Soil-Surfactant Interaction Study

The physical interaction between a nonionic surfactant and a solid soil was examined by measuring the change in weight of lard soil vs. time submersed in various nonionic solutions. Test procedures are explained in the experimental section of this report.

As shown in Figure 10, lard soil increases in weight when submersed in nonionic surfactant solutions. The rate of soil weight gain is greatest for 610-50 nonionic surfactants. As surfactant carbon chain length is increased, the rate of soil weight gain decreases.

The fact that soil weight does not decrease indicates that soil solubilization is not the primary process for removing the soil. Because soil weight increases, the key soil removal process may involve penetration or dissolution of the surfactant into the soil. Soil penetration would explain why hard-surface cleaning performance is strongly related to carbon chain length. Surfactant penetration would cause soil to swell and soften, allowing it to be more easily removed. Surfactants with smaller hydrophobes would logically penetrate or dissolve into soil at a faster rate, resulting in an improvement in cleaning performance.

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Factors Affecting Oil/Water Interfacial Tension in Detergent Systems: Nonionic Surfactants and Nonpolar Oils

K.W. DILLAN, Union Carbide Corporation, Tarrytown, NY 10591

ABSTRACT

Because earlier model detergency studies have shown that oil/water interfacial tension is critically important in oil removal processes, factors affecting the interfacial tension between detergent-range nonionic surfactant solutions and paraffin oil have been examined. For a given hydrophobe, equilibrium interfacial tension values increase with the length of the ethylene oxide chain in the hydrophile, because of the attendant decrease in overall surface activity. For a given degree of ethoxylation, commercial nonylphenol ethoxylates reduce interfacial tension more effectively than their secondary alcohol-based counterparts, and these in turn are more effective than commercial primary alcohol ethoxylates. Furthermore, monodisperse primary alcohol ethoxylates reduce interfacial tension more effectively than broad-range ethoxylates with similar cloud points. This observed order of effectiveness is attributed in part to variations in the extent of fractionation that occur as nonionic surfactants divide between the oil and water phases. Equilibrium interfacial tension values produced by commercial nonionic surfactants are significantly more dependent on concentration and temperature than those obtained with monodisperse ethoxylates. However, the time-course for lowering interfacial tension exhibited by monodisperse ethoxylates varies with concentration and temperature to a greater extent than that displayed by commercial products. These findings are accounted for by the combined effects of the changes in relative surface activity and partitioning that occur as the concentration and temperature are varied. An imidazoline-based quaternary fabric softener markedly increases the interfacial tension immediately following phase contact, whereas equilibrium values are only slightly higher in the presence of the softener. Apparently, preferential adsorption of the softener occurs at the interface, followed by adsorption of the nonionic surfactant at the new softener/water interface. Builders and electrolytes have no significant effect on the interfacial tension between aqueous nonionic surfactant solutions and paraffin oil. Terg-O-Tometer results demonstrate the correlation between oil/water interfacial tension and detergency.

INTRODUCTION

Previous investigations (1,2) have shown that nonpolar oils are removed from polyester substrates submerged in nonionic surfactant solutions by the roll-up process originally described by Adam (3). Using the Young equation (4), an expression relating the extent of roll-up, i.e., the equilibrium contact angle in the aqueous phase ($\theta_{w/s}$), to the solid/water ($\gamma_{s/w}$), solid/oil ($\gamma_{s/o}$), and oil/water ($\gamma_{o/w}$) equilibrium interfacial tensions may be cast in the form:

$$\mathrm{COS}\ \theta_{w/s} = \frac{\gamma_{s/o} - \gamma_{s/w}}{\gamma_{o/w}}. \qquad [1]$$

Model studies have demonstrated the utility of this relationship in explaining relative performance differences among nonionic surfactants (1,5). These investigations also revealed that although the resultant force acting at the 3 phase point of contact ultimately determines the value of $\theta_{w/s}$ for a given substrate and oil, variations in $\theta_{w/s}$ are usually caused by changes in $\gamma_{o/w}$. Consequently, an examination of factors affecting $\gamma_{o/w}$ is instrumental in developing an understanding of the performance properties of nonionic surfactants.

In this report, factors affecting interfacial tension in systems of interest to the detergent industry are examined. The effects of surfactant concentration and structure on the time-course of interfacial tension lowering are delineated. Because warm- and cool-water launderings are becoming more prevalent, temperature effects are also considered. Also, in view of the growing market for detergents with built-in fabric-softening capabilities, the effects of softeners on interfacial tension are cursorily treated. Finally, a brief discussion of the effects of builders and electrolytes on interfacial tension provides a basis for future research. In selected instances, the practical implications of the data and the correlation with laboratory detergency evaluations are addressed.

