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Behavior of Surfactant Mixtures in Model Oily-Soil Detergency Studies

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ABSTRACT

A study of roll-up in a model oily-soil detergent system has shown that the addition of a second surfactant in a minor amount to an effective detergent can either enhance or inhibit roll-up. Which effect takes place depends on the relative surface activity of the components, the levels used, and, for ionic surfactants, the electrolyte content. Addition of anionic surfactants can reduce the performance of an effective nonionic under low ionic strength/low hardness conditions. However, in high ionic strength/high hardness solutions, where the anionic is effective, the situation is reversed and addition of the nonionic component can, in some cases, reduce the rate of roll-up. Roll-up behavior appears to be controlled by the oil/water interfacial tension. When the interfacial tension increases above a critical value, roll-up is inhibited. A theory that has been used to predict surface tensions of mixtures is also useful in estimating oil/water interfacial tensions. The theory provides an understanding of why the interfacial tension can rise when mixed micelles are formed.

INTRODUCTION

It is generally accepted that the roll-up process is the primary mechanism by which nonpolar oily liquids, e.g., mineral oil, are removed from low energy surfaces (1). For polar oils, emulsification can also play a role in the removal process. Earlier work in our laboratory (2) showed that surfactant structure is important in determining the efficiency of oil roll-up in a model detergency system. For detergent range ethoxylated alcohols, the type of hydrophobe determines roll-up efficiency—which has the order, alkylphenol > secondary alcohol > primary alcohol. The degree of ethoxylation is also a major factor, as shown in Figure 1, where for a primary alcohol there is a sharp decline in oil removal efficiency as the degree of ethoxylation increases.

There appears to be a strong dependence of the rate of roll-up in the model experiments on the oil/water interfacial tension (3). For example, the rate of removal increases and the interfacial tension continues to decrease as the surfactant concentration is increased beyond the critical micelle concentration (CMC). Of the three types of commercial nonionics mentioned above, the alkylphenol ethoxylates have the lowest oil/water interfacial tension when compared at the same ethylene oxide content and surfactant concentration—a fact which is consistent with their superiority in roll-up. Also, addition of oleic acid to the oil phase reduces the mineral oil/water interfacial tension, facilitates the roll-up process and minimizes the differences in performance among the ethoxylated alcohols.

The present study was undertaken to determine how mixtures, particularly of dissimilar surfactants, e.g., nonionic/ionic, perform in model roll-up experiments and how they are affected by ionic strength and divalent ions. Since many commercial detergents contain surfactant mixtures, it was felt that such a study could lead to a better understanding of the formulation principles underlying the achievement of superior oily-soil removal.

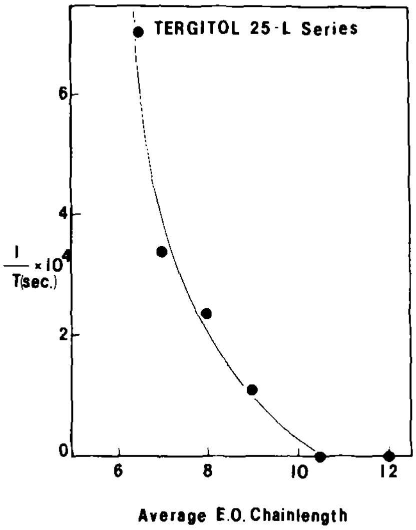

FIG. 1. Removal efficiency (expressed as the reciprocal of removal time) as a function of average EO chainlength in the TERGITOL® 25-L series at 0.1% concn.; mineral oil.

