Subscripts

M, L, G = membrane, liquid, gas phase
o = at entrance
m = mean value
a = atmospheric
i = membrane-liquid interface

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Explaining Solubilization Kinetics

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Solubilization rates of fatty acids in pure detergent solutions are controlled by mixed micelle desorption and diffusion. Solubilization rates in partially saturated detergent solutions also involve exchange of fatty acids between the solid and the solution. These conclusions depend on models like those used in gas-solid catalysis and in tracer diffusion.

SCOPE

This paper develops and verifies theories of solubilization kinetics in aqueous detergent solutions. It includes both the physical basis of the equations and the experiments necessary to verify them. However, these systems can show chemical eccentricities which are detailed in a companion paper (Chan et al., 1976).

Except at high dilution, detergent solutions contain micelles, thermodynamically stabilized aggregates which typically are 40Å in diameter (Kratohvill and Dellicolli, 1970). These micelles, which characteristically contain about one hundred detergent molecules, have a water soluble hydrophillic surface but a water insoluble hydrophobic central core. Many smaller and larger micelles are known; for example, bile salt micelles may contain less than ten molecules (Small et al., 1969). Solubilization occurs when water insoluble molecules, that is, oils, lipids, long chain fatty acids, and the like, are incorporated into the micelles. The resulting mixed micelles retain their hydrophillic shell and their hydrophobic core.

Previous investigations of solubilization have concentrated on equilibrium studies, not kinetic ones. For example, they have contained accurate determinations of the size and charge of the mixed micelles. They have included measurements of the maximum amounts which can be solubilized by specific detergents (Elworthy et al., 1968). When these earlier studies did involve kinetics, they often used poorly defined experiments from which definite conclusions were difficult to draw.

Previous investigations of other aspects of detergent kinetics have concentrated on removal from fibers of soils of greases and particles (Jones, 1961; Schott, 1972). Once removed, the soils can be suspended in detergent solutions rather than incorporated into thermodynamically stable micelles. The studies, which were largely carried out in rapidly stirred solutions, have been explained in terms of two limiting mechanisms, a roll-up mechanism and a penetration mechanism (Schwartz, 1971). The roll-up mechanism suggested that the detergent's principal function is to alter the contact between soil and fiber; the penetration mechanisms showed that diffusion of the detergent into the soil is important. While these experiments are tremendously useful in providing a qualitative picture, they do not provide an exact description of the mass transfer rates involved in detergency. This paper presents such a description for the mass transfer rates important in one aspect of detergency, solubilization.

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CONCLUSIONS AND SIGNIFICANCE

Solubilization rates of fatty acids are controlled by two sequential steps: desorption of the mixed micelles from a fatty acid surface and diffusion of these mixed micelles away from the surface. When the detergent solution is rapidly stirred, the desorption is rate limiting; when the solution is only slightly stirred, the diffusion is rate limiting. Under commonly encountered conditions, including those similar to washing machines, both steps are important for anionic, cationic, and nonionic detergents.

These conclusions result from solubilization rates measured with a rotating disk of radioactively tagged fatty acid. The interpretation of the results requires two complementary theories. When the detergent solution initially contains no fatty acid, the results can be correlated with a modal similar to that used to explain gas-solid catalysis (Laidler, 1965; Aris, 1975). This model, which contains two adjustable parameters, predicts that the reciprocal of the solubilization rate should vary linearly with the reciprocal of the detergent concentration. The intercept on this plot is independent of detergent flow, but the slope increases as detergent flow decreases. These predictions are verified.

When the detergent solution is partially saturated with fatty acid, the results can only be explained by modifying the model to account for the exchange of tagged and untagged fatty acids. These modifications are similar to those necessary to explain tracer diffusion (Cussler, 1976). They show how radioactive tracers in detergent solutions can give results which differ by more than an order of magnitude.

The theory of solubilization presented here has two complimentary parts. The first, valid for solubilization in pure detergent solution, is based on the mechanism shown in Figure 1. This mechanism contains five steps. First, detergent molecules diffuse through the bulk solution to the surface. Second, these molecules are adsorbed on the surface. Third, it reacts to form a mixed micelle containing both detergent and the material being solubilized. Fourth, the micelle is desorbed, and fifth, it diffuses away.

This model and its mathematical formulation parallel the Langmuir-Hinshelwood models (Hougen and Watson, 1943) used in gas-solid catalysis. However, solubilization may differ from heterogeneous gas phase reactions because the reactions involved have no simple stoichiometric basis. Moreover, the micelle may not remain intact during solubilization, since it always is in rapid equilibrium with unaggregated detergent. As a result, the steps in Figure 1 imply more major approximations than those in gas-solid catalysis.