EXPERIMENTAL

Interfacial tensions were measured using the spinning drop technique (6) under conditions where the infinite length assumption was valid. In the time-course of interfacial tension lowering studies, time zero corresponds to the time spinning of the drop begins; generally, a 6-8 μL drop of oil was injected into the tube containing an aqueous surfactant solution using an "agla" micrometer syringe (Burroughs Wellcome & Co. Ltd., London, United Kingdom) 2-3 min before time zero. The surfactant was initially present in the water phase only.

Detergency experiments were conducted in a Terg-O-Tometer (7), which is a thermostatically controlled, constant-temperature bath in which 4 separate 2 L beakers are mounted, each fitted with a motor-driven agitator of scaled proportions. Each beaker contained 4 (4" x 3") nylon swatches impregnated primarily with mineral oil and carbon black (8), 4 (4" x 3") clean 65% polyester/35% cotton bulking cloths, and 1 L of a 0.05% surfactant solution. Tests were run in duplicate using a 10 min wash and a 2 min rinse at 25 C. Performance was evaluated via the reflectance technique (9) using a Hunter D-25 Color/Difference meter (10-12). Percentage of detergency was calculated using the equation (13):

$$\text{Percent Detergency} = (R_W - R_S)/(R_O - R_S), \qquad [2]$$

where R_W is the reflectance of the laundered swatches; R_S is the reflectance of the soiled swatches; and R_O is the reflectance of the swatches before soiling. At the 95% confidence level, the least significant difference is 2 detergency units.

Sodium chloride, calcium chloride (dihydrate) and magnesium chloride (hexahydrate) of ACS reagent grade were purchased from Fisher Scientific Company, Fairlawn, NJ. Laboratory grade triethanolamine and paraffin oil were also from Fisher Scientific Company. Food-grade white mineral oil was supplied by Atlantic Richfield and technical-grade sodium tripolyphosphate was purchased from FMC Corporation. An imidazolinium quaternary fabric softener (Methyl-1-oleyl amido ethyl-2-oleyl imidazolinium-methy sulfate) was supplied in isopropanol by Sherex Chemical Company. Table I describes the nonionic surfactants.

Water was boiled under basic conditions for 1 hr, distilled from basic potassium permanganate and again distilled at neutral pH.

The ethoxylate adduct distribution of TERGITOL NP-9 was determined using normal-phase liquid chromatography; gas chromatography of the silylated derivative was used for TERGITOL 25-L-9. Because the numerous isomers in TERGITOL 15-S-9 make the ethoxylate adduct distribution difficult to determine experimentally, the distribution was approximated using the Poisson distribution. The actual distribution is expected to be only slightly broader (28).

RESULTS AND DISCUSSION

Effects of Surfactant Composition

Figures 1-3 depict the time-course of the lowering of interfacial tension for 0.05% solutions of primary alcohol ethoxylates, secondary alcohol ethoxylates and nonylphenol ethoxylates, respectively, against white mineral oil at 25 ± 1 C. Consistent with results reported by others working with aliphatic hydrocarbons (14-17), equilibrium interfacial tension values increase as the average ethylene oxide chain length on a given hydrophobe increases. This

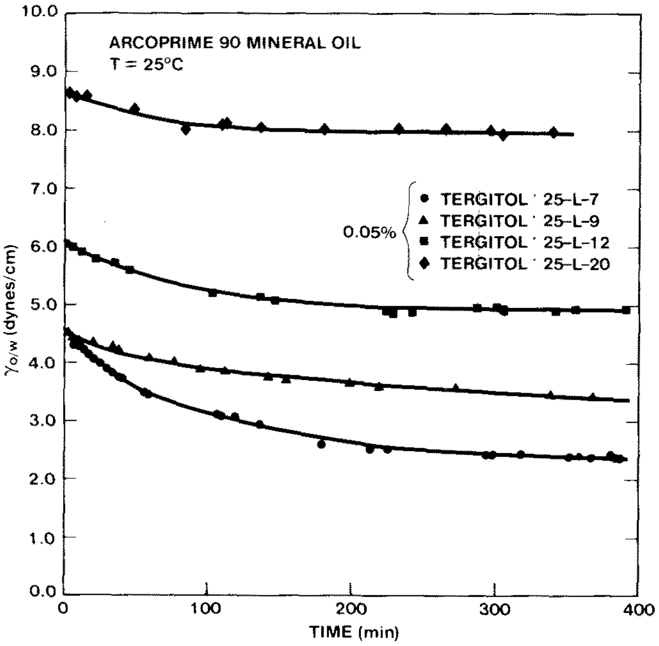

FIG. 1. Time-course of lowering of interfacial tension for commercial primary alcohol ethoxylates.

