The Interaction of Dimethyl Ditallow Ammonium Chloride and Sodium Linear Alkylbenzene Sulfonate[1]

Dewey L. Smith[a], Michael F. Cox[a], G.L. Russell[a], Gary W. Earl[b], Phillip M. Lacke[b], Richard L. Mays[b] and Jean M. Fink[b]

[a]Vista Chemical Co., P.O. Box 500, Ponca City, OK 74601, and [b]Sherex Chemical Co., P.O. Box 646 Dublin, OH 43017

The interaction of a commercial sample of dimethyl ditallow ammonium chloride (Adogen® 470E) and sodium alkylbenzene sulfonate (C-550 LAS) in aqueous solution was examined. Interaction was very strong, with the ion pair association constant estimated to be 1×10^6 l/mol.

At laundry use level concentrations, the mixtures were turbid. The highest turbidity was found at equimolar concentrations of C-550 LAS and Adogen® 470E. Turbidity was assumed to be due to the formation of an insoluble 1:1 complex.

Both filtered and unfiltered mixtures of C-550 LAS and Adogen® 470E were evaluated for detergency, softening and antistat performance. As the mixtures approached 1:1 stoichiometry, detergency decreased and softening and antistat performance improved. Lower detergency was explained by the loss from solution of LAS to form a 1:1 LAS-dimethyl ditallow ammonium complex. Improved softening and antistat perfromance were explained by adsorption of the insoluble complex on the cloth.

In recent years, the consumer has expressed a preference for laundry products that are convenient to use. For example, laundry liquids have enjoyed increasing popularity over powders; in part because of their perceived convenience. Another example of the importance of convenience in laundry products is the emergence of so-called "softergents." Softergents seek not only to remove soil from clothes but also to soften. Liquid softergents are especially convenient products.

Most commercial liquid softergents are combinations of nonionic surfactants, which are added for detergency, and cationic surfactants, which are added for softening and static control. Anionic surfactants usually are not included in softergent formulations because they interact with cationic surfactants.

This study examines mixtures of an anionic surfactant, sodium linear alkylbenzene sulfonate (LAS), and a cationic surfactant, dimethyl ditallow ammonium chloride, and reports how physical and performance properties change as a result of anionic-cationic interaction.

EXPERIMENTAL

Materials. For all but conductance measurements, commercial C-550 LAS was used. The composition is given in Table 1. For conductance measurements, commercial C-550 LAS was desalted and deoiled prior to use. The composition of the deoiled and desalted sample is also given in Table 1.

Dimethyl ditallow ammonium chloride used in all measurements was also a commercial product, Adogen® 470E fabric softener concentrate. The properties of this material are given in Table 1.

Concentration range of mixtures. Detergency, static decay and softening measurements were made on mixtures of C-550 LAS and Adogen® 470E over the range 10^{-3} M-10^{-4} M. This range corresponds to typical laundry use concentrations.

Detergency. Two series of solutions were evaluated for detergency and soil deposition. In one series, C-550 LAS was mixed with Adogen® 470E and the detergency of the mixtures was evaluated. In the second series the mixtures were first vacuum filtered through a Whatman 42 filter, and the detergency of the filtrate was then evaluated. Three mineral oil-soiled permanent press cloths and three unsoiled permanent press cloths were washed in a

TABLE 1

Composition of Materials

C-550 LAS	
Wt % active	53.92
Av mol wt	320.6
Wt % Na_2SO_4	0.97
Wt % Unsulfonated alkylate (free oil)	1.29
C-550 LAS (deoiled and desalted)	
Wt % active	93.78
Wt % Na_2SO_4	< 0.1
Wt % Unsulfonated alkylate (free oil)	2.13
Adogen ® 470E	
Av mol wt	545
Wt % active	71.97
Wt % ethanol	17.45
Wt % water	6.54

TABLE 2

Detergency Testing Procedures

Testing apapratus	Terg-O-Tometer
Wash cycle	10 min
Rinse cycle	5 min
Wash temperature	100°F (38°C)
Water hardness	DI water
Number of soiled cloths (3″ × 4.5″)	3 permanent press
Number of unsoiled cloths (for deposition)	3 permanent press
Soil	mineral oil and red dye
Cloth	permanent press
Test procedure	Vista CRS Lab Method 303-74[b]
Reflectance measuring device	Gardner (Model XL 20 Colorimeter)

[a]65% Dacron/35% cotton with a permanent press finish (Test Fabrics S/7406).

[b]Similar to ASTM Standards, Part 30, 465-466 (1977).

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[1]Presented May 10, 1988 at the 79th Annual AOCS Meeting, in Phoenix, Arizona.

Terg-O-Tometer pot. The change in reflectance of the cloth before and after washing was used to evaluate detergency and soil deposition. Further details are given in Table 2.

Elemental sulfur determination. Sulfur content was determined with a LECO sulfur analyzer on cloths washed in equimolar mixtures of C-550 LAS and Adogen® 470E. In this test, the washed and dried cloth is combusted in oxygen and the resulting sulfur trioxide is determined quantitatively by IR. The amount of sulfur originally present is then calculated.

Softening. Softening of terry cloth washed in both the filtered and unfiltered mixtures was evaluated in a subjective panel test. The five-person panel ranked the softness of each cloth within a series of either three or four cloths. When included, the fourth cloth was a control washed in either 10^{-3} M C-550 LAS (a harsh control) or 10^{-3} M Adogen® 470E (a soft control). The cloths were ranked with the softest cloth receiving the highest ranking. Therefore, when a control was included (four cloths), the rankings ranged from 4 to 1. Without a control, the rankings potentially ranged from 3 to 1.

Static decay measurements. After detergency testing, the cloths were equilibrated for 24 hr at 50% relative humidity. Antistat properties of the washed cloth were evaluated with an Electro-Tech Systems Model 406 C static decay meter. The instrument was zeroed and a static charge was impressed on the cloths by an initial 5000 V charge. The time for the charge to decay to 500 V was recorded automatically. Three soiled cloths and three unsoiled cloths were tested for each C-550 LAS and Adogen® 470E mixture. One of the soiled cloths and one of the unsoiled cloths were read three times. The other two cloths were read only once if they agreed with the first cloth. If agreement was not good, the other two cloths were both read twice. For all replicates the readings were averaged.

Precipitation boundary diagram. Stock solutions of C-550 LAS and Adogen® 470E were heated in a water bath to the wash temperature of 100°F. After equilibration, five ml of C-550 LAS solution was mixed with five ml of Adogen® 470E solution.

After approximately 10 min of equilibration at 100°F, the turbidity of the mixtures was measured with a Hach DR 3 spectrophotometer set to 500 nm.

Quantitative analysis of mixtures. Mixtures of C-550 LAS and Adogen® 470E were quantitatively analyzed for precipitate, C-550 LAS concentration and Adogen® 470E concentration. To this end, stock solutions of C-550 LAS and Adogen® 470E were mixed and then vacuum filtered through a 0.2-micron filter to remove precipitate. The precipitate was then weighed. The filtrate was retained to determine cationic and anionic surfactant concentration.

To remove chloride anions that interfere with the cationic surfactant determination, the filtrate was passed through Amberlyst® A-26, an anion exchange resin. The chloride-free filtrate was then reacted with disulfine blue, an anionic dye that forms a colored complex with Adogen® 470E. The colored complex was extracted with chloroform. The amount of Adogen® 470E originally present in the filtrate was determined by colorimetric comparison of the unknown with an Adogen® 470E/disulfine blue calibration curve.

A similar colorimetric technique was used to determine the concentration of C-550 LAS in the filtrate. In this case, methylene blue was used to form a colored complex with C-550 LAS. The concentration of LAS in the filtrate was determined by reference to a previously prepared LAS/methylene blue calibration curve.

