The Effect of Surfactant Structure on the Rate of Oil Solubilization into Aqueous Surfactant Solutions[1]

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Reduced washing temperatures decrease the rate of the various processes in a laundry cleaning cycle. This implies that fast acting detergents are needed if acceptable washing performance is to be maintained within a realistic period of time. An important factor is the rate of oily soil removal which, among other things, is a function of the molecular structure of the surfactants used in the detergent. To support the selection of proper surfactants we have established relationships between chemical structure and rate of oil solubilization for a series of alkylarenesulfonates with various alkyl chain lengths, points of attachment of the phenyl group at the alkyl chain, and aromatic substitution patterns. It is shown that oil solubilization kinetics are very sensitive to the geometry of the surfactant structure: for a set of isomeric alkylarenesulfonates the rate of oil solubilization can be made to vary by more than an order of magnitude by changing the substitution pattern around the aromatic ring. The results offer a predictive tool for the design of molecules with the proper surface activity under a wide set of experimental conditions.

Reduced washing temperatures slow down the various processes involved in the laundry cleaning process. Adjustments of the composition and nature of the surfactant components in laundry products may have to be considered to maintain satisfactory washing performance within a reasonable period of time. An important kinetic aspect of the washing process is the rate of removal of oily stains.

Several mechanisms have been proposed for the solubilization of oils into micelles. One mechanism involves dissolution of the solubilizate into the aqueous phase, followed by adsorption onto the micellar surface and subsequent incorporation. This mechanism is advocated by Kahlweit (1), Volkov (2), Arytyunyan (3) and Schwuger (4), although each favors a different step as the rate-limiting one. A second mechanism in essence consists of diffusion of the micelle toward the oil droplet, followed by demicellization, adsorption of monomeric surfactant molecules onto the oil/water interface, incorporation of solubilizate and desorption of the "swollen" micelle. Chan (5) and Carroll (6) support this mechanism. The difference in views about the mechanism of solubilization is not in the least caused by the use of different solubilizates and surfactants. Even more complicated to interpret are data obtained in the presence of a third (solid) phase such as fabrics (7), polyester films (8,9) or aluminum foil (10).

This work deals with the relationship between surfactant structure and rate of oil solubilization, using anionic alkylarenesulfonates. The emphasis will be put on phenyl positioning, aromatic substitution pattern and alkyl chain length of the surfactant. Furthermore, the effects of external experimental parameters such as temperature and concentrations will be discussed.

EXPERIMENTAL

Isomerically pure model sodium alkylarenesulfonates were synthesized following known procedures (11). The other alkylarenesulfonates were prepared from commercial olefins (Shell Higher Olefin Process) via a proprietary alkylation process and standard SO_3 sulfonation. Dobanol ethoxylates are nonionics based on synthetic alcohols; they are specified with a code in which the first number refers to the alkyl chain length and the last represents the number of ethylene oxide units, e.g. Dobanol 25-9 is based on C_{12}-C_{15} alcohols condensed with nine moles of EO.

The method used for the determination of the rate of oil solubilization, which was developed by Benson (Westhollow Research Center, Houston, Texas), consists of determining the decrease in turbidity of a macroemulsion of a model oil upon addition of a surfactant. This procedure gives consistent and reproducible data, albeit the turbidity is not an intrinsic parameter because it relates to experimental conditions. Injection of 25 μl of a model hydrocarbon containing 5% w Dobanol 45-3 into 50 ml water produces a turbid macroemulsion upon stirring with a nonaerating IJstral stirring device. At t_0, a concentrated surfactant solution is injected and the decrease in turbidity is followed with a Metrom E616 Photometer equipped with fiber optics at a wavelength of 650 nm. The turbidity data are sampled and the time elapsed to reach, e.g., 75 and 50% of the initial turbidity recorded. This yields t_{75} and t_{50} with the corresponding turbidities T_{75} and T_{50}. The solubilization rate is then arbitrarily defined as:

$$\text{rate} = (T_{75} - T_{50})/t_{75} - t_{50})$$

with a rate constant $K_m(50/75)$:

$$K_m(50/75) = \left(\frac{-2}{T_{75} + T_{50}} \right) \left(\frac{T_{75} - T_{50}}{t_{75} - T_{50}} \right)$$

Occasionally, $K_m(90/100)$ is used. K_m is a pseudo rate constant because the turbidity is not linearly proportional to the amount of unsolubilized oil.

