

Performance and Stability of the Organosilicone Surfactant L-77: Effect of pH, Concentration, and Temperature

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Studies on the effect of the organosilicone surfactant Silwet L-77 (0.1% w/v) on uptake of [^{14}C]GA₃ (0.5 mM GA₃, pH 3.0) by sour cherry leaves (*Prunus cerasus* L. Montmorency) showed a significant decline in GA₃ absorption when the treatment solution was prepared 12 h prior to application compared to a freshly prepared solution. Surface tension of a freshly prepared solution (22.4 mN m⁻¹) increased rapidly after a 76-min lag period. Gas chromatographic analysis revealed that Silwet L-77 degraded at pH 3.0 with a half-life of 43 min. Degradation velocity was dependent on pH. Slopes of the surfactant (0.1%) degradation curves at pH 3, 4, 5, 9, and 10 were 361.9, 69.2, 12.3, 6.2, and 14.8 mN m⁻¹ day⁻¹, respectively. Duration of the lag phase was linearly related with concentration between 0.025 and 0.4%. No lag phase was apparent below the critical micelle concentration (cmc = 0.008%). Degradation increased significantly with an increase in temperature from 15 to 35 °C. A related surfactant, Silwet L-7607, and two experimental organosilicone surfactants (0.1% and pH 3) also degraded significantly within 3 h. The significance of this degradation is discussed in relation to spray application.

Surfactants are widely used in formulation and spray application to increase efficacy of foliar-applied agrochemicals (McWorther, 1985). Several studies suggest that Silwet L-77 (L-77) is an effective wetting agent which enhances pesticide penetration into foliage of a wide range of plant species (Zabkiewicz and Gaskin, 1989; Gaskin and Kirkwood, 1989). Most of this enhancement has been attributed to stomatal infiltration rather than cuticular penetration (Field and Bishop, 1988; Neumann and Prinz, 1974; Zabkiewicz et al., 1988). L-77 promotion of stomatal infiltration is related to its effectiveness in markedly reducing the surface tension of aqueous spray solutions (Stevens et al., 1989).

During our initial studies with sour cherry, we obtained excellent wetting of sour cherry leaves and increased uptake of GA₃ with freshly prepared L-77 solutions; however, wetting and penetration decreased dramatically within hours of preparing buffered (pH 3.0) GA₃ solutions.

The purpose of this study was to identify the cause of this phenomenon and quantify the effect of selected factors on the stability of L-77 at low pH.

EXPERIMENTAL PROCEDURES

Plant Material. Leaves recently expanded were detached (mid-July) from current season's shoot growth of non pesticide sprayed sour cherry (*Prunus cerasus* L. Montmorency) trees grown at the Horticultural Research Center in East Lansing. Leaves were positioned in glass vials with petioles immersed in deionized water, and the vials were transferred to a growth chamber providing a day/night temperature of 25/20 ± 1 °C and relative humidity of 43/53 ± 5%, respectively. Light was supplied for 16 h at 150 μmol s⁻¹ m⁻².

Chemicals. Silicone-based surfactants used in this study were Silwet L-77 (lot 2133KP050287), Silwet L-7001, Silwet L-7602, and Silwet L-7607 [poly(alkylene oxide) modified poly(dimethylsiloxane) copolymers, Union Carbide, Tarrytown, NY] and two experimental surfactants X2-5309 and Q2-5152 (Dow Corning, Midland, MI). Surfactant solutions (0.1% w/v) were prepared with deionized water in methanol-rinsed glassware. The relationship of pH and surfactant concentration on degradation (as indexed by change in surface tension) was investigated at 0.0025, 0.025, 0.05, 0.1, 0.2, and 0.4% w/v. Except for the lowest concentration, all were above the critical micelle concentration (cmc = 0.008%, Figure 1). All surfactant solutions were buffered with 20 mM citric acid and titrated to pH 3.0 by using NaOH