TABLE I

Nonionic Surfactants

Commercial trade name	Hydrophobe	Average moles ethylene oxide	Cloud point °C (1.0% aqueous
TERGITOL 25-L-3[a]		3	–
TERGITOL 25-L-7	C12-15 Primary alcohol	7	50
TERGITOL 25-L-9		9	60
TERGITOL 25-L-12		12	90
TERGITOL 25-L-20		20	>100
TERGITOL 15-S-7	C11-15 Secondary alcohol	7	37
TERGITOL 15-S-9		9	60
TERGITOL 15-S-12		12	90
TERGITOL NP-7		7	20
TERGITOL NP-8	Branched nonylphenol	8	45
TERGITOL NP-9		9	54
TERGITOL NP-10		10	60
TERGITOL NP-13		13	83
Nikkol BR-6SY[b]		6	52

[a] TERGITOL is a registered trademark of Union Carbide Corporation, USA.

[b] A monodisperse ethoxylate from Nikko Chemical Company.

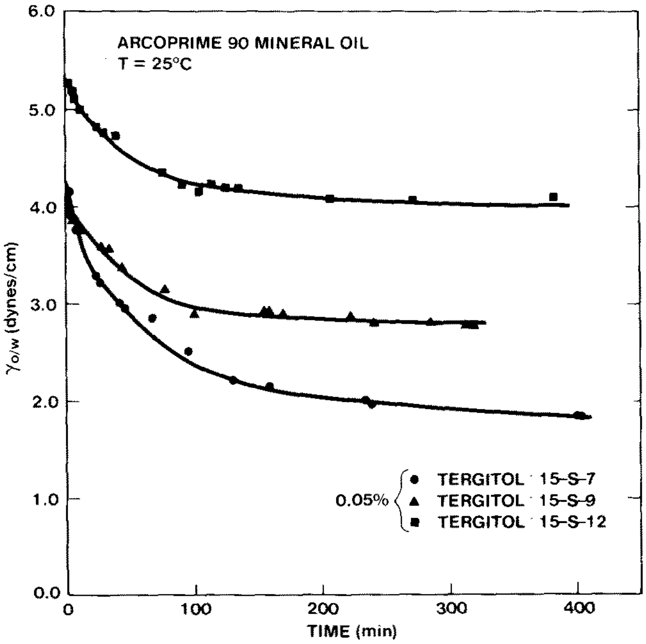

FIG. 2. Time-course of lowering of interfacial tension for commercial secondary alcohol ethoxylates.

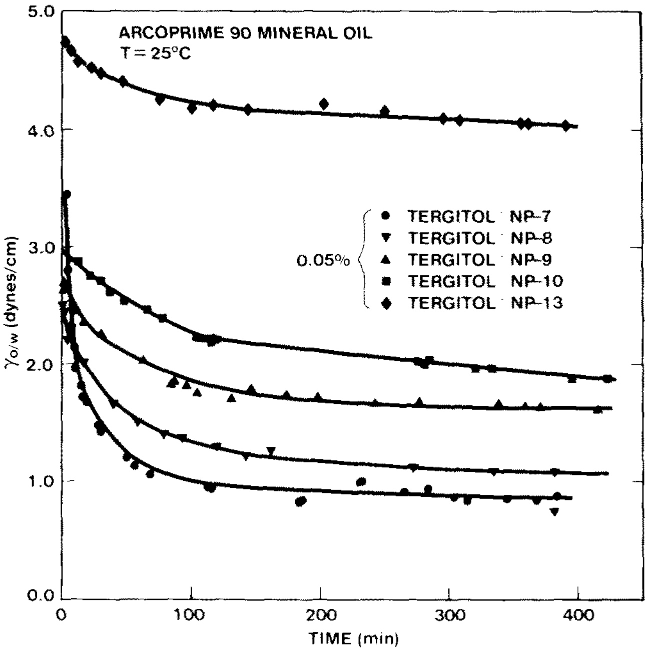

FIG. 3. Time-course of lowering of interfacial tension for commercial nonylphenol ethoxylates.

trend has also been observed at the air/water interface (1,5,18-21) and is attributable to the decrease in surface activity accompanying an increase in the degree of ethoxylation. Changes in the molecular orientation of the surfactant at the oil/water interface as the ethylene oxide content varies may also affect interfacial tension (14). In contrast with trends reported for the air/water interface (5), for a given degree of ethoxylation, solutions containing nonylphenol ethoxylates reduce equilibrium interfacial tension more effectively than solutions of secondary alcohol ethoxylates and these, in turn, produce lower equilibrium interfacial tensions than solutions of their primary alcohol-based counterparts. Furthermore, while equilibrium surface tension values are rapidly attained above the CMC (5,22), time effects are evident at the oil/water interface, especially with the least water-soluble members of each surfactant family. These effects are not experimental artifacts, as shown by the fact that they can be eliminated by pre-equilibrating the oil and water phases before measuring the interfacial tension.