The second part of the theory is based on the mechanism shown in Figure 2. This new mechanism describes solubilization of a radioactively tagged material in a detergent solution saturated with untagged but chemically identical material. As such, it is an extension of diffusion theories of two identical solutes to systems containing simultaneous diffusion and chemical reaction (Dunlop, 1965; Curran et al., 1967; Albright and Mills, 1965; Cussler, 1976).

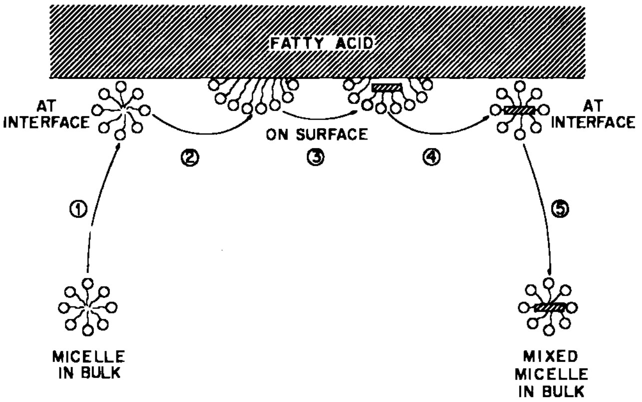

Fig. 1. Schematic mechanism for initial solubilization. Mixed micelle desorption and diffusion [steps (4) to (5)] are assumed to control stearic acid solubilization.

The mechanism in Figure 2 is in many ways similar to that in Figure 1. For example, steps (1) and (5) in Figure 2 are similar to step (5) in Figure 1; all refer to mixed micelle diffusion. Steps (2) and (4) in Figure 2 are essentially the reverse and forward reactions of step (4) in Figure 1. However, step (3) is different. Before, it described detaching material from the solid surface; now it represents exchange of untagged material for tagged material. Figure 2 also includes a sixth step, micelle exchange, in which tagged and untagged material exchange positions in the bulk solution. The mathematical basis of both mechanisms is given in the next section.

THEORY

The mathematical description of solubilization is best divided into two parts. First, for initial solubilization, the theory is a straightforward parallel to Langmuir-Hinshelwood kinetics (Hougen and Watson, 1943; Chan, 1976). Second, for solubilization in partially saturated solutions, the theory is an interesting application of ternary mass transfer (Cusser, 1976).

Initially, the solubilization rate is assumed to be controlled by steps (4) to (5) in Figure 1. If these steps

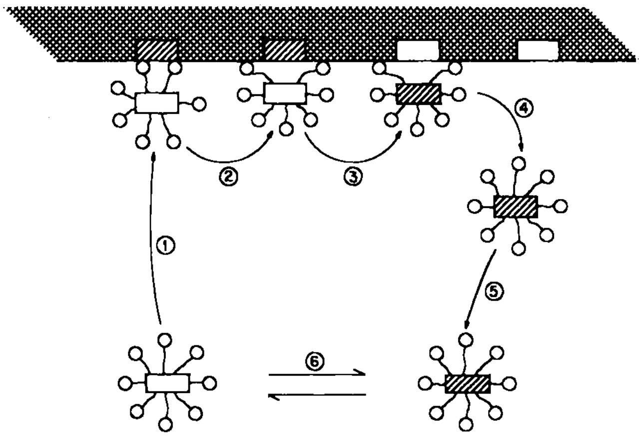

Fig. 2. Schematic mechanism or solubilization in saturated solutions. This mechanism involves exchange of untagged fatty acid (the plane rectangles) for radioactively tagged fatty acid (the shaded rectangles).

Table 1. Consequences of the Initial Solubilization Mechanism in Figure 1

Controlling steps	Form of equation	Number of adjustable parameters	Dependence on flow	Dependence on detergent concentration
1,2	rate $= K_La\,[F(\mathrm{sat})]$	One	$\frac{1}{K_La} \propto \frac{1}{\sqrt{Re}}$	rate $\propto [F(\mathrm{sat})]$
1,5	rate $= K_La\,[F(\mathrm{sat})]$	One	$K_La \propto \sqrt{Re}$	rate $\propto [F(\mathrm{sat})]$
1,2,3	Quadratic	Three	Complex	Complex
2,3	rate $= \frac{v_{\max}[F(\mathrm{sat})]}{K_m + [F(\mathrm{sat})]}$	Two	None	$\frac{1}{\text{rate}} \propto \frac{1}{[F(\mathrm{sat})]}$
4,5	rate $= \frac{v_{\max}[F(\mathrm{sat})]}{K_m + [F(\mathrm{sat})]}$	Two	$v_{\max} \neq f(Re)$ $K_m \propto \frac{1}{\sqrt{Re}}$	$\frac{1}{\text{rate}} \propto \frac{1}{[F(\mathrm{sat})]}$

