DCM	TX-100	66 ± 3	856 ± 44	2670 ± 176	4505 ± 432	7637 ± 618
	NAA	227 ± 9	305 ± 9	361 ± 19	485 ± 29	732 ± 68
Citrus CM	TX-100	63 ± 2	1040 ± 27	1955 ± 121	3677 ± 141	4617 ± 212
	GA_3	18 ± 3	1520 ± 98	4355 ± 143	3714 ± 250	N.D.

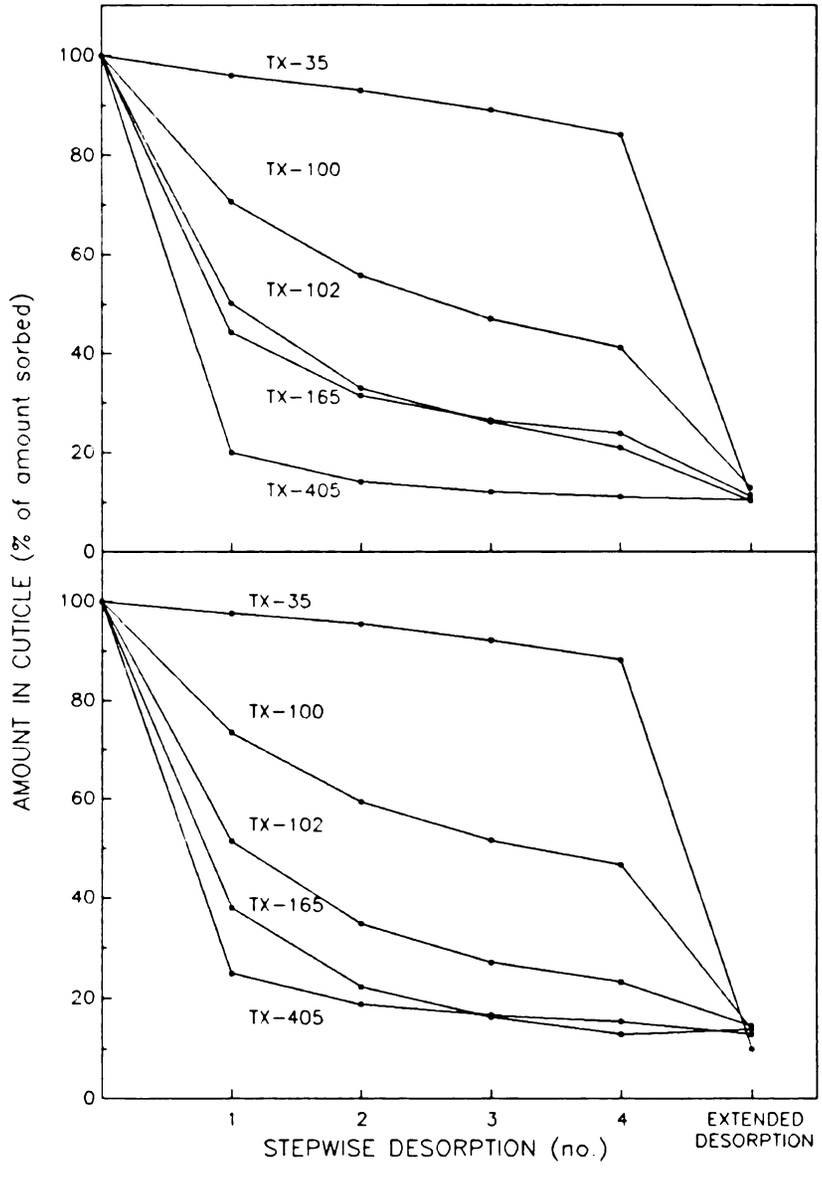


Figure 23. Desorption of Triton X surfactants (OP+nEO) from enzymatically isolated tomato fruit cuticles (upper, CM; lower, DCM). Oxyethylene chain length: TX-35, 3; TX-100, 9.5 EO; TX-102, 12.5 EO; TX-165, 16 EO; TX-405, 40 EO. Initial sorption concentrations were 1.59 mmol·kg^{-1} for all surfactants. Each stepwise desorption was against 20 mM citrate buffer solution (1.5 mL, pH 3.2) at 22°C. Extended desorption was for 300 h. See materials and methods in Section III.