The differences in the time-course of interfacial tension lowering at the air/water and oil/water interfaces cannot be accounted for strictly in terms of adsorption phenomena. Instead, the effects of a partitioning process at the oil/water interface, where the various components of the nonionic surfactant are fractionated between the oil and aqueous phases, must be considered. That nonionic surfactants divide between aliphatic oils and water is well established (18,23-25). Crook et al. (18,24) showed that when commercial octylphenol ethoxylates dissolved in water are equilibrated with iso-octane, the surfactant is fractionated, with the short-chain adducts being concentrated in the oil and the long-chain ethoxylates being concentrated in the water. Because the nonionic surfactant/paraffin oil systems in the present investigation resemble the systems examined by Crook and coworkers, assuming that a fractionation process is similarly operative is reasonable. Accordingly, immediately following phase contact, various ethoxylate adducts diffuse from the bulk solution to the oil/water interface and compete for adsorption sites. The highly surface-active short-chain ethoxylates have a higher affinity for oil than for water (24), and therefore tend to migrate into the oil phase. Consequently, for the first few minutes following phase contact, the interface contains predominately long-chain ethoxylates, and these highly water-soluble species are relatively ineffective in reducing interfacial tension. Gradually, an equilibrium distribution of species between the oil and water phases is approached and the net transfer of low ethoxylates into the oil ceases to occur. In addition, long-chain ethoxylates at the interface are slowly displaced by more highly surface-active components that diffuse to the interface from the bulk solution. As these processes proceed, interfacial tension continuously decreases until complete equilibrium is achieved. That surfactants having the lowest cloud points exhibit the most pronounced changes in $\gamma_{o/w}$ with time is consistent with this explanation, for these materials contain the largest weight fraction of oil-soluble species and therefore may be expected to partition most appreciably into the oil phase.

In addition to being responsible for the time effects at the oil/water interface, fractionation of nonionic surfactants between the oil and water phases is also at least partially responsible for the fact that for a given degree of ethoxylation, nonylphenol ethoxylates produce the lowest equilibrium oil/water interfacial tensions (5). This contention is again based on the work of Crook et al. (18,24), where lower oil/water interfacial tension values were shown to be produced by single-species octylphenol ethoxylates rather than with normal-distribution compounds. Crook and coworkers (18) argued that fractionation of the normal-distribution material is responsible for this occurrence, i.e., because the short-chain adducts in commercial ethoxylates are so oil soluble, little driving force is available for them to orient at the oil/water interface. Consequently, the average molecular weight of the surfactant in the aqueous phase increases, and only relatively long-chain adducts are appreciably adsorbed at the interface. The fact that a normal-distribution 5 mol ethoxylate was found to correspond to a single-species 7 mol ethoxylate in interfacial tension lowering, was cited by Crook et al. (18) as supporting evidence for this explanation. The implication of this work for the present study is that, for a given degree of ethoxylation, nonionic surfactants having narrow ethylene oxide distributions, i.e., those having relatively few low ethoxylates,

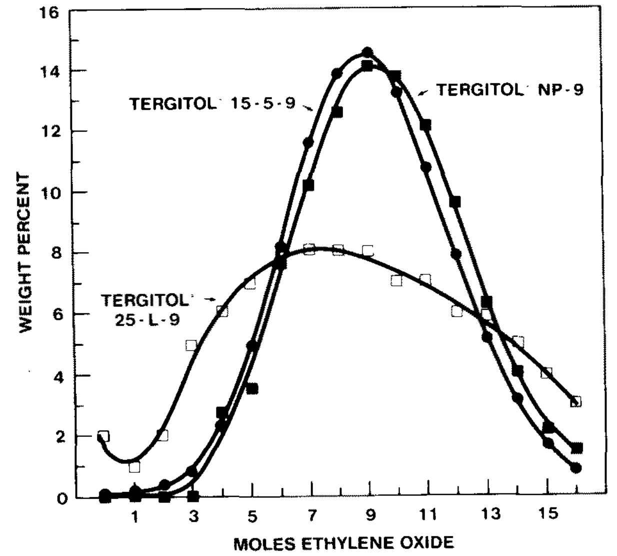

FIG. 4. Ethoxylate adduct distributions for commercial nonylphenol, secondary alcohol and primary alcohol 9 mol ethoxylates.