are rate controlling

$$\frac{d[M]}{dt} = k_5a[M_i] \tag{1}$$

$$\frac{d[M_i]}{dt} = k_4[M_s] - k_{-4}[M_i]\,[S] - k_5a[M_i] = 0 \tag{2}$$

$$[M_s] = K_3[B_s] \tag{3}$$

$$[B_s] = K_2[B]\,[S] \tag{4}$$

$$[S_o] = [S] + [B_s] + [M_s] \tag{5}$$

Combining, we obtain

$$\frac{d[M]}{dt} = \frac{\left\{\dfrac{k_4\,K_3\,[S_o]}{1+K_3}\right\}[B]}{\left\{\dfrac{k_{-4}\,[S_o] + k_5a}{k_5aK_2\,(1+K_3)}\right\} + [B]} \tag{6}$$

In our experiments, we do not measure $d[M]/dt$ or $[B]$ but the fatty acid concentrations $d[F]/dt$ and $[F(\mathrm{sat})]$. Because $d[F]/dt$ is proportional to $[d[M]/dt]$ by assumption and $[F(\mathrm{sat})]$ is proportional to $[B]$ by experiment, Equation (6) can be rewritten as

$$\left(\frac{d[F]}{dt}\right)^{-1} = \left\{\frac{1+K_3}{nk_4\,K_3\,[S_o]}\right\} + \left\{\left(\frac{\xi}{nK_2K_3}\right)\left[\frac{1}{k_4\,[S_o]} + \frac{1}{k_5a\,K_4}\right]\right\}\frac{1}{[F(\mathrm{sat})]} \tag{7}$$

This equation has two adjustable parameters equal to the quantities in braces.

If steps (4) to (5) in Figure 1 are rate controlling, Equation (7) predicts that a plot of $(d[F]/dt)^{-1}$ vs. $1/[F(\mathrm{sat})]$ will be linear. Moreover, the intercept of this plot is independent of k_5 and hence should be independent of flow. The slope of this plot does depend on k_5 and so should depend on flow. For the rotating disk experiments in this work, k_5 is proportional to the square root of the Reynolds number. As a result, the slope of the plot suggested by Equation (1) should be proportional to the reciprocal of the square root of the Reynolds number.

If steps (4) to (5) are not rate controlling, these characteristics will not be observed. This is partially illustrated in Table 1, where equations are summarized for some other rate controlling steps. In this table, k_1 and k_5 are assumed to vary with the square root of the Reynolds number, since this will be true in the experiments below.

In addition to these results for initial solubilization, a mathematical description for solubilization in partially saturated solutions is needed. This description requires examining the role of the radioactive tracer in somewhat greater detail. In initial dissolution experiments, the tracer and the untagged solute are always present in the same ratio of concentrations. For example

$$\frac{[F^*]}{[F^*] + [F]} = \frac{[F^*(\mathrm{sat})]}{[F^*(\mathrm{sat})] + [F(\mathrm{sat})]} \tag{8}$$

However, when tagged material in the surface dissolves in a solution which is initially completely saturated with untagged material, the concentration ratio is not constant; instead, the assumption is that

$$[F^*(\mathrm{sat})] - [F^*] = [F] - [F(\mathrm{sat})] \tag{9}$$

In other words, the solubilization of tagged material must be balanced by the precipitation of untagged material. These fluxes become zero only when the fraction of tagged material present in solution is the same fraction as is present in the surface.

The rate expressions for initial dissolution can now be written as

$$\frac{d}{dt}[F^*] = K_La\,[F^*(\mathrm{sat})] \tag{10}$$

and

$$\frac{d[F]}{dt} = K_La\,[F(\mathrm{sat})] \tag{11}$$

The solubilities $[F^*(\mathrm{sat})]$ and $[F(\mathrm{sat})]$, which are proportional to the detergent concentration $[B]$, must sum to the total solubility present in solution. The overall mass transfer coefficient K_L also varies with the total detergent concentration, as shown by comparing Equation (7) with Equation (11).