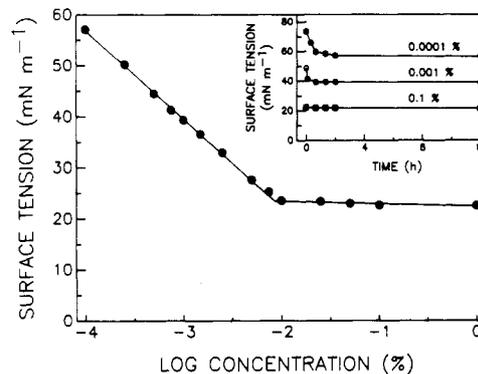


Figure 1. Effect of L-77 concentration (w/v) on equilibrium surface tension (all determinations at pH 7, solutions equilibrated for 2 h). (Inset) Effect of concentration of L-77 on time required to reach equilibrium surface tension.

except for the pH study, for which a composite buffer (2.9 mM citric acid, 2.9 mM KH₂PO₄, 2.9 mM H₃BO₃, 2.9 mM diethylbarbituric acid) was used. In this experiment pH was adjusted to 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, and 10.0 with NaOH. All studies were performed at 24 ± 1 °C except the temperature experiment, during which surfactant solutions were held in water baths at 15, 25, or 35 ± 1 °C. All solutions were vigorously stirred during incubation.

[1,7,12,18- ^{14}C]GA₃ (specific activity 7 mCi mmol⁻¹, radiochemical purity 99%; Amersham Corp., Arlington Heights, IL) was added to 0.1% L-77 surfactant solution to yield a GA₃ concentration of 0.5 mM.

Absorption of [^{14}C]GA₃. Fifteen 0.24-μL droplets of spray solution (0.1% L-77, 0.5 mM GA₃, pH 3.0), prepared 1 or 12 h prior to treatment, were applied to the median portion of the adaxial or abaxial surface of sour cherry leaves between 2 and 4 h after the beginning of the light period. Buffer solution containing only radiolabeled GA₃ served as control. Leaves were removed from the growth chamber 24 h after treatment. Spray deposits were removed by rinsing with 10 mL of acetone/water (3:2 v/v). The epicuticular wax was removed by stripping with cellulose acetate as described by Silcox and Holloway (1986). The cellulose acetate strips were then dissolved in dioxane-based scintillation cocktail. The remainder of the leaf tissue was air-dried and oxidized for 3 min in a biological oxidizer (Model OX-400, Harvey, Hillsdale, NJ). $^{14}\text{CO}_2$ was trapped in a toluene-based scintillation cocktail. Radioactivity was determined

by scintillation spectrometry (Model 1211 Rackbeta, LKB Wallac, 20101 Turku 10, Finland). Counts were corrected for efficiency and background. Total recovery was always greater than 95%. For autoradiography, leaves were treated with five 0.24- μ L droplets on either side of the midrib on the adaxial or abaxial surface. After the droplets dried, the leaves were mounted on poster board, covered with Mylar (Mylar 50M-30, Du Pont, Wilmington, DE), frozen, and exposed for 30 h at -20°C to Kodak diagnostic film (X-Omat AR). The film was developed in a Kodak X-Omat (Eastman Kodak, Rochester, NY).

Surface Tension Measurements. Degradation of L-77 was followed by measuring surface tension in the concentration (% w/v) range 0.01–0.0001 (Figure 1). Ten milliliters of surfactant solution was pipetted into methanol-rinsed glass Petri dishes, and surface tension was determined by using a Fisher Model 20 surface tensiometer (Fisher Scientific, Pittsburgh, PA). Due to the length of the equilibration time at concentrations below the cmc (Figure 1, determined at neutral pH, cmc = 0.008%) and the rapid rate of degradation at pH 3, it was not possible to measure the equilibrium surface tension. Hence, duplicate measurements (three replications) were taken on each sample within 1.5 min after transfer of the solution to the Petri dish. In the temperature study, 10-mL aliquots of surfactant solution were removed and stirred for 10 min for equilibration to ambient temperature ($24 \pm 1^{\circ}\text{C}$) before surface tension was measured as previously described.

The time course of change in surface tension was followed as an index of degradation. Lag times, characterized by constant surface tension, and slopes of the degradation curve were calculated by using the method of least-squares analysis. The slope was obtained by fitting a linear regression line during the phase of increasing surface tension of a plot of surface tension vs time. Lag times were calculated by solving the regression equation for time at surface tension γ_0 , where γ_0 represents the mean surface tension of the initial readings during the phase of constant surface tension. Each determination was replicated three times.