Ion pair formation constant. To measure the equilibrium constant for the reaction

$$(\text{LAS})^- + (\text{Adogen® 470E})^+ \rightleftarrows (\text{LAS-Adogen® 470E}) \quad [1]$$

the method described by Mukhayer and Davis (1) was used. The method is based on measuring the conductance of an anionic and cationic surfactant solution separately and then adding the conductances to predict the conductance of their mixture. Next the mixture is made and the conductance is determined. Deviation of the actual conductance from the predicted conductance is assumed to be due to the formation of a nonconducting ion pair. The ion pair is shown on the right hand side of equation [1].

Conductivity was measured with a YSI model 34 conductivity meter fitted with a YSI dipping cell electrode (cell constant = 0.103 cm^{-1}). Solutions were prepared using DI water that had passed through a Millipore column (R = 17 MOhm-cm^{-1}). Prior to conductance measurements, the solutions were thermostated in a double-walled beaker. The temperature was controlled to 25.0 ±0.1°C with a Lauda® RC 6 circulating bath. Thermal equilibrium was maintained with a mixing bead and a magnetic stirrer. To ensure that conductivity did not change due to carbon dioxide absorption from the atmosphere, all conductance measurements were performed under nitrogen.

RESULTS

Precipitation boundary diagram. The absorbance at 500 nm of the C-550 LAS and Adogen® 470E mixtures served as a measure of the amount of precipitate formed. The higher the absorbance, the more precipitate was formed. The absorbance data for the grid of mixtures is shown in Figure 1.

Quantitative analysis of solutions. The results of the quantitative analysis of the solutions are given in Table 3. The next to the last column in Table 3 is the weight of precipitate solubilized and is defined as:

$$\text{Wt solubilized} = (\text{wt in}) - [(\text{wt LAS}) + (\text{wt complex}) + (\text{wt Adogen® 470E})] \quad [2]$$

To measure the percent solubilized, the weight solubilized was divided by the total weight of C-550 LAS and Adogen® 470E put into each mixture. The results are shown as the last column in Table 3.

Taking the average molecular weights for C-550 LAS and Adogen® 470E given in Table 1, assuming a 1:1 stoichiometric complex, and taking the volume of the mixture as 30 ml, it is possible to convert the weights given in Table 3 to molar concentrations of LAS and Adogen® 470E. Assuming the activity of the "free" precipitate and the solubilized precipitate is unity, the solubility product for the reaction

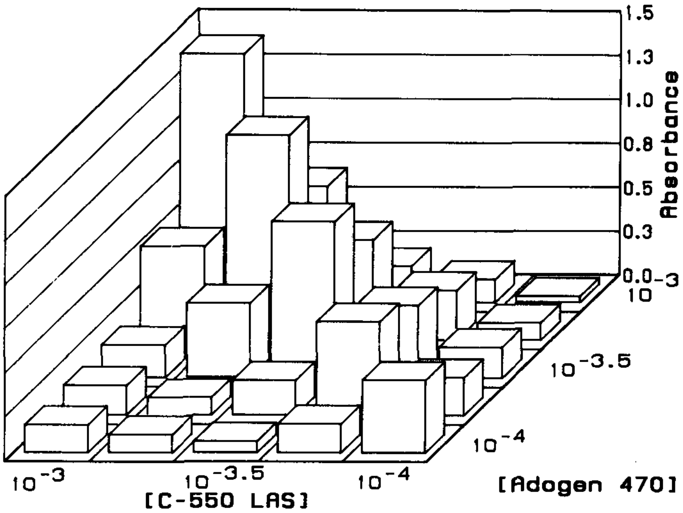

FIG. 1. Absorbance vs concentration of C-550 and Adogen® 470E mixtures.

TABLE 3

Mass Balance Data

(C-550 LAS)/ (Adogen® 470E)	Wt C-550 LAS (mg)	Wt Adogen® 470E (mg)	Wt precip (mg)	Wt in (mg)	Wt sol (mg)	Percent sol (%)
$10^{-3}/10^{-3}$	0.2	0.3	23.4	26.0	2.5	9.6
$10^{-3}/10^{-3.5}$	6.4	0.0	2.0	14.8	6.4	43.2
$10^{-3}/10^{-4}$	9.8	0.0	0.8	11.22	0.6	5.4
$10^{-3.5}/10^{-3}$	0.5	11.7	0.2	19.4	7.0	36.1
$10^{-3.5}/10^{-3.5}$	0.7	0.2	7.6	8.2	-0.3	-
$10^{-3.5}/10^{-4}$	1.7	0.0	1.8	4.7	1.2	25.5
$10^{-4}/10^{-3}$	0.0	15.6	0.1	17.3	1.6	9.2
$10^{-4}/10^{-3.5}$	0.2	3.6	0.1	6.1	2.2	36.1
$10^{-4}/10^{-4}$	0.0	0.1	2.3	2.6	0.2	7.7

TABLE 4

Solubility Product

Concentration	K_{sp}
[(C-550 LAS)/(Adogen ® 470E)]	$(\mathrm{mol/l})^2$
$10^{-3}/10^{-3}$	3.8×10^{-10}
$10^{-3.5}/10^{-3.5}$	7.0×10^{-11}
$10^{-4}/10^{-4}$	2.0×10^{-11}

TABLE 5

Ion Pair Association Constant

Concentration	$K_{\text{ion pair}}$
[(C-550 LAS)/(Adogen ® 470E)]	(mol/l)
$10^{-8.66}/10^{-8.64}$	1.5×10^{6}
$10^{-8.54}/10^{-8.65}$	1.3×10^{6}
$10^{-8.44}/10^{-8.65}$	1.2×10^{6}
$10^{-8.37}/10^{-8.65}$	1.1×10^{6}
$10^{-8.30}/10^{-8.65}$	1.1×10^{6}
$10^{-8.25}/10^{-8.65}$	1.0×10^{6}

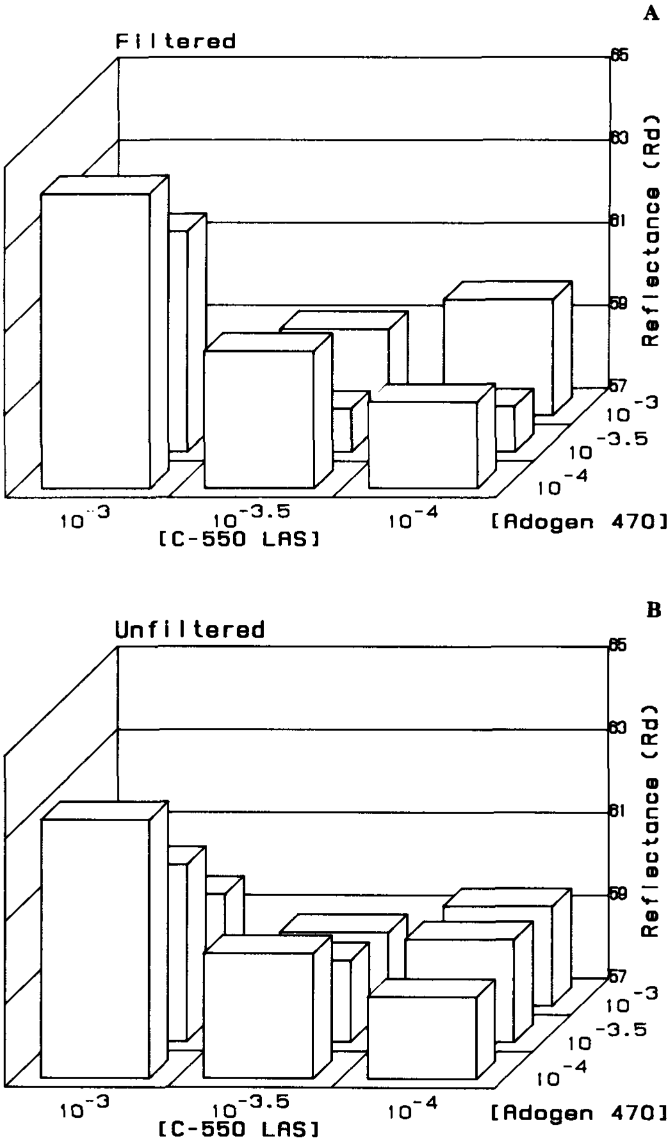

FIG. 2. Reflectance of sebum-soiled permanent press cloths washed in filtered (A) and unfiltered (B) mixtures.

