Relationship of Soil Removal to Hydrophile-Lipophile Balance

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ABSTRACT

Concentration-detergency curves were developed for 28 soil-surfactant systems. These systems consisted of three single component soils and nonionic surfactants from two homologous series. An optimum surfactant concentration was shown to exist for each soil-surfactant system and was found to be related to the hydrophile-lipophile balance of the surfactant. From data developed, a relationship is apparent between the hydrophile-lipophile balance of the soil and the hydrophile-lipophile balance of the surfactant (of either homologous series) most effective for removing this soil. The relationship points the way for optimization of surfactant type and concentration for a specific soil based upon hydrophile-lipophile balance calculations.

INTRODUCTION

The development of a theory for the mechanism of detergency has been the purpose of many investigations. As a result of these investigations, three basic detergency mechanisms (1) for liquid soils have been recognized: emulsification, roll-back (formation of globules by oily soil in aqueous solution), and solubilization. These mechanisms operate in combinations or separately depending upon the particular system.

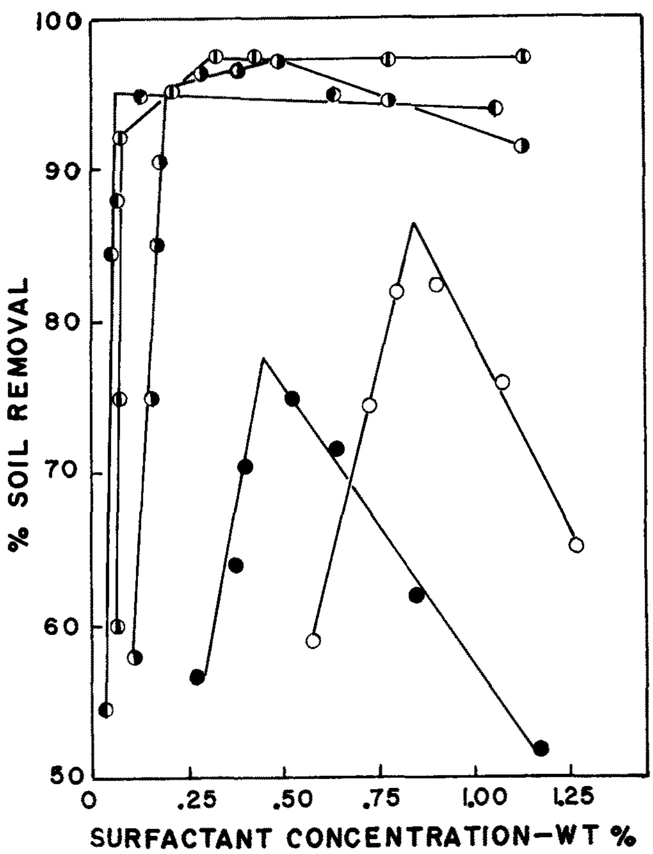

FIG. 1. Detergency of tridecanol ethoxylates using oleic acid soil. Ethylene oxide units/surfactant molecule: ○, 12; ●, 15; ◑, 20; ◐, 30; ⦶, 40.

The theory of detergency has not been developed to a state where it usually can be predicted for a given surfactant-soil system. The possibility of useful correlations existing between detergency and physicochemical factors believed to influence the above detergency mechanisms has been investigated. These physicochemical factors include micellar solubilization (2, 3), electrical forces, such as ζ potential (4), critical micelle concentration (3, 5), surface tension at critical micelle concentration (5), soil dipole moment (5), soil viscosity (5), and hydrophile-lipophile balance (HLB) of surfactant (6, 7). These references are examples only and are not intended to be complete. Correlations between the above physicochemical factors and detergency have been shown in some instances, but the application of these correlations to the selection of an efficient surfactant for a given soil is, at best, generally difficult. Indeed, the usual method of surfactant selection for a given recurring soil is a time consuming screening test or selection based upon experience without regard to close matching of soil and surfactant.

In the present study, a relationship is indicated that would enable a close match between a known soil and surfactant without the usual screening test. For each of the soil-surfactant combinations studied, it is shown that there exists an optimum surfactant concentration, which relates to the HLB of the soil and the HLB of the most effective surfactant in a homologous series.