should reduce $\gamma_{o/w}$ most effectively. Indeed, Figure 4 reveals that commercial nonylphenol and secondary alcohol ethoxylates contain lower percentages of oil-soluble adducts than primary alcohol ethoxylates. The actual distribution of TERGITOL 15-S-9 is expected to be slightly broader than the Poisson distribution shown here as an approximation (28). This accounts for the superior performance of nonylphenol ethoxylates, which have nearly true Poisson distributions (29-30). Differences in hydrophobe structure also affect relative surfactant performance, but the expected order of effectiveness, based on relative linearity, is exactly the opposite of what is observed. Thus, for these commercial families, the differences in ethylene oxide distribution have a greater effect on oil/water interfacial tension lowering than the differences in hydrophobe structure. Variations in ethylene oxide distribution also account for the observed order of effectiveness in surface tension reduction (5), for surfactants having the highest concentration of highly surface-active low ethoxylates produce lower surface tensions than those having relatively few low ethoxylates (18).

The effects of surfactant partitioning on $\gamma_{o/w}$ may be further examined in the absence of hydrophobe variations by adding various amounts of a low ethoxylate to a high ethoxylate. Figure 5 reveals that the addition of a small amount of TERGITOL 25-L-3 to TERGITOL 25-L-20 produces a moderate reduction in the equilibrium value of $\gamma_{o/w}$, but continued addition has little or no effect. Although the 60/40 blend of TERGITOL 25-L-20 and TERGITOL 25-L-3 has the same calculated HLB value as TERGITOL 25-L-9, a comparison of Figures 1 and 5 reveals that the latter surfactant produces a significantly lower interfacial tension against mineral oil than the former. These data are again readily explained in terms of Crook's arguments (18). The short-chain adducts in TERGITOL 25-L-3 are so oil soluble that little driving force is available for them to adsorb at the interface. Consequently, the majority of the low ethoxylates migrate into the oil, are solubilized in the interior of TERGITOL 25-L-20 micelles or are simply dispersed as insoluble globules in solution. The moderate reduction in $\gamma_{o/w}$ obtained by adding TERGITOL 25-L-3 suggests that some of the material does adsorb at the oil/water interface, however.

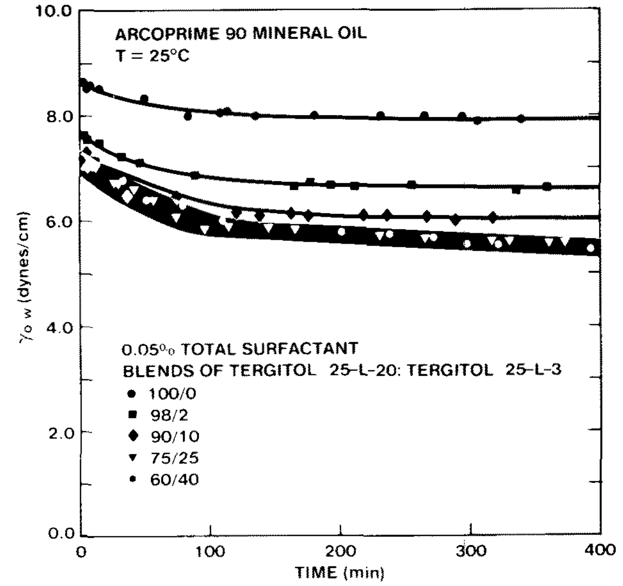

FIG. 5. Time-course of lowering of interfacial tension for blends of high and low primary alcohol ethoxylates.

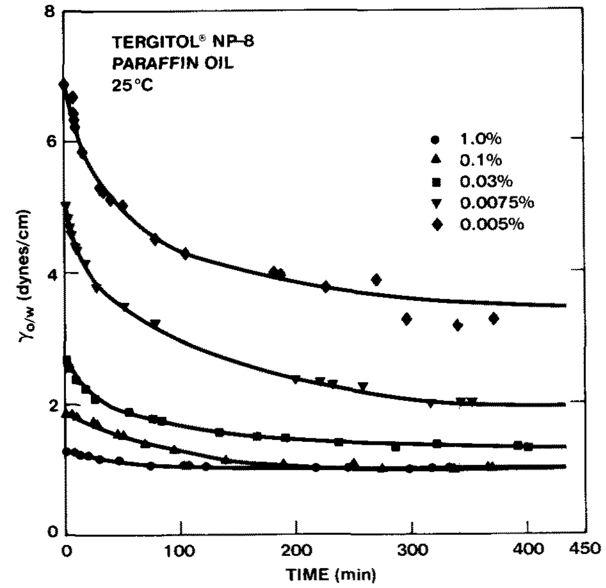

FIG. 6. Time-course of lowering of interfacial tension at various concentrations for a commercial nonylphenol ethoxylate.