$$(\mathrm{LAS})^- + (\text{Adogen® 470E})^+ \rightleftharpoons (\text{LAS-Adogen® 470E})_s \quad [3]$$

can then be calculated. These values are presented in Table 4.

Ion pair association constant. The ion pair association constant for reaction [1] can be calculated from conductivity data and is shown in Table 5.

Detergency results. Reflectance data for soiled cloths washed in filtered and unfiltered mixtures are shown in Figures 2A and 2B, respectively. Figures 3A and 3B show the reflectance values for the unsoiled cloths washed in the filtered and unfiltered mixtures, respectively.

Elemental sulfur analysis. The results of the elemental sulfur analysis for the cloths washed in equimolar concentrations of C-550 LAS and Adogen® 470E are shown in Table 6.

Static decay measurement results. The static charge decay times from cloths washed in the filtered and unfil-

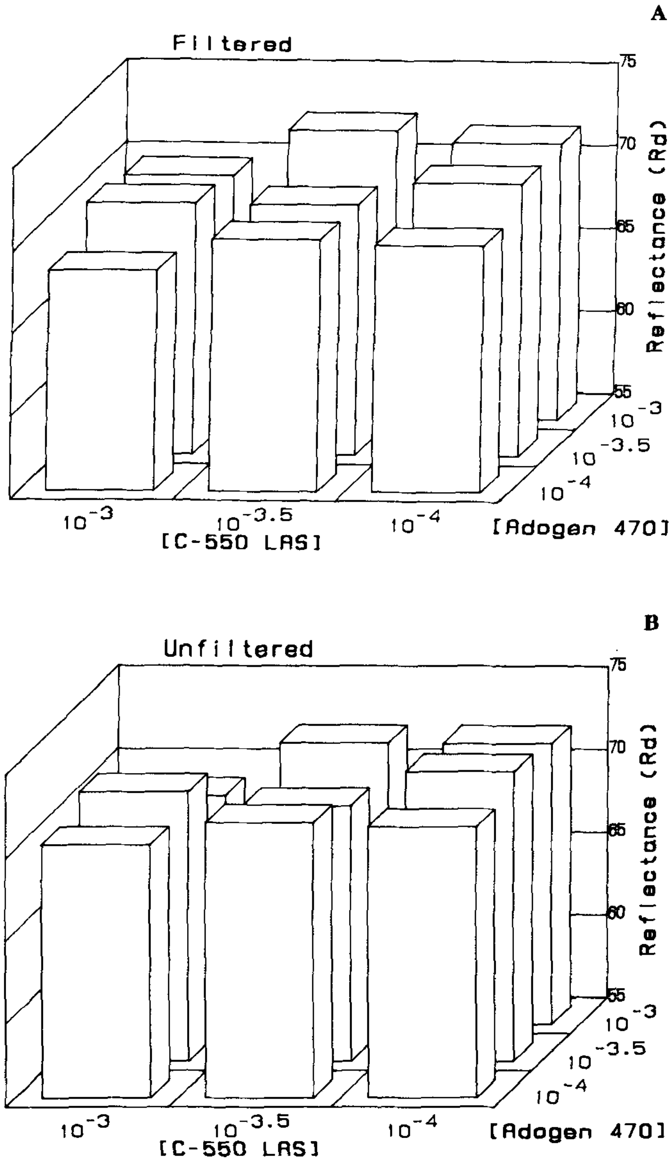

FIG. 3. Reflectance of initially clean permanent press cloths washed in filtered (A) and unfiltered (B) mixtures.

TABLE 6

Sulfur Content of Washed Cloths

Concentration	Wt sulfur/g of cloth
[(C-550 LAS)/(Adogen ® 470E)]	(μg/g)
$10^{-3}/10^{-3}$	5450
$10^{-3.5}/10^{-3.5}$	2020
$10^{-4}/10^{-4}$	450

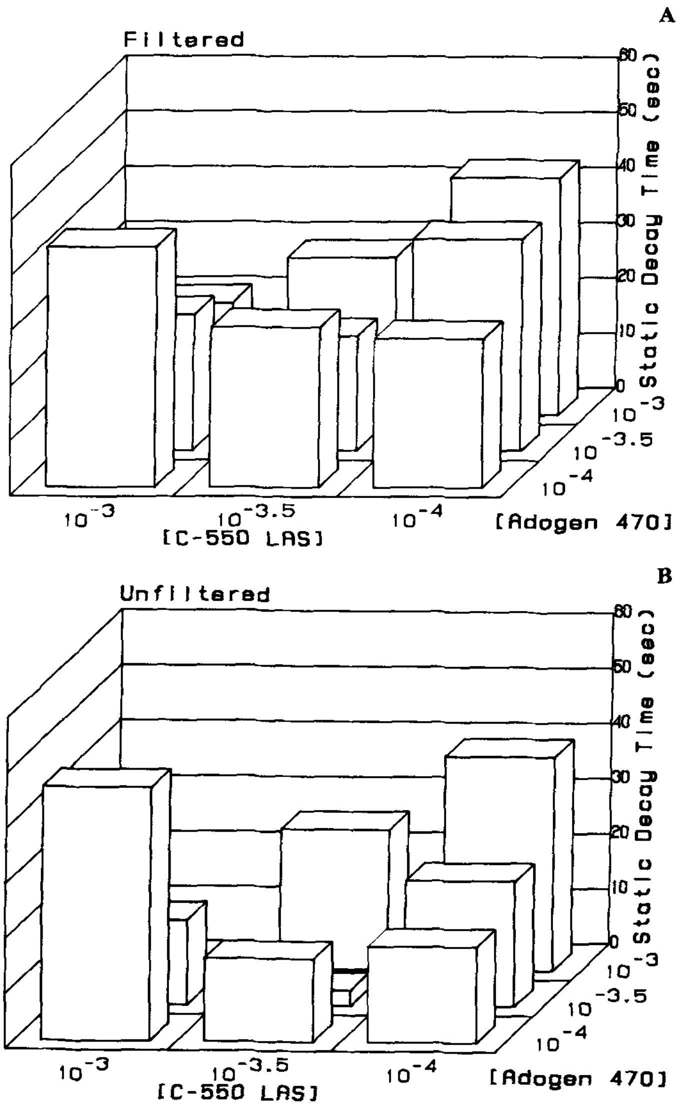

FIG. 4. Static decay times of sebum soiled permanent press cloths washed in filtered (A) and unfiltered (B) mixtures.

tered mixtures are shown in Figures 4A and 4B, respectively. The static charge decay times from the unsoiled cloths washed in the filtered and unfiltered mixtures, respectively, are shown in Figures 5A and 5B.