In the turbidity decay curves the starting turbidity (T_{100}) is normalized to an arbitrary value of one.

To establish standard experimental conditions allowing a clear discrimination between the effects of different surfactant structures on K_m, we carried out some initial experiments with two anionic surfactants, namely isomerically pure p-(3-dodecyl) benzenesulfonate (3-Φ-C_{12}-LAS) and $C_{11\text{-}12}$-alkyl-o-xylenesulfonate ($C_{11\text{-}12}$-o-LXS). With these anionics as the only surfactant, no decrease in turbidity was observed,

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which may well be attributed to the low Krafft point of the pure anionics (for 3-Φ-C_{12}-LAS: 4 C and C_{11-12}-o-LXS: 28 C). A nonionic is required to obtain a measurable solubilization rate. For Dobanol 25-9 the anionic/nonionic ratio has been fixed arbitrarily at 1. The selection of the nonionic was based on the data in Figure 1, which shows the effect of chain length and ethylene oxide number of the nonionic. The effects of calcium ions and surfactant concentration are shown in Figures 2 and 3, respectively. For standard conditions both concentrations were set at 10 mmol/l (at the plateau part of the curves). On the basis of these data the following standard experimental conditions have been selected: Oil phase, n-hexadecane containing 5% w of Dobanol 45-3; amount of oil, 500 μl/l; temperature, 25 C; [Ca^{2+}], 10 mmol.l^{-1}; surfactant, anionic/Dobanol 25-9 (equimolar); and total surfactant concentration, 10 mmol.l^{-1}, well above the CMC (12).

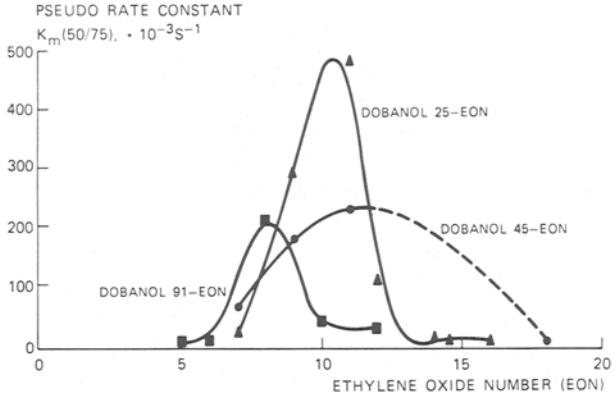

FIG. 1. Effect of alkyl chain length and ethylene oxide number of alcohol ethoxylates on the pseudo rate constant of n-hexadecane solubilization into C_{11-12}-o-LXS/Dobanol ethoxylate solutions (Temp. 25 C; [Ca^{2+}] = 10 mmol.l^{-1}; [C_{11-12}-o-LXS] = 5 mmol.l^{-1}; [nonionic] = 5 mmol.l^{-1}).