Transmittance Measurements. Turbidity of 3-mL aliquots of surfactant solution was measured at 300 nm by using a Gilford spectrophotometer (Model Response TM, CIBA-Corning Diagnostics, Oberlin, OH). Buffered solutions without surfactant served as the reference. Each determination was replicated twice.

Loss of Parent Compound. Ten-milliliter aliquots were taken at selected time intervals after initial preparation, frozen in liquid nitrogen, and lyophilized. Residues were dissolved in 0.2 mL of water, partitioned against 2 mL of chloroform, and salted-out into the organic phase by addition of NaCl. The organic phase was dried with anhydrous Na_2SO_4 . GLC analysis was carried out with a Varian Model 3740 gas chromatograph (Varian, Walnut Creek, CA) at the following operating conditions: temperatures of injector and flame ionization detector were 230 and 350 $^{\circ}\text{C}$, respectively. Gas flow rates were 30 mL min^{-1} H_2 , 300 mL min^{-1} air, 1 mL min^{-1} He as carrier gas, and 30 mL min^{-1} N_2 as makeup gas using the splitless method. Separation was performed on a DB-1 fused silica capillary column (30 m \times 0.3 mm i.d.; J&W Scientific Inc., Folsom, CA) temperature programmed from 50 to 320 $^{\circ}\text{C}$ at 6 $^{\circ}\text{C}$ min^{-1} . Peaks were integrated by using a Spectra Physics integrator (Model SP 4100; Spectra Physics, San Jose, CA; chart speed 5 mm min^{-1}). Since L-77 is a mixture of oligomers, several peaks were detected (Figure 2). Peaks with retention times (RT) of 26.8, 30.8, 34.4, 37.6, 40.6, and 43.4 min, representing 47% of the total peak area detected, were assigned to the parent compounds and measured over time. Each sample contained 80 ng of 1-octanol as an internal standard (RT 7.6 min). Data shown are based on single measurements and were corrected for sensitivity by using the internal standard.

Statistics. Data were subjected to analysis of variance where appropriate, and means were compared by using Duncan's multiple range test ($P = 0.05$). Standard errors of the means were included in all graphs and in most cases were smaller than data points.

Terminology. In this paper the term "solution" is not limited to true solutions, but is used also for stable dispersed emulsions.

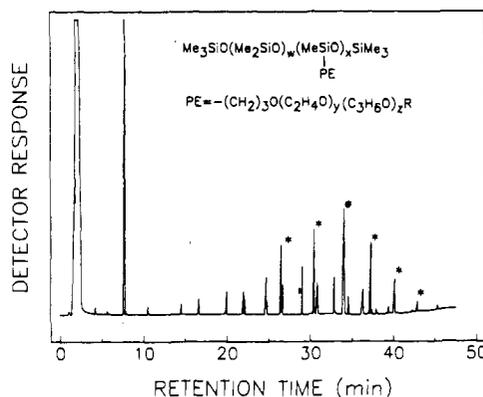


Figure 2. GLC trace of L-77. Peaks marked by an asterisk were assigned to the parent compound(s), and their cumulative areas were measured during degradation. The formula given represents the general structure for the Silwet surfactants, and for L-77 w and z are 0, x is 1, y is 7.5, and R is CH_3 .

Table I. Effect of Age of L-77/ GA_3 Solution on Absorption of GA_3 through Adaxial and Abaxial Leaf Surfaces of Detached Sour Cherry Leaves^a

leaf surface	GA_3 absorbed, % of applied		
	control	L-77 at solution age of	
		1 h	12 h
adaxial	0.6de ^b	2.9cd	0.4e
abaxial	5.9b	23.4a	3.6c

^a Conditions: 0.1% L-77, 0.5 mM GA_3 , pH 3.0, $25 \pm 1^{\circ}\text{C}$. ^b Means followed by the same letter are not significantly different at $P = 0.05$, Duncan's multiple range test.