Softening results. Softening by the various mixtures was measured for both filtered and unfiltered solutions. It is important to realize that the results are for relative softening and that comparisons are appropriate only within a softening panel. Results are summarized in Figures 6-11. The upper portion of each figure shows the softening of the cloth washed in the filtered mixture. The lower portion of each figure shows softening of the cloth washed in the unfiltered mixture. The number above each bar is the average softness ranking.

Figure 6 shows the effect on softening of an increase in initial equimolar concentrations. The effect on softening of changing the concentration of Adogen® 470E with (LAS) = 10^{-4} M, $10^{-3.5}$ and 10^{-3} M is shown in Figures 7, 8, and 9, respectively. The effect of holding the concentration of Adogen® 470E constant and changing the C-550 concentration is shown in Figures 10 and 11 for (Adogen® 470E) = 10^{-4} M and 10^{-3} M, respectively.

In most softening tests of this study, softness ranking between filtered and unfiltered mixtures cannot be made. However, the softness tests shown in Figure 12 were performed so comparisons between filtered and unfiltered mixtures could be made.

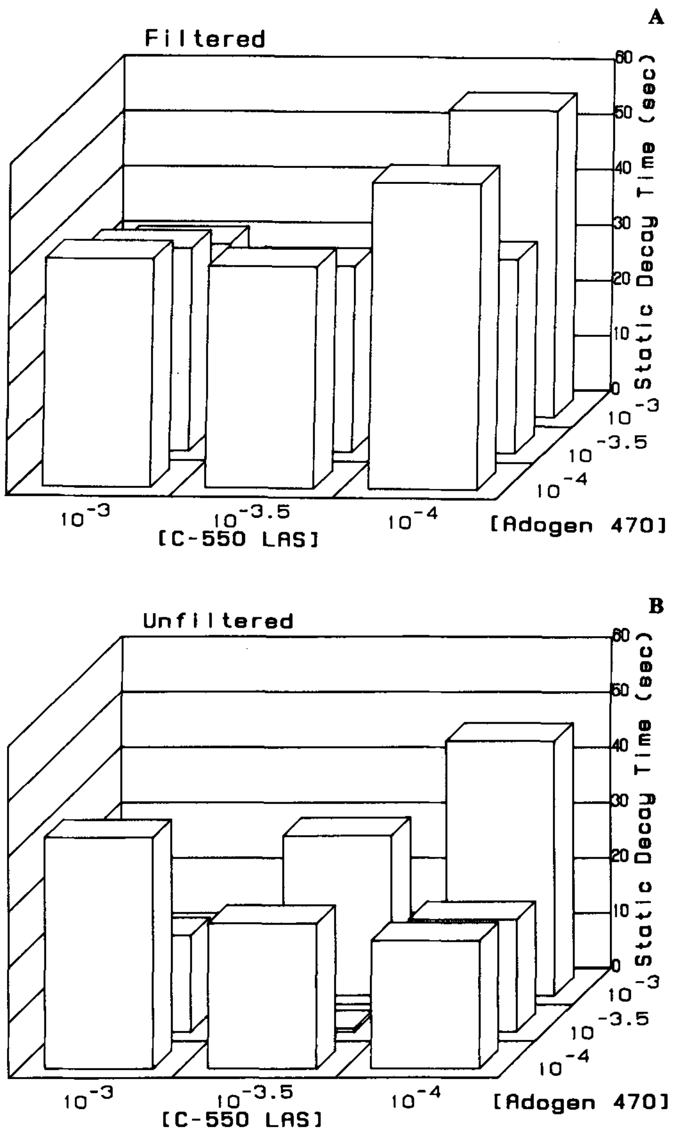

FIG. 5. Static decay times of initially clean permanent press cloths washed in filtered (A) and unfiltered (B) mixtures.

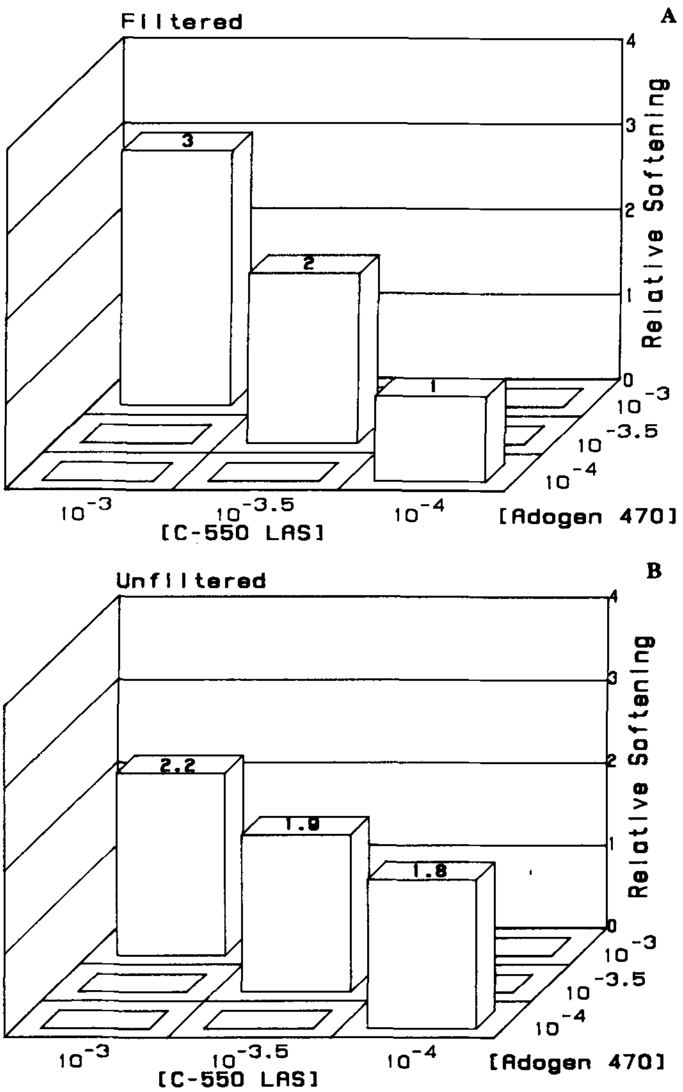

FIG. 6. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking.

DISCUSSION

There are two factors which favor association of surfactant anions and cations. First, association is favored by opposite charges on the ions. Because of attraction of opposite charges, ions take up an equilibrium separation set by the dielectric constant of water and the solvation shield around each ion (2). Second, for surface active ions, association is favored by the tendency of hydrophobes to associate in water (3). Hydrophobic association can be very significant if the surfactant ions have large hydrophobes.

For example, Mukayer and Davis have found that, below 19 C, the interaction of benzyl triphenyl phosphonium chloride and sodium dodecyl sulfate (SDS) is driven more by hydrophobic association than by electrostatic attraction (3). At higher temperatures, however, the dielectric constant of water decreases and electrostatic attraction dominates association. Because both surfactant ions of this study have large hydrophobes, hydrophobic association may be important, especially at low temperatures.

Below the concentration where visible phase separation occurs, the combined effects of hydrophobic association and electrostatic attraction are expressed in the ion pair association constant. The ion pair association constant evaluated by conductance is shown in Table 5 for (C-550 LAS) = $10^{-8.66}$ M - $10^{-8.25}$ M and (Adogen® 470E) = $10^{-8.64}$ M - $10^{-8.65}$ M. Because the ion pair association constant is approximately 10^6 l/mol, one can conclude that the interaction is very strong between C-550 LAS and Adogen® 470E in dilute solution.

The ion pair association constant between benzyl triphenyl phosphonium chloride and SDS is found to be approximately 0.15 l/mol (1). The much smaller ion pair association constant for these two surfactants may be due to the smaller hydrophobe of benzyl triphenyl phosphonium chloride. A larger hydrophobe would be expected to promote association and increase the association constant.