Effects of Surfactant Concentration and Temperature

In earlier studies of the roll-up process (5), a dependence of oil removal time on surfactant concentration was noted above the CMC for several nonionic surfactants. This phenomenon was shown not to result from changes in $\gamma_{s/w}$ and/or $\gamma_{w/a}$, and was attributed to the decrease in $\gamma_{o/w}$ that accompanied an increase in surfactant concentration. Unfortunately, experimental limitations associated with the Wilhelmy plate technique (26-27) thwarted efforts to determine the relative importance of kinetic and thermodynamic factors. Thus, the time-course of interfacial tension lowering has now been studied as a function of concentration. Representative data shown in Figure 6 for TERGITOL NP-8 reveal that both kinetic and thermodynamic factors are important, i.e., lower equilibrium interfacial tension values are approached at a faster rate as the concentration is increased. Because similar behavior is not observed at the air/water and solid/water interfaces (5), where adsorption occurs rapidly and is constant in amount above the CMC, the previously described partitioning phenomenon is probably responsible. Because the rate of transfer of surfactant molecules from the bulk solution to the interface and from the interface into the oil varies with concentration, the time required to achieve appreciable partitioning and to have highly surface-active species adsorbed at the interface decreases with concentration. Furthermore, because the total number of highly surface-active adducts available to adsorb at the interface increases with concentration, the effectiveness of the surfactant increases with concentration. Thus, lower equilibrium interfacial tensions are approached more rapidly as the total surfactant concentration is increased.

Figure 7 reveals the effects of concentration on the time-course of the lowering of interfacial tension for hexaethylene glycol dodecyl ether. Although the rate of lowering of interfacial tension is more dependent on concentration than that observed for commercial ethoxylates, the value of the equilibrium interfacial tension shows less of a concentration dependence. Because this material has an appreciable solubility in oil, the dependence of the rate of equilibration on concentration is caused by the extensive partitioning that takes place. The rate of migration of surfactant to the interface and into the oil is controlled by diffusion and therefore varies with concentration. That the equilibrium interfacial tension varies little with concentration is to be expected for a pure ethoxylate, for no fractionation occurs as a result of partitioning. That is, the nature of the adsorbed species at the interface is independent of concentration.

For a given nonionic surfactant, optimum performance characteristics are generally attained at a temperature slightly below the cloud point. In theory, the balance between surface activity and water solubility is optimal at this temperature. Thus, equilibrium $\gamma_{o/w}$ values are expected to decrease with increasing temperature, at least up to the cloud point. Representative data in Figure 8 for TERGITOL 15-S-9 show that, indeed, equilibrium interfacial tension values decrease with increasing temperature. However, the change in $\gamma_{o/w}$ with time is significantly greater at temperatures near the cloud point than at lower temperatures, suggesting that partitioning of the surfactant between the 2 phases is more extensive near the cloud point. This result is consistent with previous studies (24) in which partition coefficients for octylphenol ethoxylates were found to decrease with increasing temperature and may also explain why nonionic surfactants generally do not perform well in practice when used at temperatures above the cloud point. That is, the interfacial tension during the first few minutes following phase contact is often more important than the equilibrium value.

Figure 9 shows the effects of temperature on the time-course of the lowering of interfacial tension exhibited by hexaethylene glycol dodecyl ether. The dependence of equilibrium interfacial tension on temperature is less significant than that observed with commercial ethoxylates, presumably, because the adsorbed species at the interface is independent of temperature. The only factor that acts to decrease the equilibrium interfacial tension with temperature is the increased surface activity of the ethoxylate. On the other hand, the change in $\gamma_{o/w}$ with time varies greatly as a function of temperature. This may be attributed to the change in the extent of partitioning with temperature, because the affinity of the nonionic surfactant for the oil increases markedly near the cloud point.

Effects of Fabric Softeners and Builders

Many of today's liquid laundry detergents dispense cationic softeners directly into the wash cycle. Although these products save time and are convenient for the consumer, formulating softener-containing products that give adequate detergency performance is challenging. To develop some understanding of how a cationic softener affects detergency, a brief investigation into their effects on $\gamma_{o/w}$ has been conducted. The results illustrated in Figure 10 for TERGITOL 25-L-7 are typical of those observed when an imidazolinium quaternary softener (Methyl-1-oleyl amido ethyl-2-oleyl imidazolinium-methyl sulfate) is added to a commercial nonionic surfactant solution. The softener has a modest effect on equilibrium interfacial tension values, but the time-course of lowering of interfacial tension is greatly altered. The higher the softener concentration, the more marked the effects. These data suggest that the cationic softener competes quite effectively with the nonionic surfactant for initial adsorption sites at the interface, but if given sufficient time, the nonionic surfactant is able to either displace much of the softener at the interface or, more likely, it forms a monolayer at the new high-energy interface created by the softener. Considering the time frame of a normal wash cycle, the implication of these findings is clear: softeners may adversely affect the ability