RESULTS

GA_3 absorption by the abaxial surface of sour cherry leaves was markedly enhanced on addition of a freshly prepared (within 1 h of treatment) L-77 solution (Table I). However, a significant depression of absorption was observed when the solution was made up 12 h before treatment. A similar trend was found for the astomatous adaxial surface, but the effect of L-77 was not significant in comparison with the control. However, less GA_3 was again absorbed from an aged solution.

Within 12 h of preparation of the solution, spreading of the droplets on sour cherry leaves changed dramatically (Figure 3). Droplets of a freshly prepared solution of GA_3 and L-77 spread rapidly over the leaf (Figure 3B,E), whereas little spreading occurred in the absence of L-77 (Figure 3A,D) or when the solution was prepared 12 h before treatment (Figure 3C,F). Generally, the adaxial surface was easier to wet than the abaxial. Areas over veins, particularly on the adaxial surface, were preferentially wetted (Figure 3B).

Surface tension of L-77 solutions (0.1%) at pH 3 (22.4 mN m^{-1}) increased in a sigmoidal pattern with time after preparation of the solution (Figure 4A). After an initial lag phase of 76 min, during which time surface tension remained constant, surface tension increased in 104 min from about 22.4 to 50 mN m^{-1} . Surface tension approached a plateau in about 3 h after preparation of the solution and attained a value of about 56.5 mN m^{-1} within 24 h.

As indexed by transmittance and visual ratings the L-77 solutions underwent two dramatic changes in clarity during the first 3 h after preparation (Figures 4B and 5). Immediately after preparation, L-77 (0.1%, pH 3.0) formed a hazy (cloudy, stable dispersion) aqueous solution at room temperature (Figures 4B and 5, stage a). Transmittance then increased, reaching a maximum after 45 min (Figures 4B and 5, stage b), and then decreased (Figures 4B and

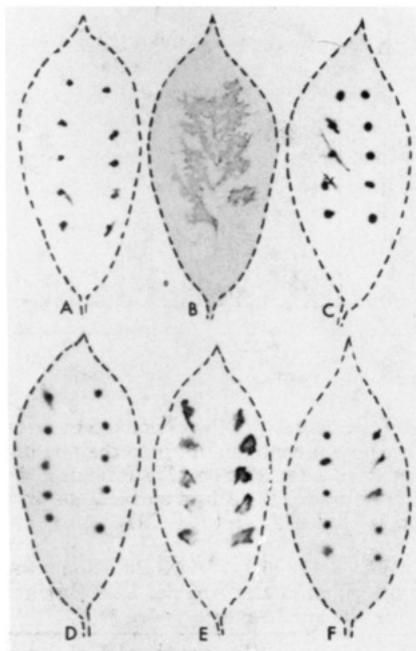


Figure 3. Autoradiographs of adaxial (A–C) and abaxial (D–F) sour cherry leaf surfaces treated with radioactive GA_3 with or without L-77. Solutions were freshly prepared or allowed to stand for 12 h before use. (A, D) GA_3 alone, 1 h; (B, E) GA_3 + L-77, 1 h; (C, F) GA_3 + L-77, 12 h. Conditions: 0.1% L-77, 0.5 mM GA_3 , pH 3.0, $25 \pm 1^\circ C$.

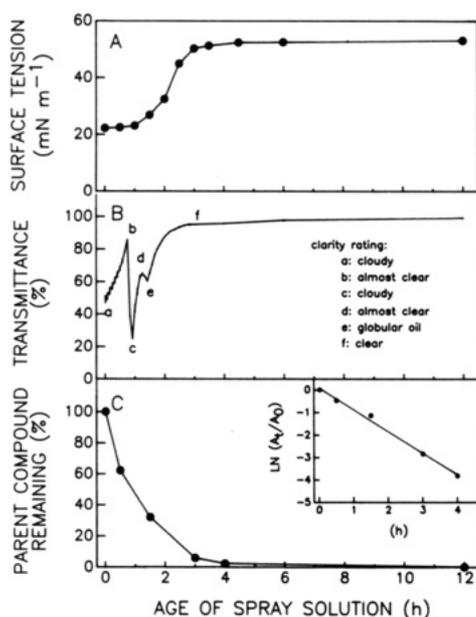


Figure 4. Time course of L-77 degradation at pH 3.0 as indexed by surface tension (A), turbidity (B), and loss of parent compound(s) (C). Conditions: 0.1% L-77, pH 3.0, $24 \pm 1^\circ C$.