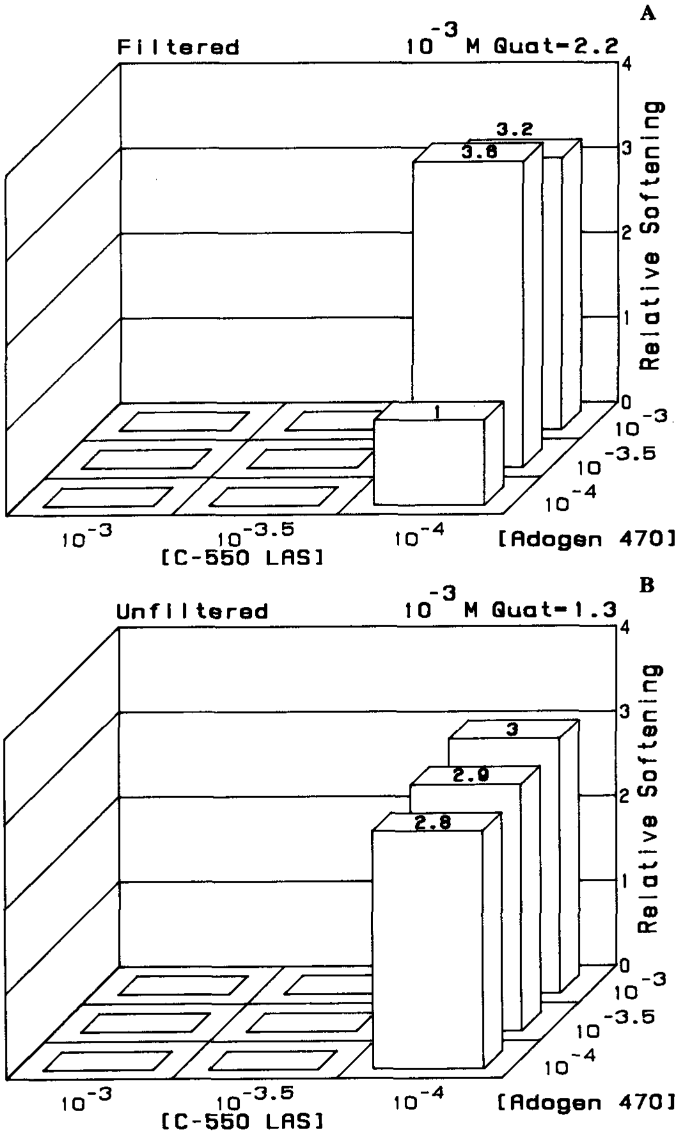

FIG. 7. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking. Ranking of the control is shown in the upper right corner of each figure.

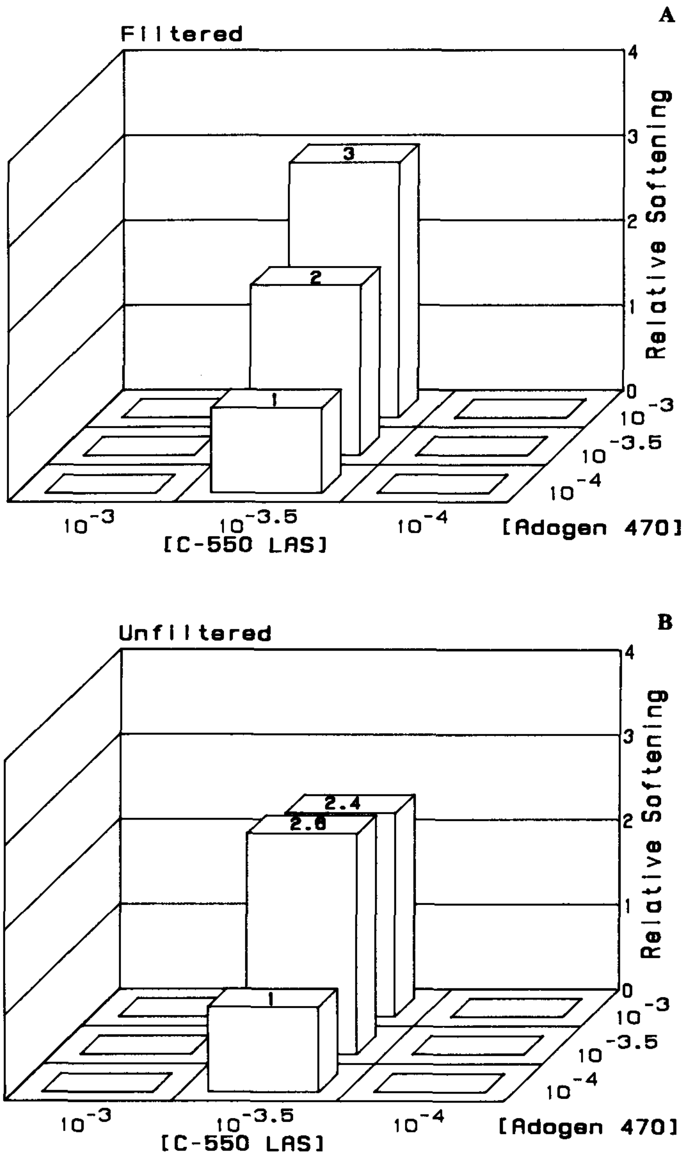

FIG. 8. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking.

Ion pair association constants were measured at 10^{-8} M where solutions are clear. In contrast, performance data were measured at 10^{-4} M through 10^{-3} M, where solutions were turbid. Turbidity can arise by the aggregation of ion pairs as the concentration is increased (4). In the range 10^{-4} M through 10^{-3} M, the extent of turbidity is shown as absorbance (Figure 1).

In Figure 1, absorbance is greatest along the line (C-550 LAS) = (Adogen® 470E). This trend is expected if C-550 LAS and Adogen® 470E form a 1:1 complex. This trend is further illustrated in Table 3 by the order of magnitude increase in weight of precipitate as the concentrations of both C-550 LAS and Adogen® 470E increase from 10^{-4} M - 10^{-3} M. Similar 1:1 complexes have been reported for either benzyl triphenyl phosphonium chloride or trimethyl ammonium bromide with SDS, and alkyl trimethyl ammonium bromide with sodium alkyl sulfates and sulfonates (1, 5-6).

An interesting feature of Figure 1 is the low absorbance values obtained when either C-550 LAS or Adogen® 470E exceeds the concentration of the other. For example, as C-550 LAS is added to a solution with (Adogen® 470E) = 10^{-4} M, the absorbance decreases from the maximum corresponding to a 1:1 complex until the absorbance is less than that of a solution of Adogen® 470E alone. Table 3 shows that the decrease in absorbance is accompanied by a decrease in the weight of precipitate. A decrease in turbidity with increasing surfactant concentration has been reported in other systems and ascribed to solubilization of the complex into micelles (1). In the concentration region we studied, both Adogen® 470E and C-550 LAS should form micelles. A plot of surface tension vs concentration is given in Figure 13 for Adogen® 470E and C-550 LAS. Mixed micelles should form even more readily (7). In our performance study, it is likely that mixed micelles of C-550 LAS and Adogen® 470E were present.