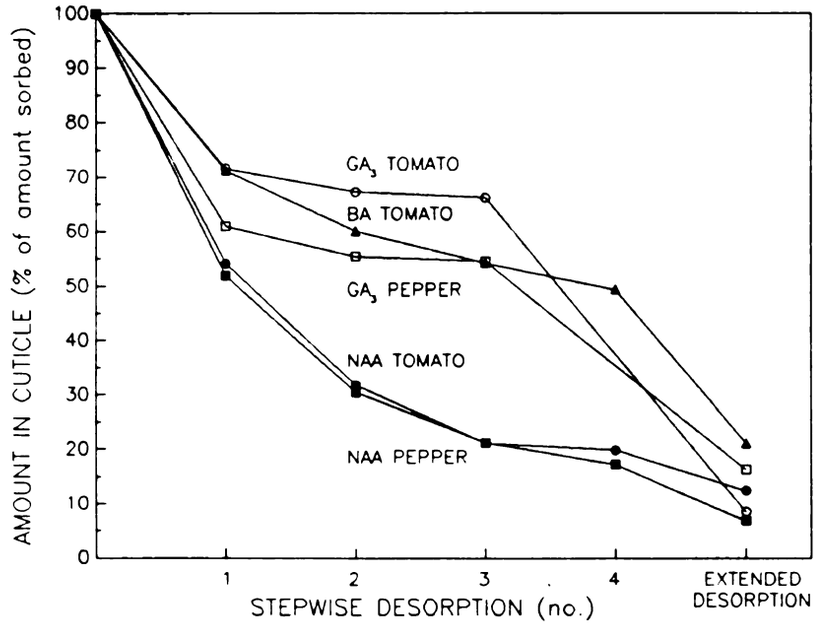


Figure 24. Desorption of gibberellic acid (GA_3), naphthyleneacetic acid (NAA), and benzyladenine (BA) from isolated tomato and pepper fruit CM. Technique described in paper II. Initial sorption concentrations were: BA, 0.10 $\mu mol \cdot kg^{-1}$; GA_3, 7.98 $\mu mol \cdot kg^{-1}$; NAA, 0.46 $\mu mol \cdot kg^{-1}$. Each stepwise desorption was against 20 mM citrate buffer solution (1.5 mL, pH 3.2) at 22°C. Extended desorption was for 300 h. See materials and methods in Section III.

Appendix VI: Cuticular transport properties 4: Effect of concentration and temperature on diffusion of an octylphenoxy surfactant

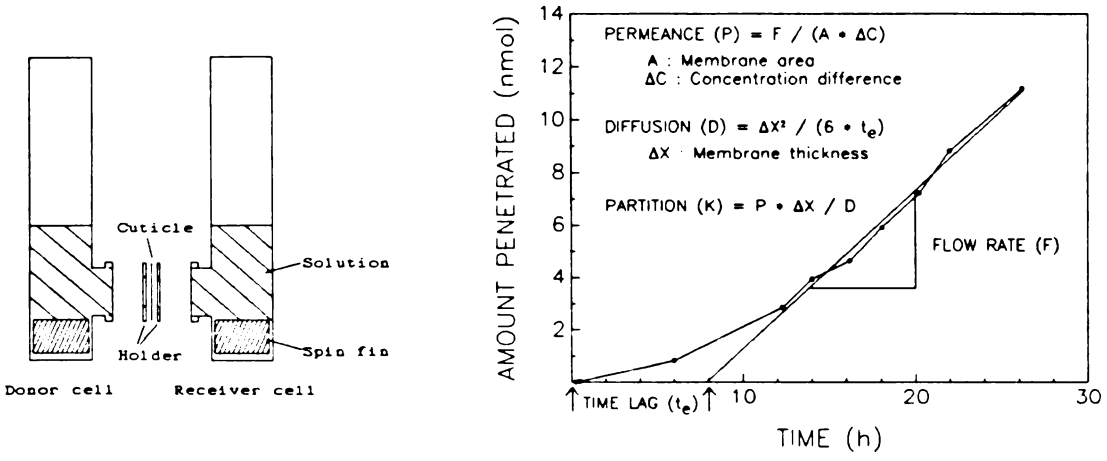


Figure 25. Infinite dose diffusion cell (left) and sample diffusion data and calculations (right).