The parallel equation is now assumed for dissolution in a solution which contains no tagged material but is saturated with untagged material:

$$\frac{d[F^*]}{dt} = K_L{}^*a([F^*(\mathrm{sat})] - [F^*]) \tag{12}$$

Again, $K_L{}^*$ is an overall mass transfer coefficient. However, because it includes steps in the mechanism in Figure 2 as well as those in Figure 1, it is numerically different than K_L in Equations (10) to (11). While Equation (12) seems reasonable, it must be checked by experiment.

Solubilization in partially saturated solutions can now be described in terms of the results in these limiting cases. Such a solution can be idealized as three distinct components: tagged fatty acid, untagged fatty acid, and a mixed solvent of water and detergent. Mass transfer in such a ternary system requires a more general form of rate equation

$$\frac{d[F^*]}{dt} = k_{11}a\,([F^*(\text{sat})] - [F^*]) + k_{12}a\,[F(\text{sat})] - [F]) \quad (13)$$

where the k_{ij}'s are ternary mass transfer coefficients. These coefficients can be calculated from ternary diffusion coefficients and from binary mass transfer correlations (Toor, 1964; Stewart and Prober, 1964). The ternary diffusion coefficients for two identical solutes have been shown to be (Curran et al., 1967; Cussler, 1976)

$$D_{11} = \frac{[F^*]}{[F^*] + [F]} D + \frac{[F]}{[F^*] + [F]} D^* \quad (14)$$

$$D_{12} = \frac{[F^*]}{[F^*] + [F]} (D - D^*) \quad (15)$$

In this case, the binary diffusion coefficient D and the tracer diffusion coefficient D^* are the eigenvalues of the diffusion coefficient matrix.

The binary mass transfer correlation required in earlier studies is used to calculate the eigenvalues of the k_{ij} which correspond to the eigenvalues of the D_{ij}. Physically, these eigenvalues refer to special situations in which the ternary system behaves as a binary. The apparent mass transfer coefficients in these special situations are equal to the eigenvalues.

While the theoretically required correlation is not known, Equations (10) to (12) do show that the system behaves as a binary for initial solubilization and for solubilization in saturated solutions. The mass transfer coefficients measured in these situations (K_L and K_L^*) must be equal to the eigenvalues of the mass transfer coefficient matrix. In this sense, systems containing radioactive tracers are unusual because the eigenvalues are easily found. Commonly they must be discovered by trial and error.

With this basis, the k_{ij} can easily be calculated (Cussler, 1976):

$$k_{11} = \frac{[F^*]}{[F^*] + [F]} K_L + \frac{[F]}{[F^*] + [F]} K_L^* \quad (16)$$

$$k_{12} = \frac{[F^*]}{[F^*] + [F]} (K_L - K_L^*) \quad (17)$$

Combination of Equations (13), (16), and (17) now yields

$$\frac{1}{a[F^*]} \frac{d[F^*]}{dt} = \left\{ K_L^* + (K_L - K_L^*) \frac{[F(\text{sat})] - [F]}{[F(\text{sat})] + [F]} \right\} \quad (18)$$

The quantity in braces represents the apparent overall mass transfer coefficient in a partially saturated solution. It is clearly a function of concentration. Since it can be measured experimentally, part of the solubilization theory is checked below.

EXPERIMENTAL

All chemicals were used as received. Sodium dodecyl sulfate (BDH Chemicals) was 99% pure by surface tension. Lauric (Aldrich), palmitic (Fisher), stearic (Eastman), and benzoic (Aldrich) acids were 99.5, 95, 97, 99.9% pure, respectively. ^{14}C tagged samples of these four acids were supplied by New England Nuclear and were at least 97% pure by thin layer chromatography.

All solubilization experiments were made by the rotating disk method (Levich, 1962; Chan, 1976). Disks of a mixture of tagged and untagged fatty acids 2.5 cm in diameter were made in a pellet press. These disks contained 10 μCi/g of radioactivity. They were then attached to a Bodine Gearmotor, Model 541, controlled by a Bodine D-C Motor speed controller, Model 902. To start an experiment, the disk was placed in a 400 cm^3 beaker containing detergent solution which had been prepared by weight. Samples of 1 cm^3 of the detergent solution were taken at various times. The radioactivity in these samples was determined by a Searle Analytic Isocap/300 liquid scintillation counter. The kinematic viscosity of these detergent solutions was measured with Cannon-Ubbelohde viscometers.

This procedure was tested by measuring the dissolution of benzoic acid in water, which is known to be diffusion controlled (Eisenberg et al., 1955). The theoretical expression for this process is (Levich, 1962)

$$\frac{kR}{D} = 0.61 \left(\frac{R^2\omega}{\nu} \right)^{1/2} \left(\frac{\nu}{D} \right)^{1/3} \quad (19)$$

The result here is (Chan, 1976)

$$\frac{kR}{D} = 0.65 \left(\frac{R^2\omega}{\nu} \right)^{1/2} \left(\frac{\nu}{D} \right)^{1/3} \quad (20)$$

Thus, the accuracy should be about 7%, although the precision may be higher.