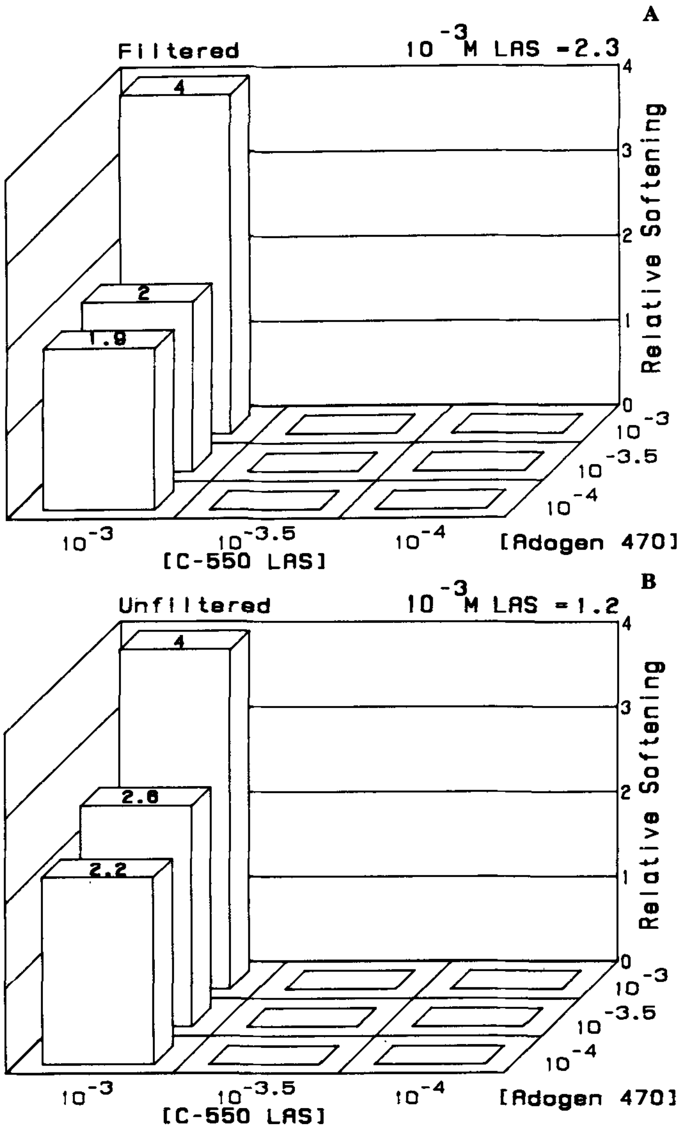

FIG. 9. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking. Ranking of the control is shown in the upper right corner of each figure.

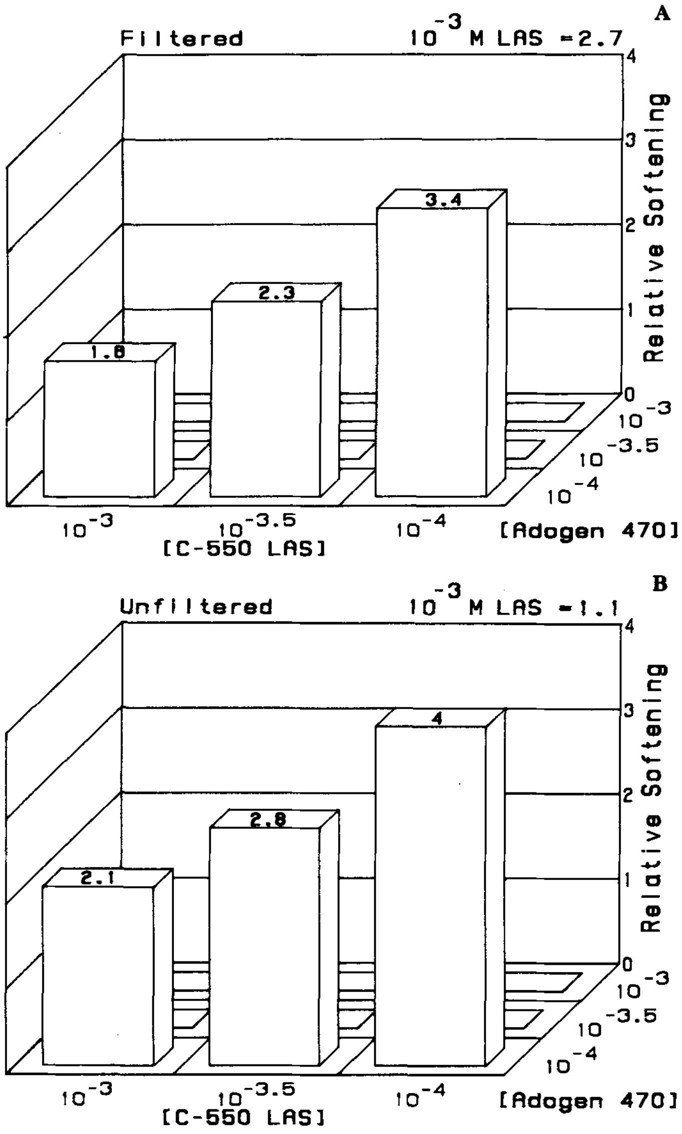

FIG. 10. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking. Ranking of the control is shown in the upper right corner of each figure.

In summary, four species probably were present in the solutions of this study: soluble monomer of both C-550 LAS and Adogen® 470E, an insoluble 1:1 stoichiometric complex of C-550 LAS with Adogen® 470E, and mixed micelles which contained solubilized complex. Though all probably were present to some extent in all of the mixtures of the performance study, different species may have become dominant as the composition of the mixtures varied.

Detergency. Reflectance data are shown in Figures 2 and 3. Reflectance data are best interpreted by examining the reflectance along concentration diagonals, i.e., the equimolar diagonal and gradients parallel to the equimolar diagonal. Equimolar mixtures had the lowest reflectances in the grid. Low reflectance could result because of two reasons. First, if LAS is tied up in the 1:1 complex, it is not available for cleaning. Second, if the complex is adsorbed on cloth, it would act as an additional soil. What little "free" LAS remains in solution is probably inadequate for removal of both the original soil and the adsorbed complex.

Evidence for adsorption of the complex on cloth is provided by measurement of total sulfur of combusted cloth washed in 1:1 stoichiometric mixtures (Table 6). Higher initial concentrations of C-550 LAS and Adogen® 470E lead to high sulfur levels on combusted cloth. Because sulfur from the combusted cloth may be from adsorbed complex, increased sulfur levels are taken as indicating higher levels of adsorbed complex.

Adsorption of the complex on unsoiled cloth is illustrated in Figure 3. For the filtered mixture (Fig. 3A), the lowest reflectance is for (LAS)/(Adogen® 470E) = 10^{-3} M/10^{-4} M. This is expected because the most soil is removed from the soiled cloth at this mixture composition and is therefore available to deposit on the clean cloth (Fig. 2A). For deposition from the unfiltered mixture (Fig. 3B), the