Table XII. *The effect of cuticle orientation and waxes on the transport of TX-100 through isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Donor cell solution consisted of TX-100 (1.59 mmol · kg^{-1}) in citrate buffer (20 mM at pH 3.2) at 25°C. Receiver cell solution consisted of citrate buffer. Coefficients represent the mean values (± SE) of 12 replications.

			Transport coefficients		
Cuticle	Donor contact surface	Time lag	Permeance	Diffusion	Partition
		h	10^{-10} *m* · s^{-1}	10^{-16} m^2 · s^{-1}	
CM	Outer	8.2 ± 0.7	11.2 ± 2.4	9.8 ± 1.6	15 ± 3
CM	Inner	15.7 ± 2.0	7.2 ± 2.0	6.2 ± 1.2	16 ± 4
DCM	Outer	5.1 ± 0.3	82.7 ± 14.5	14.1 ± 1.6	75 ± 13
DCM	Inner	6.1 ± 1.0	94.0 ± 35.8	12.5 ± 2.2	80 ± 22

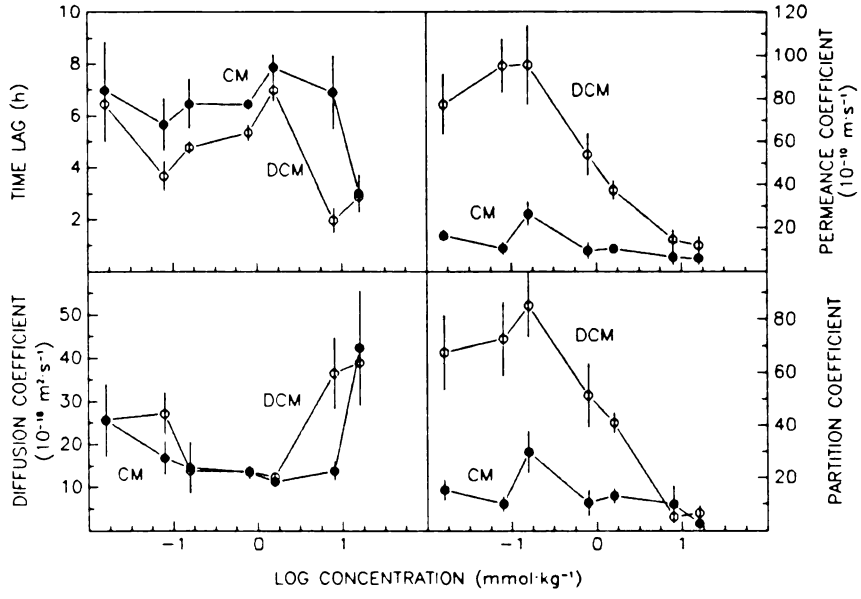


Figure 26. Effect of concentration on the diffusion time lag and transport coefficients of TX-100 through isolated tomato fruit cuticles. Bar represents SE for six replicates.