RESULTS AND DISCUSSION

The experiments are again best discussed in terms of the two situations studied, initial solubilization and solubilization in partially saturated solutions. The results for initial solubilization are exemplified by those for lauric acid given in Table 2. Similar tables for palmitic and stearic acids are given elsewhere (Chan, 1976). In all experiments, the final concentration is always less than 10% of saturation.

The theory for initial solubilization developed above assumed that mixed micelle desorption and diffusion [steps (4) to (5) in Figure 1] are rate controlling. This assumption led to three predictions [Equation (7)]:

1. The reciprocal of the solubilization rate should vary linearly with the reciprocal of solubility.

2. The intercept on this plot should be independent of flow.

TABLE 2. INITIAL SOLUBILIZATION OF LAURIC ACID IN SODIUM DODECYL SULFATE (SDS) AT 37°C*

Concentration sodium dodecyl sulfate	Solubility lauric acid	Kinematic viscosity	Reynolds number, dissolution rate†
0.80	1.92	0.735	1 149, 1.96; 2 298, 2.93; 4 596, 4.25; 6 894, 5.88
1.00	2.50	0.748	1 130, 2.45; 2 259, 3.66; 4 518, 5.40; 6 777, 6.82
1.50	3.94	0.782	1 080, 3.70; 2 160, 4.85; 4 320, 7.26; 6 480, 9.65
2.00	5.30	0.820	1 034, 4.98; 2 067, 6.87; 4 135, 9.03; 6 202, 11.2; 8 269, 12.3
3.00	8.33	0.883	956, 7.22; 1 913, 9.64; 2 869, 10.6; 3 826, 11.5; 7 651, 15.2
4.00	11.1	0.949	890, 9.2; 1 780, 10.8; 3 560, 13.2; 5 340, 15.2; 7 120, 16.5
8.00	23.2	1.263	666, 14.3; 1 332, 18.7; 2 664, 21.9; 3 996, 26.0

* Units: concentration [=] g (100 g solution)$^{-1}$; solubility lauric acid [=] 10^{-3} g cm^{-3}; kinematic viscosity [=] 10^{-2} cm^2 s^{-1}; time [=] hr; amount dissolved [=] 10^{-3} g; dissolution rate [=] 10^{-3} g cm^{-2} hr^{-1}.

† The odd values in the series are the Reynolds numbers, and the even values are the dissolution rates.

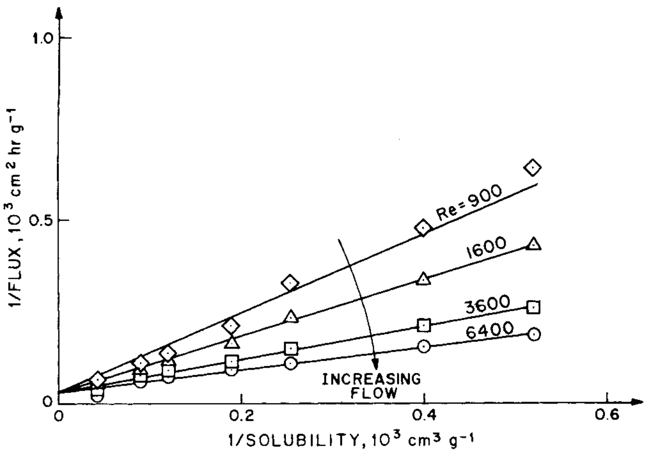

Fig. 3. Solubilization kinetics for lauric acid. The common intercept is consistent with steps (4) to (5) in Figure 1 controlling dissolution.

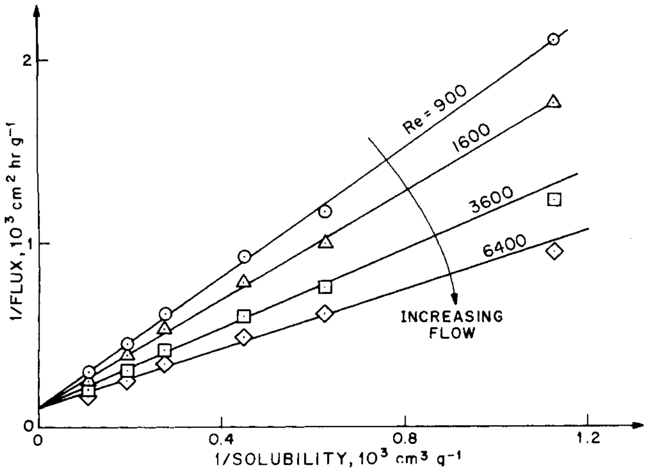

Fig. 4. Solubilization kinetics of palmitic acid. These results support the hypothesis that steps (4) to (5) in Figure 1 are rate controlling.