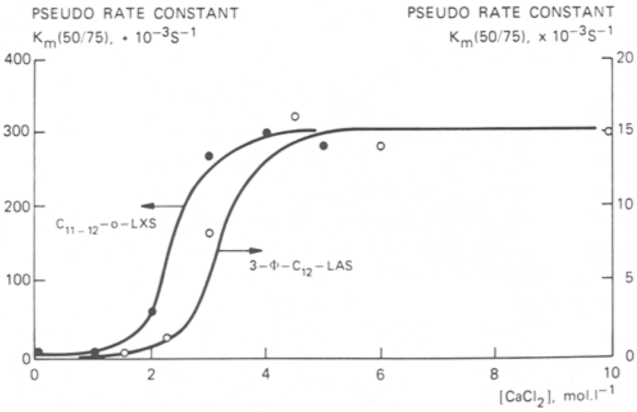

FIG. 2. Effect of calcium ion concentration on the pseudo rate constant of n-hexadecane solubilization into alkylarenesulfonate/Dobanol 25-9 solutions (3-Φ-C_{12}-LAS: temp. 40 C; [anionic] + 7.2 mmol.l^{-1}; [Dobanol 25-9] + 4.1 mmol.l^{-1}; C_{11-12}-o-LXS: temp. 25 C; [anionic] + 5 mmol.l^{-1}; [Dobanol 25-9] + 5 mmol.l^{-1}).

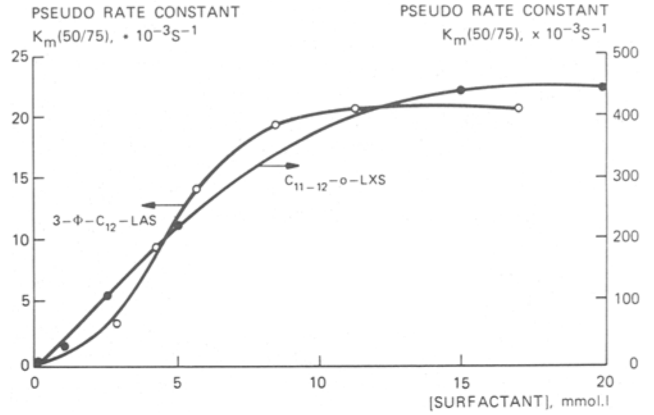

FIG. 3. Effect of total surfactant concentration on the pseudo rate constant of n-hexadecane solubilization into alkylarenesulfonate/Dobanol 25-9 solutions (3-Φ-C_{12}-LAS: temp. 40 C; [Ca^{2+}] = 10 mmol.l^{-1}; [anionic]/[nonionic] = 1; C_{11-12}-o-LXS: temp. 25 C; [Ca^{2+}] = 10 mmol.l^{-1}; [anionic]/[nonionic] = 1).

RESULTS AND DISCUSSION

Effect of molecular structure of alkylarenesulfonate. Three structural elements have been tested for their effect on the rate of n-hexadecane solubilization viz. phenyl positioning, aromatic substitution pattern and alkyl chain length.

Phenyl positioning. The effect of the point of phenyl attachment to the alkyl chain was determined with two series of isomerically pure alkylbenzenesulfonates viz. p-(x-decyl)-benzenesulfonate (x-Φ-C_{10}-LAS) and p-(x-dodecyl)-benzenesulfonate (x-Φ-C_{12}-LAS). Changing the molecular geometry from rod shaped to ball shaped by moving the phenyl group toward the middle of the alkyl chain causes a pronounced increase in the rate of solubilization. The pseudo rate constants of solubilization have been listed in Table 1; the turbidity decay curves for x-Φ-C_{10}-LAS are depicted in Figure 4.

TABLE 1

Effect of Phenyl Positioning on the Pseudo Rate Constant of n-Hexadecane Solubilization into x-Φ-C_n-LAS/Dobanol 25-9 Solutions[a]

x-Φ-C_n-LAS	Pseudo rate constant $K_m(90/100)$, $*10^{-3}$ s^{-1}
3-Φ-C_9	0.15
2-Φ-C_{10}	0.4
3-Φ-C_{10}	0.8
5-Φ-C_{10}	2.9
2-Φ-C_{12}	2.2
3-Φ-C_{12}	8.3
4-Φ-C_{12}	17.2
5-Φ-C_{12}	50.1
6-Φ-C_{12}	70.2

[a] Temperature: 40 C; 3 mmol.l^{-1} Ca^{2+}; total surfactant concentration: x-Φ-C_{10}-LAS/Dobanol 25-9: [x-Φ-C_{10}-LAS] = 3.7 mmol/l, [Dobanol 25-9] = 4.1 mmol/l – x-Φ-C_{12}-LAS/Dobanol 25-9: [x-Φ-C_{12}-LAS] = 3.1 mmol/l, [Dobanol 25-9] = 4.1 mmol/l.