EXPERIMENTAL

Materials

Arcoprime 90 white mineral oil from Atlantic Richfield has a viscosity of 91 SUS at 100 F. Oleic acid was from Sigma Chemical Company (St. Louis, MO). Heptaethyleneglycol dodecylether ($C_{12}E_7$) and sodium dodecyl sulfate were from Nikko Chemicals Co., Ltd., and cetyltrimethylammonium bromide (CTAB) from Fine Organics (Lodi, NJ). Mylar film is a DuPont polyethylene terephthalate film with a minimum of surface defects. The polyester filament yarn was obtained from Fiber Industries and was cleaned as described previously (4). The TERGITOL® nonionic surfactants used are nonylphenol, primary and secondary alcohol ethoxylates from Union Carbide Corporation. The primary (L) alcohol ethoxylates are based on C_{12}–C_{15} alcohols and the secondary (S) on C_{11}–C_{15} alcohols. The final number in each designation refers to the average number of EO units in the surfactant. Linear alkylbenzene sulfonate (LAS) was prepared by neutralization with NaOH of Calsoft LAS-99 from Pilot Chemical.

Procedures

The experimental details for the model detergency system have been described previously (1). Briefly, the method involves measuring the removal times of 2 μL oil droplets placed on a clean Mylar film which is subsequently submerged in 400 g of surfactant solution. All tests were performed at 25 C. After submersion of the film, the solution is mildly agitated.

Surface tensions were measured using a platinum Wilhelmy plate with a Cahn Model C27 electrobalance. Interfacial tensions were measured with a spinning drop interfacial tensiometer, Model 500, from the University of Texas. Total carbon analysis was performed with a Beckman Tocamaster 915B (4, 5). The UV spectrophotometer used was a Beckman Acta CV.

RESULTS

Oil Removal Performance at Low Ionic Strength

Various mixtures of nonionic and ionic surfactants were tested in the model detergency system with mineral oil and mineral oil containing 5% oleic acid, "polar mineral oil", as the model soils. The results for TERGITOL® 25-L-7 and LAS mixtures are summarized in Table I.

In distilled water, LAS solutions do not remove either type of oil, whereas TERGITOL® 25-L-7 is very effective in removing the polar mineral oil and moderately effective with mineral oil. Addition of LAS to 25-L-7 can dramatically reduce the rate of oil roll-up with the effect depending on the LAS concentration. For example, at a LAS concentration of 0.05 wt % (2:1 ratio of nonionic to anionic in Table I), oil removal from the polyester surface does not occur.

Other TERGITOL® nonionic surfactants were tested, both alone and in combination with the alkylbenzene sulfonate. The results for TERGITOL® 15-S-7 and NP-10 are summarized in Table II. In agreement with earlier work (2), both TERGITOL® NP-10 and 15-S-7 are more efficient than TERGITOL® 25-L-7 in removing the nonpolar oil. Furthermore, it is seen that the influence of LAS in decreasing the rate of soil removal is not unique to TERGITOL® 25-L-7 but occurs with all three nonionics. The results in Table II also indicate that the extent of inhibition depends on the ratio of nonionic to anionic. For example, addition of 0.005% LAS increases the roll-up time for 0.1% TERGITOL® NP-10 from 1 min to 8 min, whereas oil removal is completely arrested when this concentration of LAS is combined with 0.05% TERGITOL® NP-10.

As is well known, commercial nonionics have a distribution of chainlengths in both the hydrophobe and hydrophile. To test the efficiency of a monodisperse surfactant, heptaethylene glycol dodecyl ether ($C_{12}E_7$) was used. Mixtures of $C_{12}E_7$ with other charged surfactants, such as sodium dodecyl sulfate (SDS) and cetyl trimethyl ammonium bromide (CTAB), were also studied to determine if the behavior of mixtures found earlier is specific to LAS. The results are shown in Table III for mineral oil and polar mineral oil.