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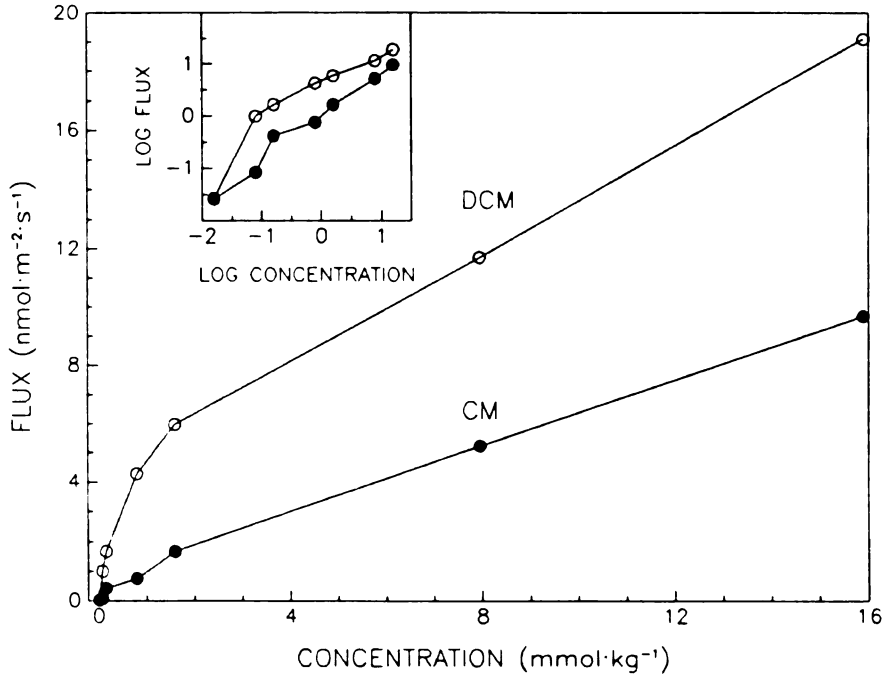

Figure 27. Effect of concentration on flux of TX-100 through isolated tomato fruit cuticles. Inset: log-log plot of flux data.

Table XIII. *Effect of oxyethylene chain length on the transport of TX surfactants through isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Donor cell solution consisted of surfactant (1.59 mmol · kg^{-1}) in citrate buffer (20 mM at pH 3.2) at 25°C. Receiver cell solution consisted of citrate buffer. EO is the average number of ethylene oxide units in hydrophile. Coefficients represent the mean values (± SE) for a minimum of six replications.

			Transport coefficients		
Surfactant	EO	Time lag	Permeance	Diffusion	Partition
	no.	*h*	10^{-10} *m* · s^{-1}	10^{-16} m^2 · s^{-1}	
			CM		
TX-35	3	5.5 ± 0.7	24.0 ± 9.1	12.4 ± 2.9	401 ± 137
TX-100	9.5	7.8 ± 0.5	10.4 ± 1.9	11.2 ± 1.1	13 ± 2
TX-102	12.5	7.6 ± 0.6	6.1 ± 1.6	14.4 ± 2.8	6 ± 2
TX-165	16	11.5 ± 1.6	3.8 ± 0.9	7.2 ± 1.6	7 ± 1
TX-405	40	10.7 ± 1.5	0.8 ± 0.4	10.0 ± 2.8	1 ± 1
			DCM		
TX-35	3	1.7 ± 0.4	95.2 ± 26.1	42.8 ± 21.4	274 ± 77
TX-100	9.5	5.8 ± 0.3	33.2 ± 4.4	14.7 ± 0.9	30 ± 3
TX-102	12.5	5.5 ± 0.7	14.2 ± 3.9	18.4 ± 2.7	11 ± 2
TX-165	16	5.9 ± 2.2	8.9 ± 1.2	22.2 ± 2.2	5 ± 2
TX-405	40	5.8 ± 1.1	4.4 ± 1.5	26.8 ± 9.5	6 ± 2

Table XIV. *Effect of temperature on the transport of TX-100 and TX-165 through isolated (CM) and dewaxed isolated (DCM) tomato fruit cuticles.*

Donor cell solution consisted of surfactant in citrate buffer solution (20 mM at pH 3.2) at 25°C. Receiver cell solution consisted of citrate buffer. Coefficients represent the mean values (± SE) for a minimum of nine replications.