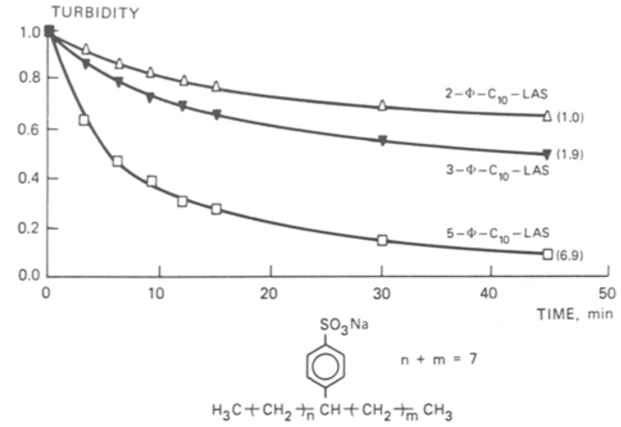

FIG. 4. Effect of phenyl attachment of p-(x-decyl)benzenesulfonate (x-Φ-C_{10}-LAS) on n-hexadecane solubilization. (Hexadecane, 40 C; [Ca^{2+}] = 3 mmol.1^{-1}; [Dobanol 25-9] = 5 mmol.1^{-1}, Relative pseudo rate constants indicated in parentheses.)

Aromatic substitution pattern. The influence of the aromatic substition pattern was studied with alkylbenzenesulfonate (LAS), alkyl-p-xylenesulfonate (p-LXS), alkyltoluenesulfonate (LTS) and alkyl-o-xylenesulfonate (o-LXS) as the anionic components. Each consists of a series of chain-length and phenyl-position isomers as determined by the manufacturing procedure. Both LAS and p-LXS are monoisomeric in terms of aromatic substitution, but o-LXS and LTS are composed of a mixture (13). The most abundant isomer is shown.

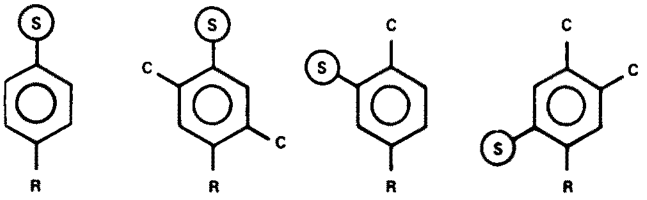

TABLE 2

Effect of Aromatic Substitution Pattern on the Pseudo Rate Constant of n-Hexadecane Solubilization into Alkylarenesulfonate/Dobanol 25-9 Solutions[a]

Alkylarenesulfonate	Pseudo rate constant $K_m(50/75)$, *10^{-3} s^{-1}
C_{11-12}-LAS	18
C_{13-14}-LAS	9.4
C_{8-10}-LTS	10
C_{11-12}-LTS	61
C_{13-14}-LTS	16
C_{8-10}-p-LXS	18
C_{11-12}-p-LXS	40
C_{13-14}-p-LXS	0.9
C_{8-10}-o-LXS[b]	150
C_{11-12}-o-LXS[b]	510 (280)[c]
C_{13-14}-o-LXS[b]	-[d]

[a] Temperature: 60 C; 10 mmol.1^{-1} Ca^{2+}; [anionic] = 5 mmol.1^{-1}; [Dobanol 25-9] = 5 mmol/1.
[b] Based on 95% 4-alkyl-1,2-dimethylbenzene (13).
[c] Figure in parentheses at 25 C.
[d] No reduction in turbidity observed.