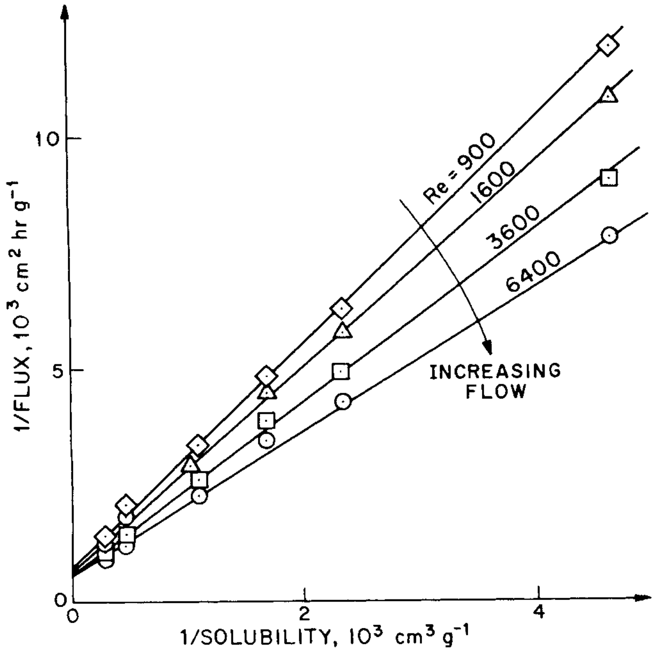

Fig. 5. Solubilization kinetics of stearic acid. These data also support the hypothesis that mixed micelle desorption and diffusion are rate controlling.

3. The slope of this plot should be proportional to the reciprocal of the square root of the disk Reynolds number.

If steps (4) to (5) do not control, this behavior will not be observed (Table 1).

The first two predictions are verified in Figures 3 to 5. The reciprocal of the solubilization rate does vary linearly with $1/[F(\text{sat})]$. The intercept on this plot is not a function of Reynolds number.

The third prediction is verified by the results in Figure 6. However, these data are not completely consistent with the physical picture given above. As shown in Equation (7), the intercept of this plot is a measure of micelle desorption. For palmitic and stearic acids, this intercept is positive and so makes physical sense; for lauric acid, the intercept is negative, suggesting that the mechanism in Figure 1 does not always hold.

These results strongly indicate that steps (3) and (4) in Figure 1 control solubilization. In more physical terms, these results show that mixed micelle desorption and diffusion commonly control rates of solubilization. Micelle diffusion to the surface, micelle adsorption on the surface, and surface reaction [steps (1) to (3)] are much less important. To see why these conclusions make chemical sense, each step in Figure 1 must be considered in greater detail.

The two diffusion steps (1) and (5) both depend on the properties of the solution but not on the properties of fatty acid surface (Tao et al., 1974). When the fluid flow across the surface is well defined, as in the case with the rotating disk, the speed of these steps can be calculated a priori from fluid mechanics. These steps differ only because of the different diffusion coefficients of the pure detergent micelle and of the mixed micelle.

Interestingly, the diffusion of mixed micelles and pure detergent can differ by a factor of five, even though the micelle molecular weights differ by much less (Sehlin et al., 1975). While no exact explanation for this difference is known, one reasonable hypothesis is that mixed micelles diffuse intact but that pure detergent diffuses both as micelles and as single molecules. One consequence in pure detergent solutions is that the diffusion coefficient varies very little with the solution's viscosity.

In contrast, the adsorption and desorption steps in Figure 1 may be radically different. Detergent adsorption may involve free detergent molecules as well as intact micelles. Since an individual detergent molecule is singly charged and requires only a small free surface for adsorption, it probably adsorbs easily and rapidly. On the other hand, aggregated detergent molecules will be multiply charged and can require a much larger area for adsorption. They will adsorb more slowly than the monomers.

Unlike adsorption, desorption probably occurs as mixed micelles. The fatty acid is much more soluble in detergent solution than in water. In other words, if fatty acid molecules are present, they will mainly be confined within the micelles. While these mixed aggregates may have a somewhat different composition near the surface than in the bulk solution, they will be large and multiply charged. Such unwieldy species will desorb slowly. These chemical considerations suggest that adsorption will be faster than desorption, consistent with our results.