Table II. Effect of Solution pH on Rate of L-77 Degradation As Indexed by Surface Tension^a

pH	slope, $mN\ m^{-1}\ day^{-1}$	duration of lag phase, days
3	361.9a ^b	0.11e
4	69.2b	0.72d
5	12.3c	6.39b
6–8	ND ^c	>40
9	6.2c	14.22a
10	14.8c	3.60c

^a Conditions: 0.1%, $24 \pm 1^\circ C$. ^b Means within a column followed by the same letter are not significantly different at $P = 0.05$, Duncan's multiple range test. ^c No degradation detected.

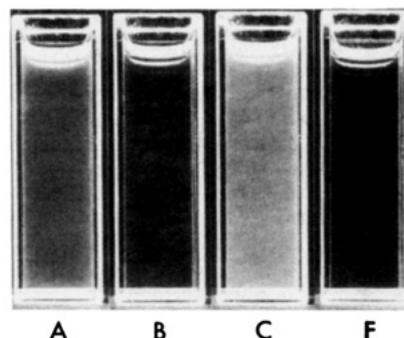


Figure 5. Photographs of acidic L-77 solution depicting changes in clarity with time after preparation. (A) Cloudy, solution immediately after preparation; (B) clear, maximum clarity occurring 45 min after preparation; (C) cloudy, 55 min after preparation; (F) clear, final stage 3 h after preparation. Conditions: 0.1% L-77, pH 3.0, $24 \pm 1^\circ C$.

5, stage c). At this point the turbidity exceeded that of the newly prepared solution. The treatment solution then cleared again, approaching asymptotically the transmittance of the buffer solution without surfactant (Figures 4B and 5, stage f). During this final clearing, very small oillike droplets formed. This phase separation was usually associated with a decrease in transmittance from stage d to stage e (Figure 4B). The oil droplets increased in size when the solution was not stirred, but were dispersed when the solution was shaken, increasing turbidity again.

The rate of disappearance of the parent compounds (L-77), as determined by GLC, gave a good fit for kinetics of a first-order reaction with a rate constant of $k = 0.96\ h^{-1}$ and a $t_{1/2}$ of 43 min at pH 3.0 (Figure 4C).

$$\ln(A_t/A_0) = 0.83 - 0.96 \times \text{time (h)}, r^2 = 0.994^{***}$$

Within 12 h after preparation of the L-77 solution the level of the parent compound decreased to below the detection limit. No attempt was made to identify and measure the product(s) formed.

Velocity of degradation, as indexed by an increase in surface tension, was dependent on pH of the spray solution. Degradation occurred most rapidly in acidic or alkaline solutions (Table II). As the pH approached neutrality, the velocity decreased and lag times increased. These changes were log linearly related to pH in the range from 3 to 5. No detectable increase in surface tension was noted over a period of 40 days at pH 6, 7, or 8.

Degradation of L-77, as measured by change in surface tension, showed an initial lag phase at concentrations above the cmc (i.e., 0.025, 0.2%, Figure 6A). At a concentration below the cmc (0.0025%), surface tension increased immediately after preparation of the solution (Figure 6A). The slope and the final surface tension increased as concentration decreased. Above the cmc the relationship between the L-77 concentration originally present in the solution and the duration of the lag phase was linear (Figure 6B).

$$\text{lag phase (h)} = -0.42 + 12.41 \times \text{concn (\%)}, r^2 = 0.982^{**}$$

Temperature had a relatively small effect on degradation in the range from 15 to $35^\circ C$ (Table III). The slopes of the degradation curves obtained at 15 and $25^\circ C$ were significantly lower than that at $35^\circ C$. As expected, lag times decreased significantly with each $10^\circ C$ increase in temperature.