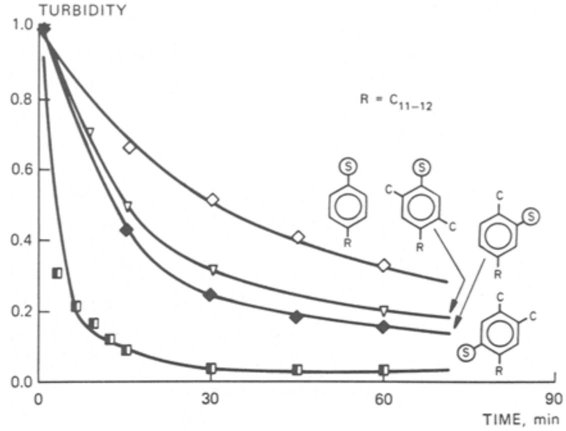

FIG. 5. Effect of aromatic substitution pattern of alkylarenesulfonate on n-hexadecane solubilization. (Hexadecane, 60 C; [Ca^{2+}] = 10 mmol.1^{-1}; [anionic] = 5 mmol.1^{-1}; [Dobanol 25-9] = 5 mmol.1^{-1}).

The turbidity decay curve for n-hexadecane solubilization by surfactant systems containing these alkylarenesulfonates is shown in Figure 5. It is evident that the solubilization rate (Table 2) is favorably affected by the close proximity of the polar sulfonate group and the lipophilic chain. The rate decreases in the order:

$$\text{o-LXS} >> \text{LTS} > \text{p-LXS} \sim \text{LAS}.$$

In o-LXS, 2-alkyl-4,5-dimethyl-benzenesulfonate is supposed to be the isomer that makes a substantial contribution to the rate of solubilization. This has been confirmed in an experiment with isomerically pure 2-(3-dodecyl)-4,5-dimethylbenzenesulfonate, which gave a pseudo rate constant [$K_m(50/75)$] of 370 $10^{-3}s^{-1}$ at 25 C as compared to a value of 280 10^{-3} s^{-1} (experimental conditions as given in Table 2) for the isomer mixture in which 2-C_{11-12}-alkyl-4,5-dimethylbenzenesulfonate constitutes ca. 75% (13). Thus, the linear alkylarenesulfonates (LAS and p-LXS) contribute less to the rate of solubilization than the ballshaped structures.

Alkyl chain length. The effect of alkyl chain length on the rate of solubilization by alkylarenesulfonates is shown in Tables 1 and 2. A graphic presentation (Fig. 6) reveals that the optimum chain length for maximum rate is C_{11}-C_{12} with n-hexadecane. The turbidity decay curve of the isomerically pure 3-Φ-C_n-LAS compounds shows a marked increase in rate by increasing the chain length from C_9 to C_{12} (Fig. 7).

Mechanistic considerations. Two main mechanistic pathways have been considered for oil solubilization. Dissolution of oil is unlikely to be the rate-limiting step because a strong contribution of the effect of surfactant structure was found. Moreover, the rate of n-hexadecane solubilization proved to be independent of the amount of oil supplied. Furthermore, a pronounced dependence of the rate on surfactant concentration was found (Fig. 3). When plotting these data as $1/K_m$ versus 1/(surfactant), a positive intercept with the $1/K_m$-axis is observed (e.g., Fig. 8).

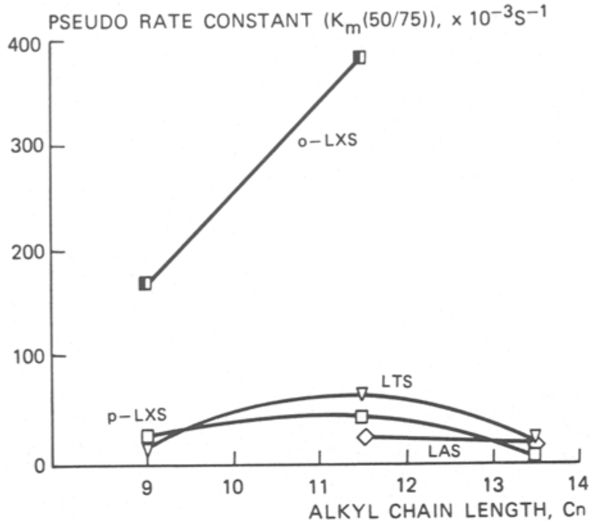

FIG. 6. Effect of alkyl chain length (C_n) of alkylarenesulfonates on the pseudo rate constant of hexadecane solubilization into an aqueous phase. (Temp. 60 C; $[Ca^{2+}]$ = 10 mmol.l^{-1}; [anionic] = 5 mmol.l^{-1}; [Dobanol 25-9] = 5 mmol.l^{-1}.)