It is seen that the purified nonionic, $C_{12}E_7$, is more efficient than TERGITOL® 25-L-7 for the nonpolar oil. As with the commercial surfactants, the rate of oil removal is

TABLE I

Oil Removal by TERGITOL® 25-L-7 and LAS Mixtures

Surfactant system	Oil type	Removal time (min)
0.1% 25-L-7	Mineral oil	48
0.1% LAS	Mineral oil	No removal
0.1% 25-L-7 + 0.05% LAS	Mineral oil	No removal
0.1% 25-L-7 + 0.005% LAS	Mineral oil	133
0.1% 25-L-7 + 0.001% LAS	Mineral oil	43
0.05% 25-L-7	Mineral oil + 5% oleic acid	Immediate removal
0.1% LAS	Mineral oil + 5% oleic acid	No removal
0.05% 25-L-7 + 0.05% LAS	Mineral oil + 5% oleic acid	No removal
0.05% 25-L-7 + 0.005% LAS	Mineral oil + 5% oleic acid	53
0.05% 25-L-7 + 0.001% LAS	Mineral oil + 5% oleic acid	5

TABLE II

Mineral Oil Removal by TERGITOL® Nonionic/LAS Mixtures

Surfactant system	Oil type	Removal time (min)
0.1% NP-10	Mineral oil	1
0.1% NP-10 + 0.005% LAS	Mineral oil	8
0.1% NP-10 + 0.001% LAS	Mineral oil	1
0.05% NP-10	Mineral oil	2
0.05% NP-10 + 0.005% LAS	Mineral oil	No removal
0.05% NP-10 + 0.001% LAS	Mineral oil	3
0.05% 15-S-7	Mineral oil	8
0.05% 15-S-7 + 0.005% LAS	Mineral oil	No removal
0.05% NP-10	Mineral oil + 5% oleic acid	Immediate removal
0.05% NP-10 + 0.02% LAS	Mineral oil + 5% oleic acid	No removal
0.05% NP-10 + 0.01% LAS	Mineral oil + 5% oleic acid	10
0.05% NP-10 + 0.005% LAS	Mineral oil + 5% oleic acid	Immediate removal
0.05% 15-S-7	Mineral oil + 5% oleic acid	1
0.05% 15-S-7 + 0.02% LAS	Mineral oil + 5% oleic acid	No removal
0.05% 15-S-7 + 0.005% LAS	Mineral oil + 5% oleic acid	27

TABLE III

Mineral Oil Removal by $C_{12}E_7$ and Ionic Surfactants

Surfactant system	Oil type	Removal time (min)
0.1% $C_{12}E_7$	Mineral oil	10
0.1% $C_{12}E_7$ + 0.005% LAS	Mineral oil	31
0.1% $C_{12}E_7$ + 0.001% LAS	Mineral oil	10
0.05% CTAB	Mineral oil	No removal
0.1% $C_{12}E_7$ + 0.05% CTAB	Mineral oil	No removal
0.1% $C_{12}E_7$ + 0.005% CTAB	Mineral oil	38
0.05% $C_{12}E_7$	Mineral oil + 5% oleic acid	Immediate removal
0.05% $C_{12}E_7$ + 0.0275% SDS	Mineral oil + 5% oleic acid	No removal
0.05% $C_{12}E_7$ + 0.0163% SDS	Mineral oil + 5% oleic acid	12
0.05% $C_{12}E_7$ + 0.005% SDS	Mineral oil + 5% oleic acid	Immediate removal
0.05% $C_{12}E_7$ + 0.0163% LAS	Mineral oil + 5% oleic acid	No removal
0.05% $C_{12}E_7$ + 0.0106% LAS	Mineral oil + 5% oleic acid	23
0.05% $C_{12}E_7$ + 0.005% LAS	Mineral oil + 5% oleic acid	Immediate removal

decreased when LAS is present above some critical concentration. Furthermore, it is observed that the other charged surfactants also inhibit oil removal in the model system when mixed with an efficient nonionic detergent. Inspection of Table III indicates that the wash solution can tolerate a higher concentration of the less surface active SDS, as compared with the more surface active LAS, before roll-up is inhibited.