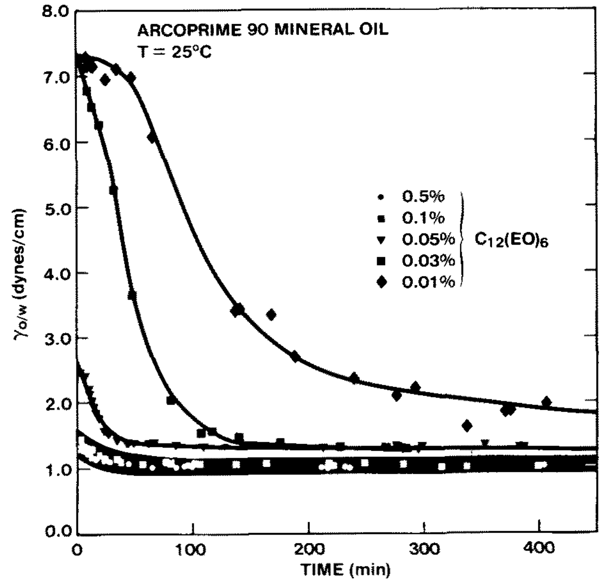

FIG. 7. Time-course of lowering of interfacial tension at various concentrations for hexaethylene glycol dodecyl ether.

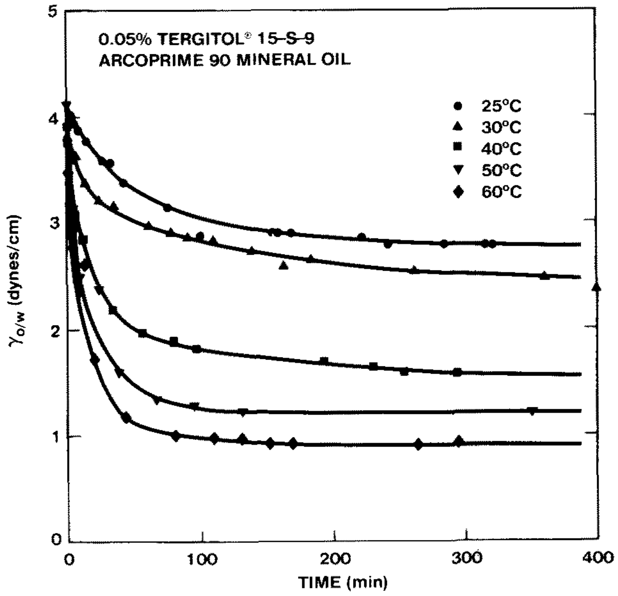

FIG. 8. Time-course of lowering of interfacial tension at various temperatures for a commercial secondary alcohol ethoxylate.

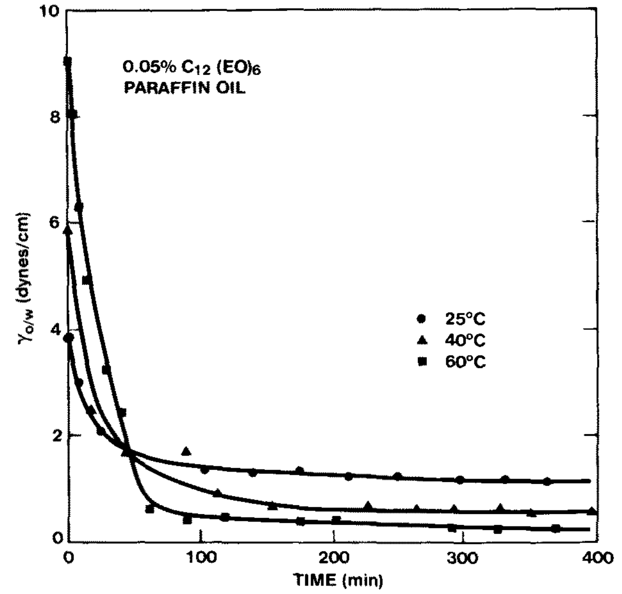

FIG. 9. Time-course of lowering of interfacial tension at various temperatures for hexaethylene glycol dodecyl ether.