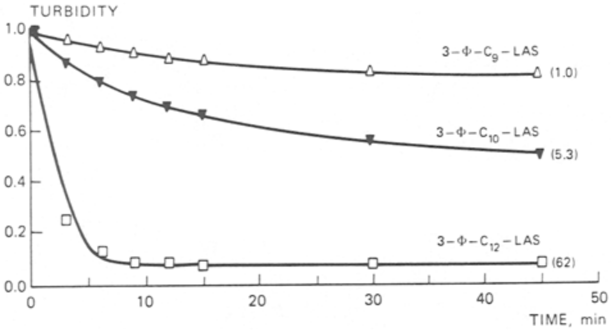

FIG. 7. Effect of alkyl chain length of p-(3-alkyl) benezenesulfonate (3-Φ-C_n-LAS) on n-hexadecane solubilization. (Hexadecane, 40 C; $[Ca^{2+}]$ = 3 mmol.l^{-1}; [anionic] = 5 mmol.l^{-1}; [Dobanol 25-9] = 5 mmol.l^{-1}. Relative pseudo rate constants indicated in parentheses.)

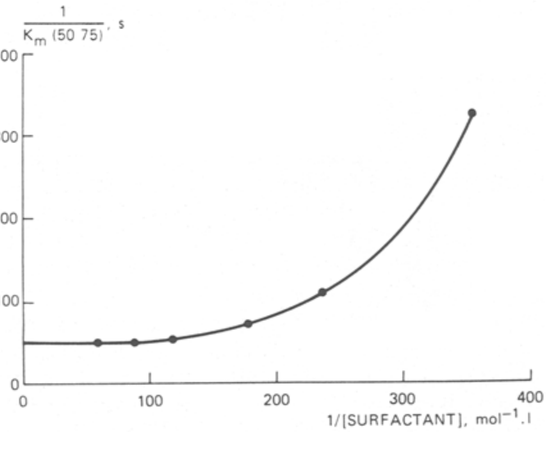

FIG. 8. Reciprocal of the pseudo rate constant versus the reciprocal of the concentration of the 3-Φ-C_{12}-LAS/Dobanol 25-9 blend. (For conditions see Fig. 2.)

TABLE 3

IFT Between n-Hexadecane/Water in the Presence of Isomerically Pure Alkylbenzenesulfonate (Dobanol 25-9 blends)[a]

Surfactant	CMC[b]	Surfactant mmol.l^{-1}	γ, mN.m^{-1}	γ, mN.m^{-1}[c]
2-Φ-C_{10}-LAS	4.63	5.3	9.0	
2-Φ-C_{10}-LAS		8.85	9.1	8.5
3-Φ-C_{10}LAS	6.04	8.7	7.9	
5-Φ-C_{10}-LAS	8.01	8.3	6.6	6.0
2-Φ-C_{10}-LAS/Dobanol 25-9		2.2/2.2	7.1	
3-Φ-C_{10}-LAS/Dobanol 25-9		2.2/2.2	6.6	
5-Φ-C_{10}-LAS/Dobanol 25-9		2.1/2.1	6.3	

[a] Temperature 25 C.
[b] Ref. 14.
[c] After 2 days aging.

Apparently, the rate is determined not by the bulk surfactant concentration, but rather by the concentration of the surfactant at the oil/water interface, at least in the case of the 3-Φ-C_{12}-LAS/Dobanol 25-9 blend (6). This is further supported by the fact that the hexadecane/water interfacial tension is lowest for the most active blends in the X-Φ-C_{10}-LAS series (Table 3).

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