Since both nonionic/anionic and nonionic/cationic mixtures displayed "negative synergism" in roll-up in low ionic strength solutions, experiments were also done with nonionic/nonionic mixtures. The results in Table IV indicate that the addition of 0.01% TERGITOL® 25-L-20 to a 0.1% TERGITOL® 25-L-7 completely inhibits removal of

TABLE IV

Mineral Oil Removal by Mixtures of TERGITOL® Nonionic Surfactants

Surfactant system	Removal time (min)
0.1% 25-L-7	48
0.1% 25-L-20	No removal
0.1% 25-L-7 + 0.01% 25-L-20	No removal
0.1% 25-L-7 + 0.001% 25-L-20	45
0.05% NP-10	2
0.1% NP-40	No removal
0.05% NP-10 + 0.01% NP-40	10

mineral oil from polyester film. Similar effects were observed with NP-10/NP-40 mixtures.

The results presented above indicate that combining a poor surfactant for oil removal with an efficient surfactant can result in poor performance in the model detergency system even though the poor surfactant may only comprise 10% of the total surfactant concentration. This effect is found with both nonionic/ionic and nonionic/nonionic mixtures.

Oil Removal Performance in the Presence of Electrolytes

The studies described in the previous section were done in distilled water and are thus models for oily soil removal in either soft water or in "overbuilt" systems.

The influence of electrolyte on the roll-up of nonionic/ionic mixtures is quite striking. The effect of NaCl in 25-L-7/LAS mixtures is shown in Figure 2. Whereas the nonionic alone is only slightly affected by salt, the salt concentration has a large effect on the removal time with LAS. In fact, the mineral oil removal time of the mixed system with 0.5 m NaCl is less than half that of the nonionic alone.

Divalent ions have an even greater effect with nonionic/LAS mixtures. As shown in Figure 3, addition of Mg^{2+} dramatically increases the oil removal efficiency of LAS. Magnesium salts of alkyl sulfonates and sulfates are generally more surface active than the corresponding sodium salt. For example, above the CMC, a solution which contains an equivalent molar amount of Mg^{2+} to LAS has a surface tension which is ca. 5 dynes/cm less than that of a LAS solution without Mg^{2+}. It can be inferred from Figure 3 that LAS with Mg^{2+} is more efficient in mineral oil roll-up than TERGITOL® 25-L-7. In this case, the TERGITOL® 25-L-7 is the less surface active component and, at a Mg^{2+} concentration of between 0.1 and 0.75 equivalents, actually impedes the removal of oil when it is the minor component. The behavior of the nonionic/anionic mixture as regards roll-up of nonpolar soil can thus be completely altered in going from distilled to salt containing (including hard) water.

Adsorption and Interfactial Tension Measurments

In order to better understand the behavior of surfactant mixtures in the model detergency studies, surfactant adsorption on polyester fiber and interfacial tensions were measured. Nonionic surfactants such as TERGITOL® NP-10 have been shown to adsorb from aqueous solution to form a monolayer on the polyester fiber (4). Adsorption isotherms for mixtures of TERGITOL® NP-10 and LAS are shown in Figure 4 as a function of the equilibrium nonionic surfactant concentration in solution. Total carbon analysis (5) and Hyamine titrations were used to determine adsorption. LAS alone absorbs only slightly on polyester

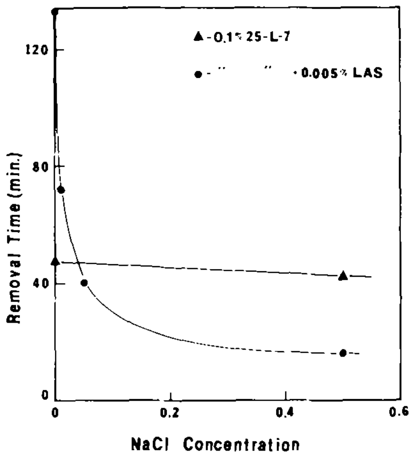

FIG. 2. Influence of the concentration of NaCl (mol/L) on removal time for mineral oil from polyester.