A comparison of stability of different silicone-based surfactants at pH 3.0 revealed that of the six surfactants evaluated, L-77, L-7607, and two experimental surfactants (X2-5309, Q2-5152) increased significantly in surface tension within 3 h (Table IV). However, surface tension

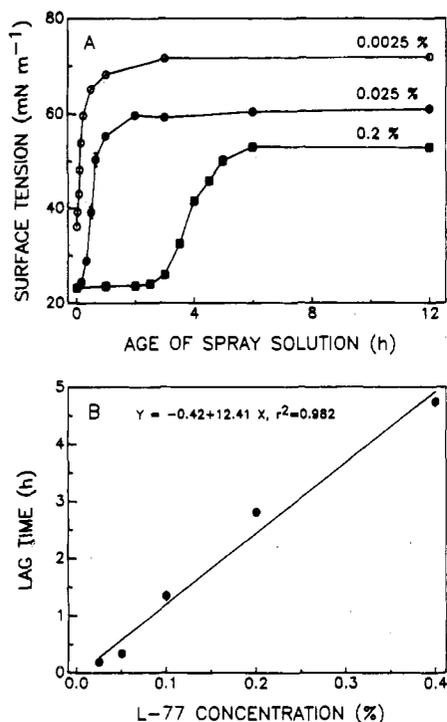


Figure 6. Effect of concentration on L-77 degradation. Conditions: pH 3.0, 24 ± 1 °C. (A) Time course of change in surface tension as affected by concentration (0.0025, 0.025, and 0.2%, w/v). (B) Relationship between duration of lag time (from zero time to first increase in surface tension) and concentration above the cmc.

Table III. Effect of Temperature on Rate of Degradation of L-77^a

temp, °C	slope, mN m ⁻¹ h ⁻¹	duration of lag phase, min
15	18.2b ^b	111a
25	16.7b	77b
35	22.7a	55c

^a Conditions: 0.1%, pH 3.0. ^b Means within a column followed by the same letter are not significantly different at $P = 0.05$, Duncan's multiple range test.

Table IV. Changes in Surface Tension of Selected Organosilicone Surfactants (0.1%) at pH 3.0 and Various Times after Preparation^a

surfactant	surface tension, mN m ⁻¹ , at solution age of				
	0 h	3 h	6 h	12 h	24 h
L-77	22.6d ^b	51.9a	55.5b	56.0c	57.2c
L-7001	36.5a	36.4b	36.5c	35.7e	36.5e
L-7602	34.3b	33.6c	33.9d	33.6f	32.5f
L-7607	24.3c	29.0d	32.8d	46.8d	53.8d
X2-5309	23.2d	28.8d	54.2b	59.8b	61.8b
Q2-5152	22.6d	50.4a	58.7a	62.1a	64.0a

^a Temperature: 24 ± 1 °C. ^b Means within a column followed by the same letter are not significantly different at $P = 0.05$, Duncan's multiple range test. Comparing the time effect, the surface tension increased significantly ($P = 0.05$) over the first 3 h (0 vs 3 h) for L-77, L-7607, X2-5309, and Q2-5152, but not for L-7001 and L-7602.

of the surfactants (emulsifiers) L-7001 and L-7602 at 0.1% and pH 3.0 remained constant over the time period monitored.

DISCUSSION

Foliar-applied agrochemicals enter the leaf via stomatal and/or cuticular routes. Penetration of stomata is dependent on stomatal morphology and the surface tension of the spray solution (Greene and Bukovac, 1974; Schönherr and Bukovac, 1972). Thus, surface tension of the

spray solution is the only factor governing infiltration of stomata on a given leaf surface assuming no variation of stomatal morphology and wettability. L-77 is among the few surfactants shown to reduce surface tension sufficiently to permit mass flow of an aqueous spray solution through the stomatal pore (Stevens et al., 1989).

Transport via the second pathway, cuticular penetration, is viewed as a diffusion process (Franke, 1967). According to Fick's first law of diffusion, the flux (J) of an active ingredient is proportional to the spray droplet/cuticle interface area (A), the permeability coefficient (P), and the concentration gradient ($C_o - C_i$). Thus, A is dependent on plant surface characteristics and the surface tension of the spray solution (Holloway, 1969, 1970). Therefore, penetration via both the stomatal and cuticular routes is strongly dependent on the surface tension of the spray solution for any given plant surface. The reduced penetration of GA₃ into sour cherry leaves (12 vs 1 h, Table I) was probably a result of the marked increase in surface tension (Figure 4A) following degradation of the surfactant (Figure 4C). The high surface tension prevented stomatal infiltration on the abaxial surface and decreased interface area on adaxial and abaxial surfaces (Figure 3).