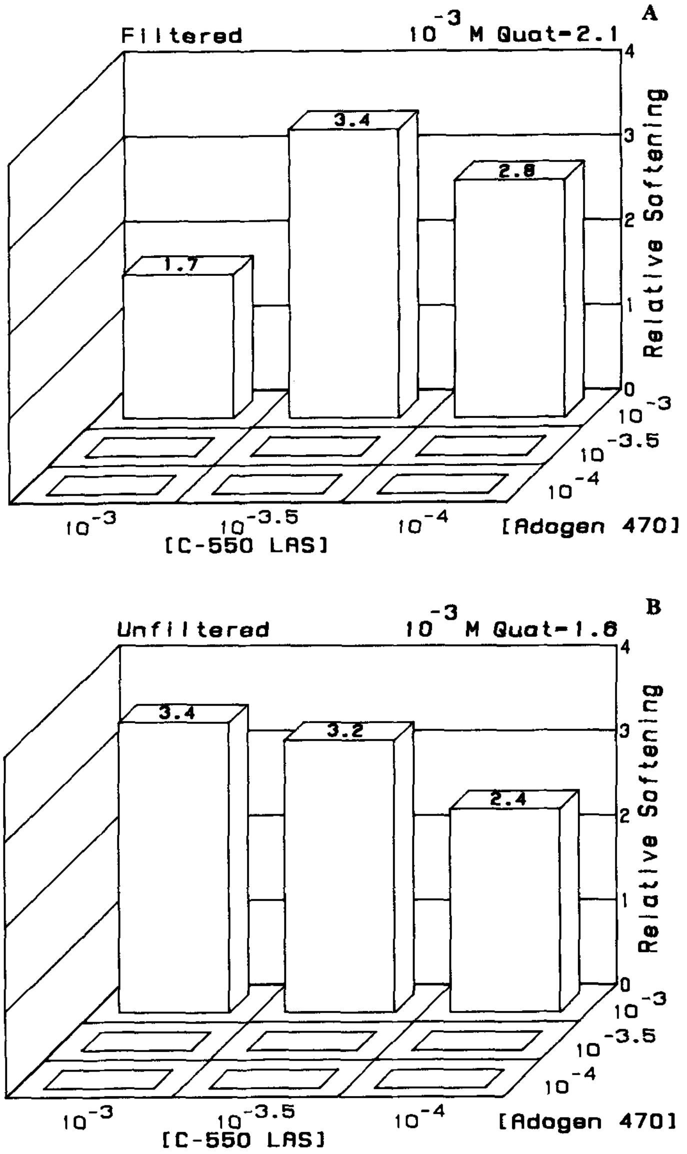

FIG. 11. Relative softness ranking of terry cloth swatches washed in filtered (A) and unfiltered (B) mixtures. Number on each bar is the average softness ranking. Ranking of the control is shown in the upper right corner of each figure.

lowest reflectances are found along the 1:1 diagonal. This is explained if the complex that is formed is adsorbed on clean cloth and lowers its reflectance.

Adsorption of the complex on clean cloth can explain the "improved" redeposition performance previously reported (8). In the cited study, the redeposition of radiolabelled sebum was monitored and showed less redeposition when LAS was added to a nonionic/cationic formulation. If the LAS-cationic complex, which is not radiolabelled, is adsorbed instead of radio-labelled sebum, then redeposition will appear to have decreased.

Reflectance increases for mixtures in which LAS is in excess of Adogen® 470E. This is shown in Figure 2. Presumably, more C-550 LAS is available to improve detergency (and also to solubilize the complex). In Figure 2, the filtered solution outperforms the unfiltered solution slightly. The unfiltered mixture probably contains some

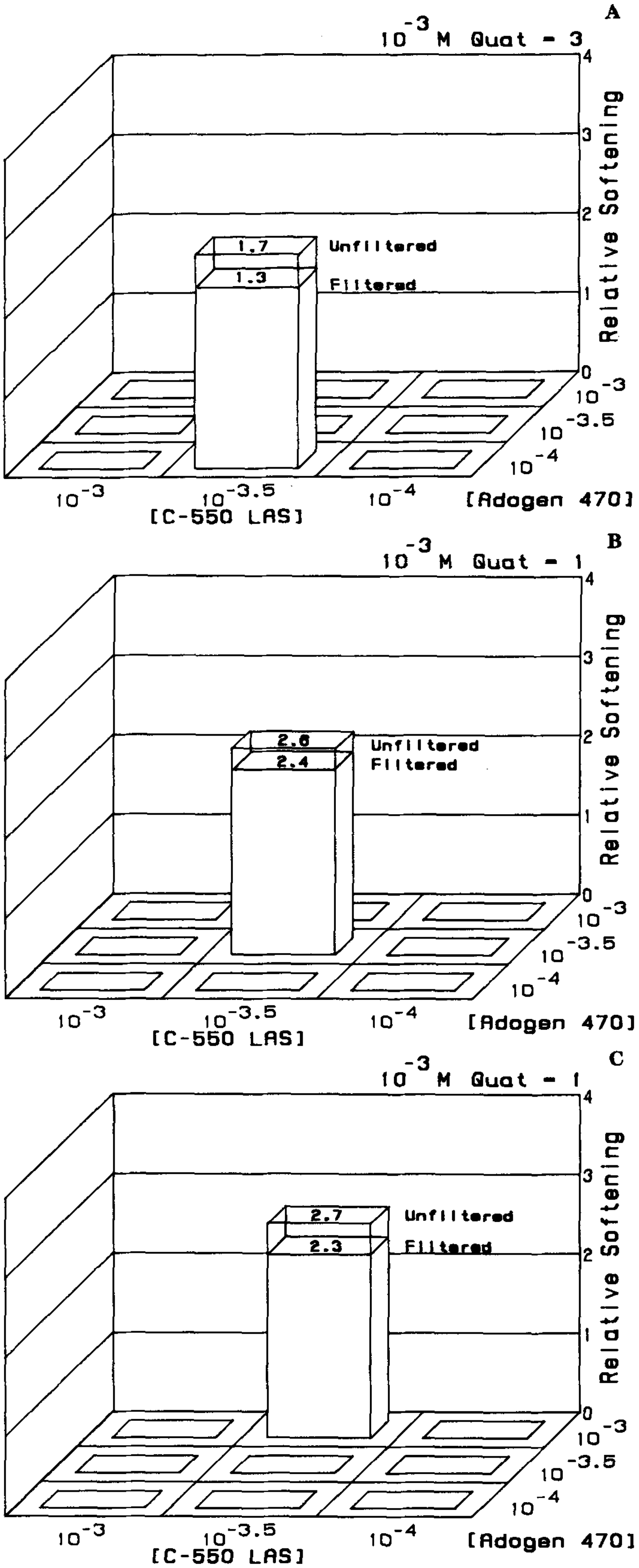

FIG. 12. Comparison of softening of terry cloth swatches washed in [C-550 LAS] = $10^{-3.5}$ and [Adogen® 470E] = 10^{-4} (A), $10^{-3.5}$ (B), and 10^{-3} (C) mixtures. Softness ranking of control is shown in the upper right corner of each figure.

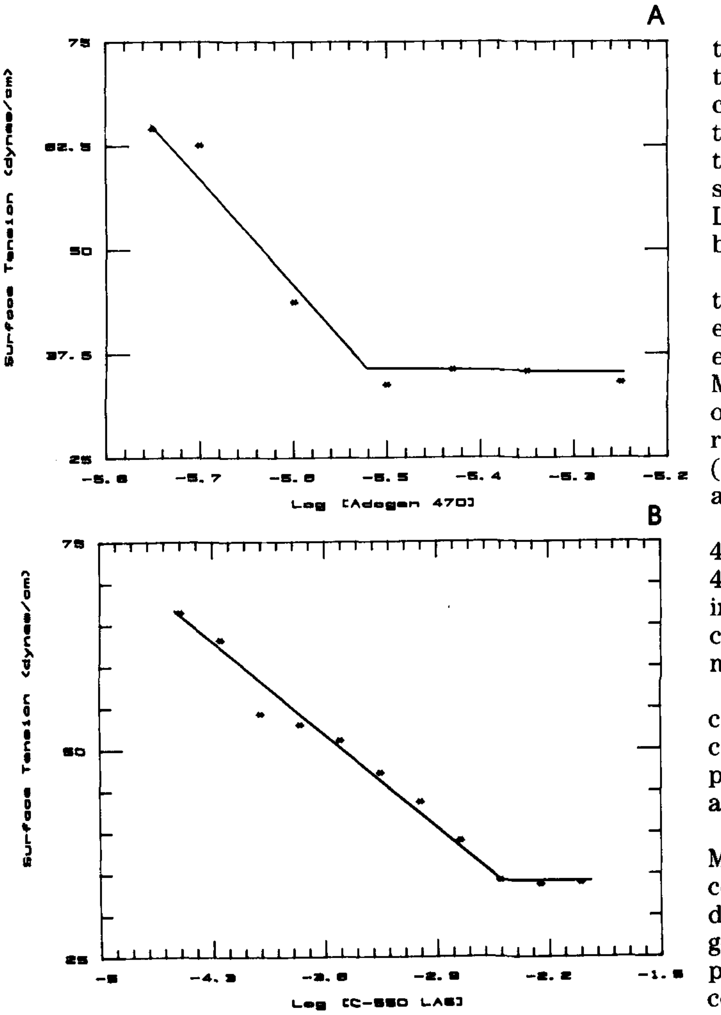

FIG. 13. Surface tension vs log (concentration) for Adogen® 470E (A) and C-550 LAS (B).