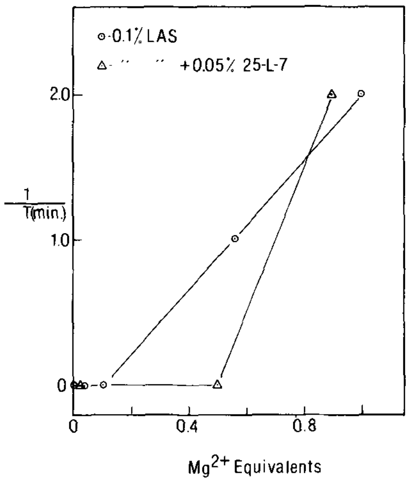

FIG. 3. Influence of Mg^{2+} on the removal efficiency for mineral oil from polyester.

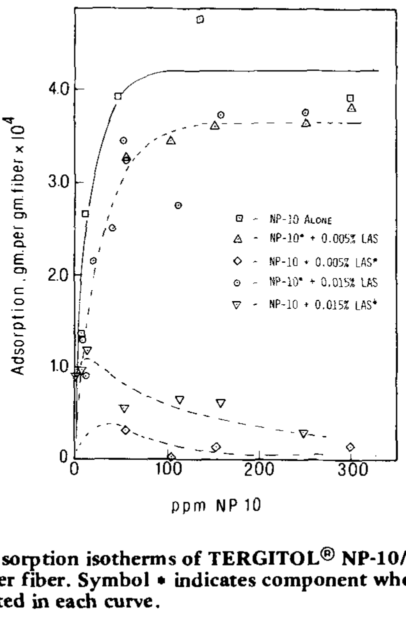

FIG. 4. Adsorption isotherms of TERGITOL® NP-10/LAS mixtures on polyester fiber. Symbol • indicates component whose adsorption is represented in each curve.

from either 50 or 150 ppm solution in distilled water, and its adsorption is further reduced on addition of nonionic. Addition of either 50 or 150 ppm LAS to TERGITOL® NP-10 results in a slight decrease in the amount of nonionic adsorbed. However, the effects are minor when compared to the oil roll-up results.

As noted previously (2, 3), the oil/water interfacial tension is an important parameter in determining oil roll-up efficiency. The interfacial tensions of TERGITOL® 25-L-7, LAS and their mixtures in distilled water are shown in Figure 5. The pronounced "aging effect" has been discussed by Dillan (3), and appears to be due to partitioning of components in the oil phase. Addition of LAS to TERGITOL® 25-L-7 increases the interfacial tension in distilled water until, at higher LAS concentrations, the interfacial tension approaches that of LAS. The effect of interfacial tension on roll-up efficiency for LAS and TERGITOL® 25-L-7 mixtures is shown in Figure 6. For these systems there appears to be a critical interfacial tension value of ca. 2.5 dynes/cm, above which no oil removal occurs. This critical tension probably depends on the degree of agitation in the detergency experiment and should not be taken as having an inherent significance. However, the results in Figures 5 and 6 indicate that addition of a less surface active component can lead to a significant increase in the interfacial tension of the mixture and so adversely influence oil removal. On changing to hard water, conditions can change drastically. Dillan (private communication) has found that the interfacial tension of LAS solutions (against paraffin oil) is less than 1 dyne/cm at $MgCl_2$ concentrations of $\geqslant$ of 0.01%. Thus, in mixtures with TERGITOL® 25-L-7 under these conditions, magnesium LAS would dominate in lowering the interfacial tension. It is accordingly expected that under certain mixing ratios and total concentrations TERGITOL® 25-L-7 could increase the interfacial tension when added to LAS in hard water. This behavior is consistent with the roll-up efficiencies depicted in Figure 3 where the nonionic surfactant can actually impede the action of LAS.