				Transport coefficient		
Cuticle	Surfactant concn	Temp	Time lag	Permeance	Diffusion	Partition
	$mmol \cdot kg^{-1}$	°C	*h*	$10^{-10}\ m \cdot s^{-1}$	$10^{-16}\ m^2 \cdot s^{-1}$	
			TX-100			
CM	0.159	5	18.5 ± 1.3	1.8 ± 0.4	4.3 ± 0.5	6 ± 1
		15	18.1 ± 1.9	2.3 ± 0.7	6.0 ± 1.5	8 ± 3
		25	8.1 ± 0.7	11.2 ± 2.3	9.8 ± 1.5	15 ± 3
		35	5.8 ± 0.3	49.8 ± 10.4	15.0 ± 1.6	45 ± 8
CM	1.59	5	13.1 ± 0.6	2.3 ± 0.6	6.8 ± 0.6	5 ± 1
		15	13.9 ± 2.3	6.9 ± 2.6	6.8 ± 1.5	15 ± 5
		25	8.3 ± 0.6	11.0 ± 2.2	10.6 ± 0.9	15 ± 3
		35	2.3 ± 0.2	45.8 ± 12.5	32.2 ± 6.1	22 ± 8
DCM	1.59	5	19.9 ± 2.3	5.6 ± 0.2	8.2 ± 1.5	13 ± 1
		15	13.2 ± 2.6	17.6 ± 8.1	13.4 ± 4.9	42 ± 28
		25	6.9 ± 0.4	37.5 ± 4.6	12.3 ± 0.7	41 ± 30
		35	1.6 ± 0.1	68.8 ± 4.0	77.5 ± 7.0	14 ± 1
			TX-165			
CM	1.59	5	16.8 ± 3.2	3.1 ± 0.7	6.1 ± 1.3	7 ± 1
		15	12.7 ± 2.2	3.4 ± 1.4	6.9 ± 1.2	6 ± 2
		25	11.5 ± 1.6	3.8 ± 0.9	7.2 ± 1.6	7 ± 1
		35	1.4 ± 0.1	27.7 ± 4.0	66.4 ± 11.3	6 ± 1
DCM	1.59	5	10.7 ± 0.8	3.4 ± 0.9	14.6 ± 2.1	4 ± 1
		15	12.5 ± 0.9	6.7 ± 3.7	11.2 ± 1.9	15 ± 9
		25	5.9 ± 2.2	8.9 ± 1.2	22.2 ± 2.2	5 ± 1
		35	1.7 ± 0.1	87.1 ± 12.6	69.6 ± 16.3	21 ± 3

Appendix VII: Glossary of terms

Absorption: Penetration of substance into the bulk of the solid or liquid (Parker 1989).

Activation energy: Energy that reactants must have for reaction to occur (Bailar et al. 1978).

Adsorption: Surface retention of substance by a solid or liquid (Parker 1989).

Adsorption isotherm: Relationship between the gas pressure or solute concentration and the amount taken up per weight of solid at equilibrium and constant temperature (Parker 1989).

Amphiphile: Molecule which has a polar head attached to a hydrophobic tail (Parker 1989).

Chemical adsorption (chemisorption): Adsorption process in which the forces involved are of the same magnitude as in chemical reactions (Osipow 1962).

Cloud point: Temperature at which turbidity appears when an aqueous solution of a nonionic surfactant is heated (Osipow 1962).

Compliance: Displacement of a linear mechanical system under a unit force (Parker 1989).

Critical micelle concentration (CMC): Concentration range in which surfactant ions or molecules begin to aggregate and form micelles (Osipow 1962).

Desorption: Removal of a sorbed substance by the reverse of adsorption or absorption (Parker 1989).

Diffusion: Movement of substance caused by random molecular motion which leads to complete mixing (Cussler 1988).

Dissolve: To cause to disperse or pass into solution (Parker 1989).

Elasticity: Property whereby a solid material changes its shape and size under action of opposing forces, but recovers its original configuration when the forces are removed (Parker 1989).

Emulsion: System consisting of two immiscible liquids, with one dispersed as small droplets in the other (Osipow 1962).