Our experiments also show that the surface reaction [step (3) in Figure 1] occurs more rapidly than the desorption. However, these experiments do not elucidate the nature of the chemical species involved. The work of Lawrence and co-workers (1961) strongly indicates that detergent reactions often involve liquid crystals as intermediates. This may well be the case here.

The theory for solubilization in partially saturated solutions carefully distinguished between the parallel mech-

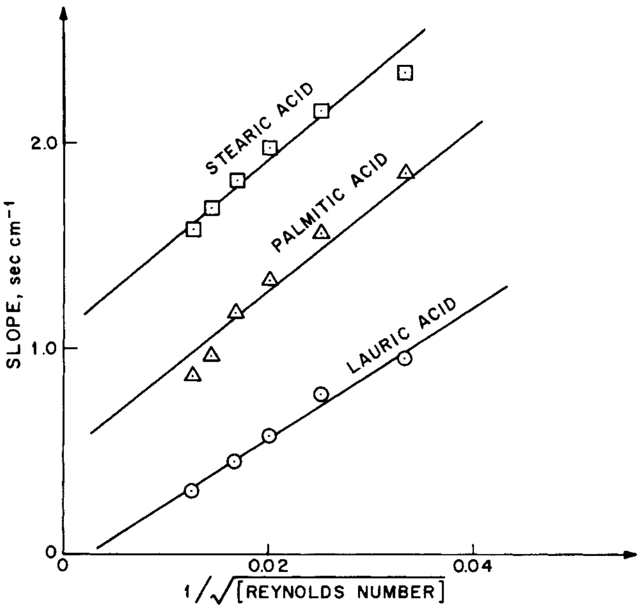

Fig. 6. The variation of solubilization with flow. The slopes shown, from Figures 3 to 5, show a variations with Reynolds number consistent with that predicted by Equation (7).

Table 3. Solubilization of Tagged Lauric Acid in 4% Sodium Dodecyl Sulfate Solutions Partially Saturated with Untagged Lauric Acid*†

Percent saturation**	Kinematic viscosity	Reynolds number, dissolution rate of tagged acid††
30	1.00	420, 0.265; 840, 0.322; 1 679, 0.37; 2 518, 0.42; 3 358, 0 504; 6 716, 0.656
60	1.065	396, 0.127; 793, 0.159; 1 586, 0.209; 2 379, 0.243; 6 344, 0.342
90	1.124	376, 0.047; 751, 0.065; 1 503, 0.096; 3 005, 0.116; 6 011, 0.136

* Temperature, 37°C.

† Units: kinematic viscosity [=] 10^{-2} cm^2 s^{-1}; time [=] hr; amount dissolved [=] 10^{-7} g; dissolution rate [=] 10^{-7} g cm^2 hr^{-1}.

** Because there are $6.40 \cdot 10^{-6}$ tagged acid/g total acid in the disk, values for 0% saturation can be found from Table 2.

†† The odd values in the list are the Reynolds numbers; the even values are the dissolution rates.

anisms in Figures 1 and 2. The chief theoretical prediction, given in Equation (18), is that the dissolution rate of tagged material is proportional to the degree of unsaturation divided by the sum of the concentration at saturation and the actual concentration present. The dissolution rate is not proportional to the degree of unsaturation alone.

This prediction is verified by the data in Table 3 and Figure 7. By comparing this figure with Equation (18), we see that the slope on this plot corresponds to $(K_L - K_L^*)$ and that the intercept corresponds to K_L^*. Accordingly, K_L is almost an order of magnitude larger than K_L^*. In other words, the mechanism shown in Figure 1 takes place about ten times faster than that shown in Figure 2. These results are consistent with the suggestions above that diffusion and reaction for mixed micelles are slower than for pure detergent micelles. The mechanism in Figure 1 includes two diffusion steps for mixed micelles; that in Figure 1 involves only one. The mechanism in Figure 2 includes adsorption of a mixed (untagged) micelle and desorption of a mixed (tagged) micelle, but that in Figure 1 only includes mixed micelle desorption.