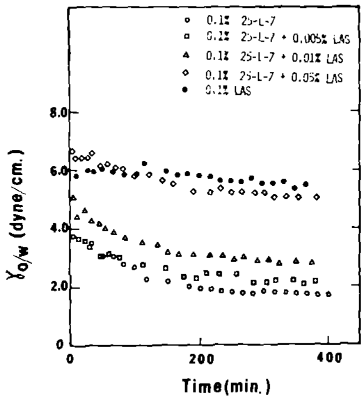

FIG. 5. Mineral oil/water interfacial tensions of TERGITOL® 25-L-7/LAS mixtures as a function of equilibration time.

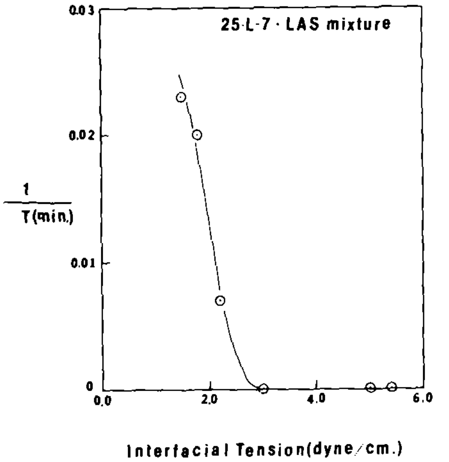

FIG. 6. Influence of interfacial tension on the removal efficiency of mineral oil from polyester film in the presence of TERGITOL® 25-L-7/LAS mixtures.

DISCUSSION

It can be readily shown from the Gibbs adsorption equation that the surface or interfacial tension of a two component surfactant mixture can increase with increasing total concentration of the less surface active species. For this to occur, the solution activity of the other surfactant must decrease. It is well known from various studies of the thermodynamics of surfactant mixtures (6–8) that, above the CMC of a surfactant mixture, the monomer activity of the more surface active component can decrease with increasing concentration of the less surface active species.

Recently Garrett (9), Ingram (10, 11) and Rosen (12) have been able to predict accurately the surface tension of mixed surfactant solutions from a knowledge of the surface tensions of the individual components. Their analysis can also be used to predict oil/water interfacial tension. However, it has to be modified to take into account partitioning of the surfactant between the oil and water phases.

When surfactant micelles are treated as a separate phase composed of completely miscible liquids, the condition for equilibrium of each surfactant species is:

$$\Delta\mu_i^\circ = RT \ln CMC_i^\circ = RT \ln \frac{C_i}{f_i^m X_i^m} \ldots i = 1, 2 \qquad [1]$$

where X_i^m and f_i^m are the mole fraction and activity coefficient, respectively, of component i in the micellar phase; C_i is the monomer concentration in the aqueous phase and CMC_i° is CMC of component i alone in water. The term $\Delta\mu_i^\circ$ represents the difference in the standard chemical potential of component "i" in the two "phases." The standard state for the "ith" surfactant in the aqueous phase is an ideal one molar solution. For the micelle phase the standard state is chosen as $X_i^m = 1$.

Equation 1 is not correct for ionic surfactants since their chemical potential in the micelle phase is strongly influenced by the type and concentration of counter-ions. Furthermore, the counter-ion concentration varies with total surfactant concentration and mixing ratio. These effects can be explicitly taken into account, as was done recently (13). Equation 1 is a useful approximation provided the CMC_i° values are chosen at the same ionic strength as the mixture and the counter-ion concentrations do not vary greatly over the surfactant concentration studied.

Equilibrium between the bulk and the interface can be analyzed in a similar way; the equilibrium condition is (9–12):

$$\Delta\mu^\circ = RT \ln C_i^\circ (\gamma) = RT \ln \frac{C_i}{f_i^s X_i^s} \ldots i = 1, 2 \qquad [2]$$

where X_i^s and f_i^s are the mole fraction and activity coefficient of component i in the surface phase. $C_i^\circ(\gamma)$ is the monomer concentration in a solution containing component i alone that would have the same interfacial tension, γ, as that of the mixture; constant temperature and pressure are assumed. By definition, $C_i^\circ(\gamma)$ is a standard state (11, 12) and may not be physically realizable. For many surfactant solutions, the surface and interfacial tensions are exponential functions of the monomer concentration near their CMC (10–12, 14, 15). Thus, $C_i^\circ(\gamma)$ can be defined by

$$\gamma = A_i + B_i \ln C_i^\circ(\gamma) \qquad [3]$$

where A_i and B_i are constants that are obtained from experiment.