Enthalpy: Heat content of a substance (Bailar et al. 1978).

Entropy: Measure of the randomness or disorder of a substance (Bailar et al. 1978).

Free energy: Thermodynamic quantity that interrelates enthalpy and entropy (Bailar et al. 1978).

Hydrophilic: Having affinity for, attracting, adsorbing, or absorbing water (Parker 1989).

Hydrophobic: Lacking affinity for, repelling, or failing to adsorb or absorb water (Parker 1989).

Hydrophobic bonding (interaction): Enhanced attraction between two particles in a solvent if the solvent-particle interaction is weaker than the solvent-solvent interaction (Adamson 1982).

Hysteresis: Dependence of the state of a system on its previous history, generally in the form of a lagging of a physical effect behind its cause (Parker 1989).

Interface: Boundary between any two immiscible phases (Rosen 1989).

Lipophilic: Having an affinity for oil (Osipow 1962).

Lipophobic: Having a repulsion for oil (Osipow 1962).

Lyophilic: Substance which will readily go into colloidal suspension in a liquid (Parker 1989).

Lyophobic: Substance in a colloid state which repels liquid (Parker 1989).

Micelle: Orientated aggregation of surfactant ions or molecules (Osipow 1962).

Molecularity: Number of reactant particles (ions, atoms, or molecules) that are involved in each individual chemical event (Laidler 1987).

Monomer: Simple molecule which is capable of combining with a number of like or unlike molecules to form a polymer (Parker 1989).

Physical adsorption (physisorption): Process in which van der Waals forces of interaction form between molecules and a solid surface (Parker 1989).

Plasticity: Property of a solid body whereby it undergoes a permanent change in shape or size when subjected to a stress (Parker 1989).

Plasticize: Softening effect of a plasticizer in which a material becomes plastic or moldable (Parker 1989).

Plasticizer: Additive that gives an otherwise rigid plastic flexibility (Parker 1989).

Reaction order: Sum of exponents of the concentrations in the rate equation (Bailar et al. 1978).

Rheology: Study of the deformation and flow of a matter (Parker 1989).

Solubilization: Spontaneous dissolving of a substance by reversible interaction with the micelles of a surfactant in a solvent to form a thermodynamically stable solution (Rosen 1989).

Soluble: Capable of being dissolved. (Parker 1989)

Solute: Substance dissolved in a solvent. (Parker 1989)

Solution: Single homogeneous liquid, solid, or gas phase that is a mixture in which the components (liquid, gas, solid, or combinations thereof) are uniformly distributed throughout the mixture (Parker 1989).

Solvent: The part of a solution that is present in the largest amount, or the compound that is normally liquid in the pure state (Parker 1989).

(Ad)sorbate: Solid, liquid, or gas which is (ad)sorbed as molecules, atoms, or ions (Parker 1989).

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(Ad)sorbent: Solid, liquid, or gas that (ad)sorbs other substances (Parker 1989).

Sorption: General term used to encompass the processes of adsorption, absorption, desorption, ion exchange, ion exclusion, ion retardation, chemisorption, and dialysis (Parker 1989).

Substance: Solid, liquid, or gas that takes the form of molecules, atoms, or ions (Parker 1989).

Substrate: Substance acted upon, as by adsorption (Osipow 1962).

Surface: Region between two contacting phases, generally a condensed and a gaseous phase (Osipow 1962).

Surface activity: Pronounced tendency of a solute to concentrate at an interface (Osipow 1962).

Surface free energy: Amount of energy required to create a given area of surface (Adamson 1982).

Surface tension: Force that is a measure of the work required to increase the area of a surface (Osipow 1962).

Surfactant (surface-active agent): Substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface (or interfacial) free energies of those surfaces (or interfaces) (Rosen 1989).

Viscoelasticity: Property of material which is viscous but which also exhibits certain elastic properties such as the ability to store energy of deformation (Parker 1989).

Wetting: Displacement of air from a liquid or solid surface by water or an aqueous solution by another (Rosen 1989).

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