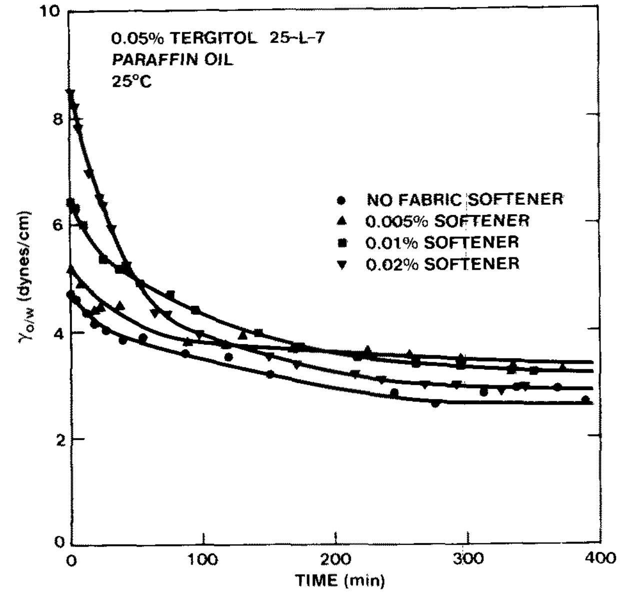

FIG. 10. Time-course of lowering of interfacial tension in the presence of various concentrations of an imidazoline-based softener for a commercial primaryalcohol ethoxylate.

TABLE II

Correlation of Percentage of Detergency with Interfacial Tension Values

Surfactant	$\gamma_{w/a}$ (dynes/cm)[a] (equilibrium)	$\gamma_{o/w}$ (dynes/cm)[b] 10 minute values	$\gamma_{o/w}$ (dynes/cm)[b] (equilibrium)	Average percentage of detergency[c]
TERGITOL NP-9	31.0	2.4	1.6	19
TERGITOL 15-S-9	29.2	3.8	2.8	13
TERGITOL 25-L-9	28.8	4.4	3.4	9
TERGITOL 25-L-7	28.2	4.2	2.4	11
TERGITOL 25-L-12	32.5	5.9	4.9	6
TERGITOL 25-L-20	38.1	8.5	7.9	3

[a] 25 C, 0.05% surfactant solutions.

[b] 25 C, 0.05% surfactant solutions, Arcoprime 90 mineral oil.

[c] Testfabrics soil on nylon, 25 C, 150 ppm hardness (Ca^{2+}:Mg^{2+} = 3:2), 0.05% surfactant.

of nonionic surfactant solutions to effect oil removal via the roll-up process. However, because detergency mechanisms other than roll-up are operative in most practical systems, and because realistic soils and formulated detergents are significantly more complex than the simple systems examined here, additional studies are required to assess more fully the effects of softeners on detergency performance.

Because commercial detergents often contain alkaline builders and electrolytes, the effects of these ingredients on $\gamma_{o/w}$ have also been considered. As expected, triethanolamine, sodium carbonate, sodium tripolyphosphate, sodium chloride and various combinations of these materials in concentrations typical of those found in a normal wash bath, have no significant effect on the time-course of lowering of interfacial tension and the equilibrium interfacial tension. This result, which is obtained regardless of whether a monodisperse or commercial nonionic surfactant is employed, emphasizes the all-important role of the surfactant in deterging nonpolar oils. On the other hand, because alkaline salts and builders are known to affect practical detergency performance, these data also illustrate a significant shortcoming of paraffin oil as a model soil, i.e., it can be used only to study the effects of surfactants. Consequently, the effects of alkalinity, softeners and electrolytes on the interfacial tension between surfactant solutions and polar, ionizing oils are being investigated and will be discussed in subsequent papers.

Correlation of Interfacial Tension Values with Detergency Performance

Whereas equilibrium $\gamma_{w/a}$ and $\gamma_{s/w}$ values are rapidly attained above the CMC (5), such is clearly not the case at the oil/water interface. Thus, when considering the correlation between detergency performance in a 10 min wash and $\gamma_{o/w}$, using interfacial tension readings taken after 10 min of phase contact is perhaps most appropriate. Table II compares, therefore, detergency results with both equilibrium and 10 min interfacial tension data for pertinent nonionic surfactants. Within the TERGITOL 25-L primary alcohol ethoxylate series, detergency varies inversely with both $\gamma_{o/w}$ and $\gamma_{w/a}$, making assessment of the relative importance of each parameter difficult. However, if the results for each of the respective 9 mol ethoxylates are compared, detergency clearly correlates well with $\gamma_{o/w}$, i.e., the lower the interfacial tension, the better the detergency performance. This is consistent with previously reported results (1,5), where TERGITOL NP-9 was more effective in removing nonpolar oils from polyester than TERGITOL 15-S-9, and both were better than TERGITOL 25-L-9. Because the relative abilities of the surfactant solutions to reduce $\gamma_{o/w}$ do not vary appreciably with time, detergency performance, not surprisingly, correlates well with both 10 min and equilibrium interfacial tension values. In general, this result is not to be expected, especially when surfactants having significantly different rates of interfacial tension lowering are compared.

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