On a broader scale, these results illustrate potential dangers in the careless interpretation of experiments with

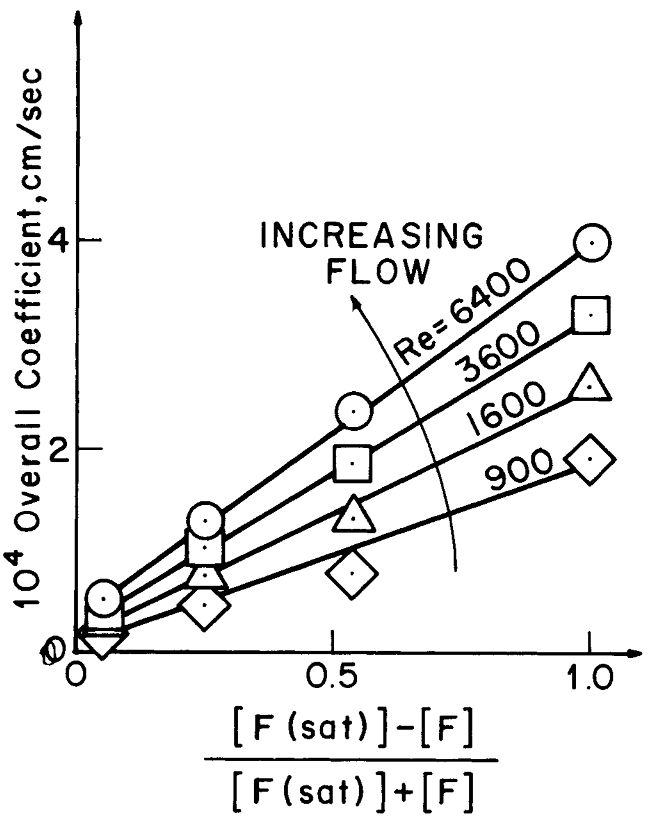

Fig. 7. Solubilization in partially saturated solutions. This plot and Equation (18) give experimental evidence of the different mechanisms in Figures 1 and 2.

radioactive tracers. Such tracers give results identical to the binary case only in solutions which contain negligible amounts of untagged material. While these effects were known to be small in diffusion, they can be considerably larger in mass transfer, as the data here show. These effects may be particularly significant in studies of tertiary oil recovery which use both detergents and tracers.

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NOTATION

a = surface area per volume, 1/cm
$[B]$, $[B_i]$, $[B_s]$ = concentration of detergent micelles in bulk solution, at interface, and on the surface, respectively, moles/cm^3
D = binary diffusion coefficient
D^* = tracer diffusion coefficient
D_{ij} = ternary diffusion coefficients
$[F]$, $[F(\text{sat})]$ = concentrations of untagged fatty acid and of untagged fatty acid at saturation, g/cm^3
$[F^*]$, $[F^*(\text{sat})]$ = concentrations of tagged fatty acid and of tagged fatty acid at saturation, g/cm^3
k_i = forward reaction rate constant for step i
k_{-i} = reverse reaction rate constant for step i
k_{ij} = ternary mass transfer coefficients, cm/s

K_L = overall mass transfer coefficient for initial dissolution
K_L^* = overall mass transfer coefficient for exchange in saturated solution
K_i = equilibrium constant of step i
K_m = combined rate constant Table 1)
$[M]$, $[M_i]$, $[M_s]$ = concentration of mixed micelles in the bulk solution, at the interface, and on the surface, respectively, moles/cm^3
n = constant, equal to $(d[F]/dt)/(d[M]/dt)$
R = radius of rotating disk
Re = Reynolds number
$[S]$ = free sites for micelle adsorption
$[S_o]$ = total sites
t = time
$v_{\max}$ = combined rate constant (Table 1)
ξ = constant, equal to $[F(\text{sat})]/[B]$
ν = kinematic viscosity
ω = angular velocity of rotating disk

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An Analysis of Slow Reactions in a Porous Particle

A one-parameter volume reaction model is developed by a simplified analytical approach to describe reaction of a gas and a consumable solid in a porous particle. In this model, a modified Thiele modulus M is introduced to take into account the effect of solid reactant depletion during the reaction.

Experimental results of an isothermal carbon-carbon dioxide reaction in the temperature range from 1 130° to 1 365°K under atmospheric pressure were analyzed by the working diagrams derived from this model. A satisfactory agreement between the experimental results and those predicted by the model indicated the applicability of this model.

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SCOPE

A number of models dealing with the reaction between a gas and a consumable solid in a porous particle have been reported. Some examples are the unreacted-core shrinking model, the homogeneous model, the zone-reaction model, and the structural model. However, the applicability of the models is often limited, either owing to simplifications or to assumptions made in deriving the models. This is especially true in reference to the solid structure. Hence, the objective of this study is to develop a simple volume reaction model that can be used to simulate the overall performance of the heterogeneous reaction. Experiments were performed to verify the validity of this model.