insoluble complex, even at high LAS concentrations. If the insoluble complex adsorbs on the soiled cloth, it constitutes an additional soil; this explains the lower reflectance.

Reflectance increases slightly compared to equimolar mixtures if Adogen® 470E exceeds LAS. Increased reflectance may be the result of increased solubilization of soil by the increased number of mixed micelles.

Deposition on the unsoiled cloth increases as the soil removed from the soiled cloth increases (Fig. 3).

Deposition on clean cloth shows only a small increase in reflectance relative to the equimolar diagonal when Adogen® 470E exceeds C-550 LAS (Fig. 3). This is probably the result of a small increase in soil removal from the soiled cloths (Fig. 2).

Static decay measurements. The static decay measurements on the soiled cloths are shown in Figures 4A and 4B for the filtered and unfiltered mixtures, respectively. The static decay measurements for the unsoiled (deposition) cloths are shown in Figures 5A and 5B for the filtered and unfiltered mixtures, respectively. In all figures, the shorter decay time corresponds to better antistat performance. As with reflectance, it is easiest to discuss the decay time differences by examining trends between diagonals.

The lowest values of static decay time are found along the stoichiometric diagonal in Figure 4. Filtering the mixtures increased static decay time. Either the adsorbed complex causes the impressed charge to decay faster, or the complex acts as an insulator and inhibits charging of the cloth. Even the unsoiled cloths showed a decrease in static decay times for the unfiltered mixture (Fig. 5). Lower static decay times for the unsoiled cloth presumably are due to adsorption of the complex.

Static decay times are higher for cloths washed in mixtures rich in C-550 LAS compared to those washed in equimolar mixtures of C-550 LAS and Adogen® 470E. For example, at (C-550 LAS)/(Adogen® 470E) = 10^{-3} M/10^{-4} M the longest static decay times for the soiled cloth occurred (Fig. 4). This is accompanied by the highest reflectance (Fig. 2). The data can be explained if the soil (red mineral oil and adsorbed complex) acted as an antistat. Removing it should increase static decay times.

Greater static decay times are found for Adogen® 470E-rich mixtures than for the equimolar mixtures (Fig. 4). This is consistent with the increase in reflectance seen in Figure 2. The increase in static decay time is greater for cloths washed in the unfiltered mixtures than the filtered mixtures.

For the unsoiled cloths, increasing Adogen® 470E concentration or C-550 LAS concentration generally increases static decay times. This may be because any complex that is formed is solubilized in micelles and cannot adsorb on the cloth to act as an antistat.

Finally, at (C-550 LAS)/(Adogen® 470E) = 10^{-4} M/10^{-3} M, high static decay times are obtained. Given the high concentration of Adogen® 470E, one might expect a decrease in static decay times. Apparently the high Adogen® 470E concentration solubilizes the adsorbed complex, and it is the antistat performance of the adsorbed complex that is being compared in Figures 4 and 5.

Softening evaluation. Average relative softness rankings of cloths washed in various mixtures are presented in Figures 6-14. Ranking of softness is subjective and so only differences in softness of 0.5 units or greater are significant. In general, softness depends on both adsorbed Adogen® 470E and adsorbed complex.

Softening performance along the stoichiometric equivalence diagonal is shown in Figure 6A for the filtered and 6B for the unfiltered mixtures. The concentration of Adogen® 470E in solution is constant in Figures 6A and 6B. This is because the concentration of Adogen® 470E depends on the concentration of LAS and the solubility product shown in Equation 3. Because the ratio C-550 LAS/Adogen® 470E did not change along the diagonal, Adogen® 470E concentration remained constant. Nonetheless, softening increased along the diagonal. Increased softening may be due to increased adsorption of the 1:1 complex. Apparently, filtering only partially removed the complex. As the initial concentrations of C-550 LAS and Adogen® 470E increased, more complex formed and passed through the filter. The complex adsorbed on the cloth during washing and acted as a softening agent.

As shown in Figure 7, for (C-550 LAS) = 10^{-4} M as Adogen® 470E concentration increased, softening increased. The increase is much smaller for the unfiltered mixture (Fig. 7B). The trends can be explained if softening is due to adsorption of both Adogen® 470E and the 1:1 complex. The relatively small change in softening for the unfiltered solution may be due to the relatively small change in adsorbed complex. At high Adogen® 470E concentrations, especially for filtered solutions, softening from Adogen® 470E adsorption must dominate. For near 1:1 mixtures, especially for unfiltered solutions, the adsorbed complex must dominate softening.

When (C-550 LAS) = $10^{-3.5}$ M and Adogen® 470E concentration is increased, similar trends are seen. In Figure 8A, increasing the concentration of Adogen® 470E increased softening. In Figure 8B, a large increase in softening is observed when the stoichiometric equivalence of C-550 LAS and Adogen® 470E was reached.

When (C-550 LAS) = 10^{-3} M and Adogen® 470E concentration increased, similar trends to lower C-550 LAS constant concentrations were seen. These are shown in Figure 9A for the filtered mixtures and Figure 9B for the unfiltered mixtures.

In Figure 10, Adogen® 470E concentration is kept constant at 10^{-4} M while C-550 LAS concentration increases. Softening decreases for both the filtered and unfiltered mixtures. The decrease could reflect a decrease in adsorption of the 1:1 complex, because Adogen® 470E was held constant. Decrease in the adsorbed complex is further supported by increased reflectance seen in Figure 2 and the increase in static decay time seen in Figure 4.

In Figure 11, Adogen® 470E concentration is kept constant at 10^{-3} M while C-550 LAS concentration increases. Softening of the filtered mixtures generally decreases as C-550 LAS concentration increases (Fig. 11A). For filtered mixtures, softening may be due primarily to adsorbed Adogen® 470E. The less Adogen® 470E removed from the cloth by C-550 LAS, the better the softening. In Figure 11B, as the equimolar ratio was approached, softening increased.

In order to show the effect of filtering, a panel was run in which a filtered, unfiltered and soft control were compared. Figure 12 shows the effect of filtering the solutions on softening (LAS) = $10^{-3.5}$ M. The differnece between filtered and unfiltered mixtures is not significant. Apparently, enough of the complex passed through the filter to provide softening. In all but the case of (C-550 LAS)/(Adogen® 470E) = $10^{-3.5}$ M/10^{-4} M (Fig. 12A), softening was better than the soft control [(Adogen® 470E) = 10^{-3} M).

In conclusion, this study has shown that the 1:1 complex of C-550 LAS and Adogen® 470E adsorbs on permanent press cloth during washing. The adsorbed complex decreases static decay time from the cloth and increases its softness. Countering these favorable trends is a decrease in detergency.

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