Equation 2 is an approximation for mixtures containing ionic surfactants because of the counter-ion effects discussed previously in connection with Equation 1. Thus, $C_i^\circ(\gamma)$ must be measured at the same ionic strength that is present in the mixture.

Equation 3, together with Equations 1 and 2 in the form:

$$X_i^m f_i^m = \frac{C_i}{CMC_i^\circ} \qquad [4]$$

and

$$X_i^s f_i^s = \frac{C_i}{C_i^\circ(\gamma)} \qquad [5]$$

allow the interfacial tension of the mixture to be computed in terms of the composition of the mixture. However, to carry out the analysis one needs expressions for the activity coefficients in the micelle, f_i^m, and surface phase, f_i^s, and a condition expressing conservation of mass.

Two types of solution models have been found to give good agreement with experiment (8, 10, 12). The ideal solution model ($f_i^m = f_i^s = 1$) is useful for mixtures of surfactants having similar polar head groups, e.g., nonionic/nonionic mixtures. For mixtures of dissimilar structures, e.g., ionic/nonionic mixtures, a regular solution model is useful. In this case

$$f_i^m = \exp - \beta_m (1 - X_i^m)^2 \qquad [6]$$

and

$$f_i^s = \exp - \beta_s (1 - X_i^s)^2 \qquad [7]$$

for i = 1, 2. The interaction constants β_m and β_s are determined experimentally (8, 11, 12). For example, to predict the surface tension of a mixture of 2 surfactants, the surface tension of each component must be known separately as a function of its concentration. This information is needed to determine CMC_i°, A_i, B_i in Equations 3–5. The surface tension of a mixture having some constant mole fraction L_i of each component is then measured as a function of the total surfactant concentration. From this information, the CMC of the mixture, C_T^* and surface tension at this CMC, $\gamma(C_T^*)$, are determined. From these values of CMC_i°, A_i, B_i, C_T^*, $\gamma(C_T^*)$ and the parameters β_m and β_s are back calculated from Equations 4–7 combined with the conservation of mass condition,

$$C_i = L_i C_T^* \qquad [8]$$

The values of β_m and β_s so obtained can then be used to compute the surface tensions of other mixtures by reapplication of Equations 4–7 and the conservation of mass condition which for a binary mixture is:

$$\frac{C_{1w}^T - C_1}{X_1^m} = \frac{C_{2w}^T - C_2}{1 - X_1^m} \qquad [9]$$

where C_{1w}^T and C_{2w}^T are the total surfactant concentrations of each component in the aqueous phase.

The above analysis can be used to compute oil/water interfacial tensions of surfactant mixtures. However, a complication arises when one or more components can partition between the oil and aqueous phases. The analysis becomes particularly complicated when micelles are formed in one or both of these phases (16), since the CMC_i° can depend on the nature of the oil, and large amounts of oil and water can be solubilized in the appropriate micellar phases. The case that will be considered here involves partitioning of only one component and ignores both micelle formation in the oil phase and appreciable solubilization of oil in the aqueous phase. Under these conditions:

$$C_1^T = C_{1w}^T + \alpha_1 \frac{(\phi)}{(1-\phi)} C_1 = C_{1w}^T + R\, C_1 \qquad [10]$$

where C_1^T is the starting concentration of "i" (all dissolved in the aqueous phase), C_{1w}^T is the equilibrium total concentration in the aqueous phase and C_1 is monomer concentration of component 1 in the water phase. α_1 is the partition coefficient and ϕ is the volume fraction of oil which is assumed to be immiscible with the aqueous phase.