The surface tension of a surfactant solution varies inversely with the concentration of surfactant monomers aligned at the liquid/air interface. At concentrations above the cmc the monomer concentration is constant; further addition of surfactant results in the formation of aggregates (micelles). Our data suggest that this classical relationship between surface tension and surfactant concentration holds also for the silicone based L-77 surfactant (Figure 1). Lack of change in surface tension at surfactant concentrations above the cmc is evidence for the formation of micelles. Whether or not these are micelles in the classical sense is not known. The surface tension of the spray solution is inversely proportional to the L-77 concentration (monomer only) below the cmc (Figure 1) when measurements are made at equilibrium, i.e., when monomers aligned at the surface are in equilibrium with monomers in the bulk solution. On the basis of these relationships the rate of surfactant degradation at concentrations below the cmc should be proportional to the rate of change in surface tension. This was confirmed in our study. Concentration of L-77 decreased with no change in surface tension during the first 76 min after preparation of the solution (Figure 4A). We propose that during the lag phase micelles serve as a "buffer", providing for a constant monomer concentration and, hence, a constant surface tension. This interpretation is also supported by the observed dose/response where at concentrations above the cmc the duration of the lag phase is proportional to the size of the micelle pool buffering the monomers (Figure 6B). No lag phase was observed below the cmc (Figure 6A).

The second phase (Figure 4A), characterized by increasing surface tension, is associated primarily with the degradation of surfactant monomers and, hence, reflects the rate of degradation. Degradation at low pH (Table II) was too rapid to permit equilibrium for surface tension measurements. Therefore, an exact degradation rate could not be derived from the surface tension data. However, the rate of degradation can be estimated from the slope of a line fitted through the phase of increasing surface tension. Thus, the increasing surface tension phase corresponds to degradation of monomers, while during the lag phase in addition to monomer degradation micelles degrade, releasing monomers and thus keeping monomer concentration and surface tension constant.

The rate of L-77 degradation fits first-order kinetics at pH 3.0. Hence, rate constant and half-life should be independent of surfactant concentration. Our results, however, indicate a decrease in slope with an increase in surfactant concentration (Figure 6A). Further, the final surface tension attained (plateau) was dependent on the initial surfactant concentration, indicating that the degradation product(s) is surface active (Figure 6) or one or more of the molecular species making up L-77 did not degrade. However, GLC studies over a 12-h period showed no significant change in distribution of the molecular species (data not presented). Thus, the observed difference in slope can be attributed to a varying product concentration depending on the initial L-77 concentration.

Of the factors investigated (pH, concentration, temperature), pH had the greatest effect on the rate of degradation. Degradation velocity decreased as pH was increased up to neutrality. This effect cannot be attributed to differences in ionic strength, since a similar degradation pattern was found over a broad range (5–50 mM NaCl) of ionic strength (data not presented).

Cleavage of siloxane bonds under acidic conditions may be catalyzed by electron donors like ethylene glycol ethers (Voronkov et al., 1978). If this occurs with the L-77 molecule, the following reaction sequence can be visualized. The first step involves the protonation of a siloxane bond, which could result in increased water solubility and account for the increased transmittance observed (Figures 4B and 5, stage b). Second, in the presence of ethylene glycol, which is part of the surfactant molecule, solvation of water protons may be reduced. Reduction in proton solvation may increase active centers for nucleophilic cleavage of the siloxane bonds (Voronkov et al., 1978), reducing both solubility of the intermediate species and transmittance, as observed between stages b and c (Figures 4B and 5). The final cleavage of the siloxane bond results in formation of a product(s) that, in the concentration range tested, is more water soluble and in clearing of the solution (Figures 4B and 5, stage f).

Degradation under acidic and alkaline conditions, resulting in a loss of surface tension over time, is of particular importance for L-77. The unique properties of this surfactant, and most likely of other surfactants of similar chemistry, are associated with the low surface tension produced in aqueous spray solutions. This important characteristic would be lost if the surfactant was degraded in the spray tank before or during the application process.

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