As an example of the behavior expected from a surfactant mixture in which only one component partitions, the analysis was applied to compute the interfacial tensions of mineral oil against aqueous solutions of $C_{12}E_7$/LAS and TERGITOL® 25-L-7/25-L-20. Here only $C_{12}E_7$ and TERGITOL® 25-L-7 have appreciable solubility in mineral oil. The values of β_m and β_s and B_i were computed by the analysis described above using surface tension data that was already available. These values together with the measured CMC_i° are collected in Table V.

The values of A_1 and A_2 were computed from a single mineral oil/water interfacial tension at a surfactant concentration where the interfacial tension no longer depended on total surfactant concentration and was thus above its CMC in the aqueous phase. These results are also given in Table V.

We recognize that the values of B_i given in Table V are only approximations for the true values, since the areas per

TABLE V

Parameters Used to Estimate Oil/Water Interfacial Tensions of Surfactant Mixtures

Surfactants		CMC_i° (molar)							
1	2	1	2	β_m	β_s	A_1	B_1	A_2	B_2
$C_{12}E_7$	LAS	1.09×10^{-4}	2.29×10^{-3}	−4.73	−3.41	−44.4	−5.05	−38.7	−7.23
25-L-7	25-L-20	1.76×10^{-5}	3.14×10^{-5}	0	0	−105.1	−9.75	−47.1	−5.31

surfactant molecule at the oil/water interface can be different from those at the water surface. This procedure was considered acceptable since the calculations are intended to illustrate the type of behavior expected for surfactant mixtures rather than to test a theory that we already know to be rather approximate.

The results are shown in Figure 7 for 0.1% concentration of $C_{12}E_7$ or TERGITOL® 25-L-7, (i.e., the surfactants that partition). The X-axis represents the concentration of the surfactant with higher interfacial tension, i.e., LAS or TERGITOL® 25-L-20. The results were computed for the several values shown in Figure 7 of the parameter R of Equation 10. Since the volume fraction of oil in rotating drop measurement of interfacial tension is ca. 0.03–0.05, these values of R span a range of α from 0 to ca. 400 which is a reasonable range for such nonionics (16).

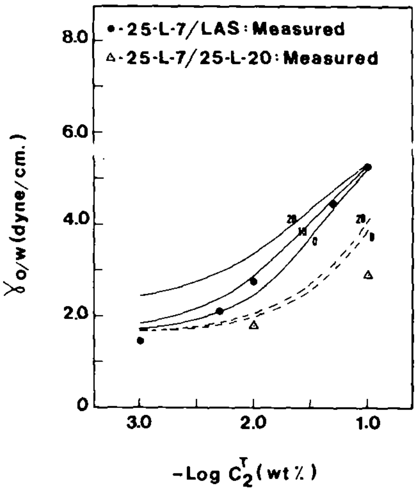

FIG. 7. Comparison of theoretical estimates of oil/water interfacial in surfactant mixtures with experimental results. Component 1 is either $C_{12}E_7$ or TERGITOL® 25-L-7 at a fixed concentration of 0.1%. C_2^T represents the total concentration of LAS or TERGITOL® 25-L-20. R represents the quantity $\alpha\phi/(1-\phi)$. In a rotating drop experiment ϕ is ca. 0.05.

Mineral oil/water interfacial tensions measured for solutions of TERGITOL® 25-L-7/LAS and TERGITOL® 25-L-7/25-L-20 are also recorded in Figure 7. Considering the approximate nature of the calculations and the fact that the actual surfactants used are themselves mixtures, the qualitative agreement between the predicted behavior and experiment is encouraging. The calculations support the view that it is the formation of mixed micelles with consequent changes in solution activity that is responsible for the increases in interfacial tensions that are observed; these, in turn, control the behavior of the mixtures in oily soil roll-up.

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