EXPERIMENTAL PROCEDURES

Materials

Two commercial grade homologous series of nonionic

TABLE I

Description of Surfactants

Surfactant	Ethylene oxide units/ molecule (n)	Mol wt
Tridecanol ethoxylates	12	728
	15	860
	20	1080
	30	1520
	40	1960
Nonylphenol ethoxylates	15	880
	20	1100
	30	1540
	40	1980
	50	2420
	100	4620

TABLE II

Empirical Group Numbers Used for Calculating HLB[a] (10)

Group	Group number
Hydrophilic groups	
-OH	1.9
$-(OCH_2CH_2)-$	0.33
-COOH	2.1
Lipophilic groups	
$-CH-, -CH_2-, -CH_3, =CH-$	0.475

[a]HLB = hydrophile-lipophile balance.

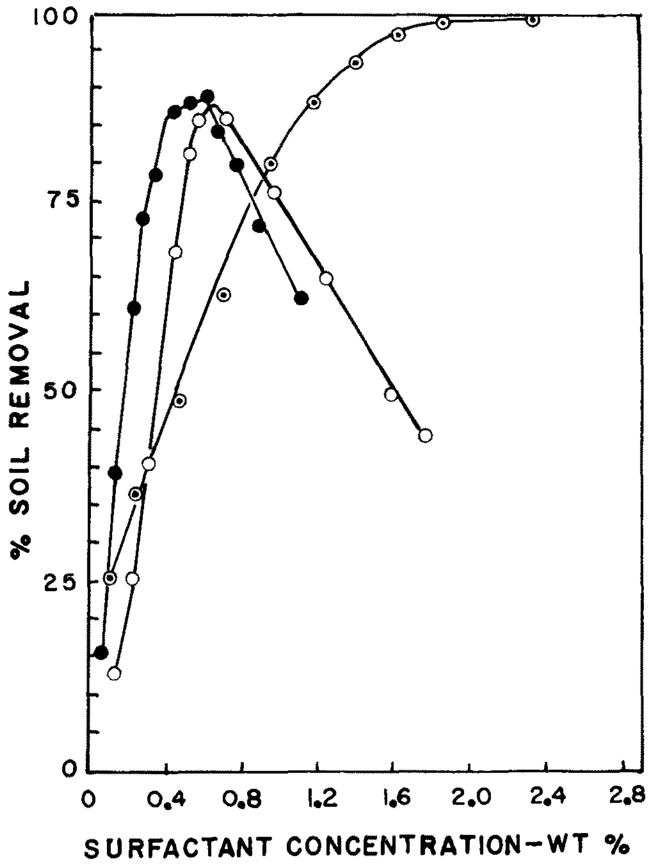

FIG. 2. Detergency of nonylphenol ethoxylates using oleic acid soil. Ethylene oxide units/surfactant molecule: ○, 15; ●, 20; ⊙, 100.

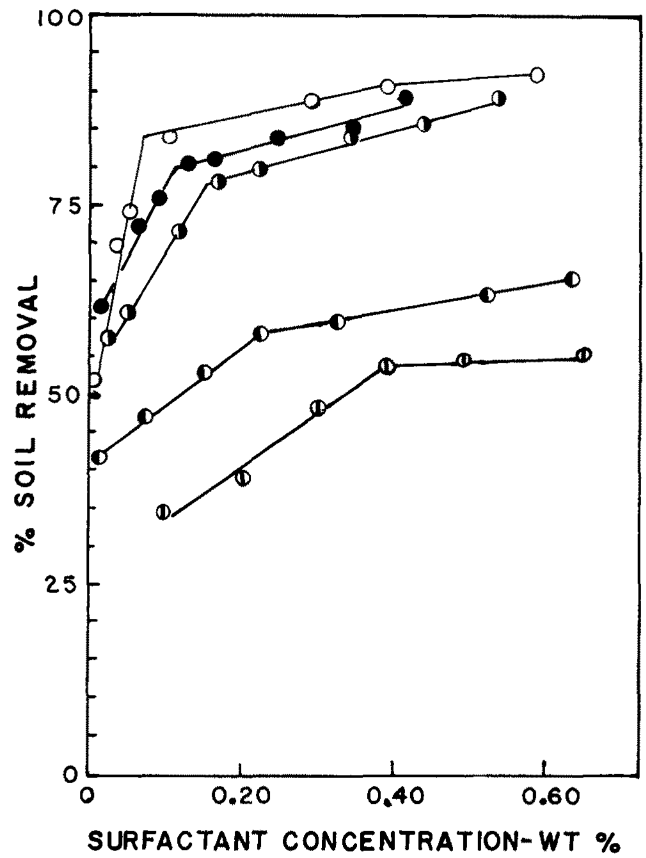

FIG. 4. Detergency of tridecanol ethoxylates using tetramethylpentadecane as soil. Ethylene oxide units/surfactant molecule: ○, 12; ●, 15; ◑, 20; ◐, 30; ⦶, 40.

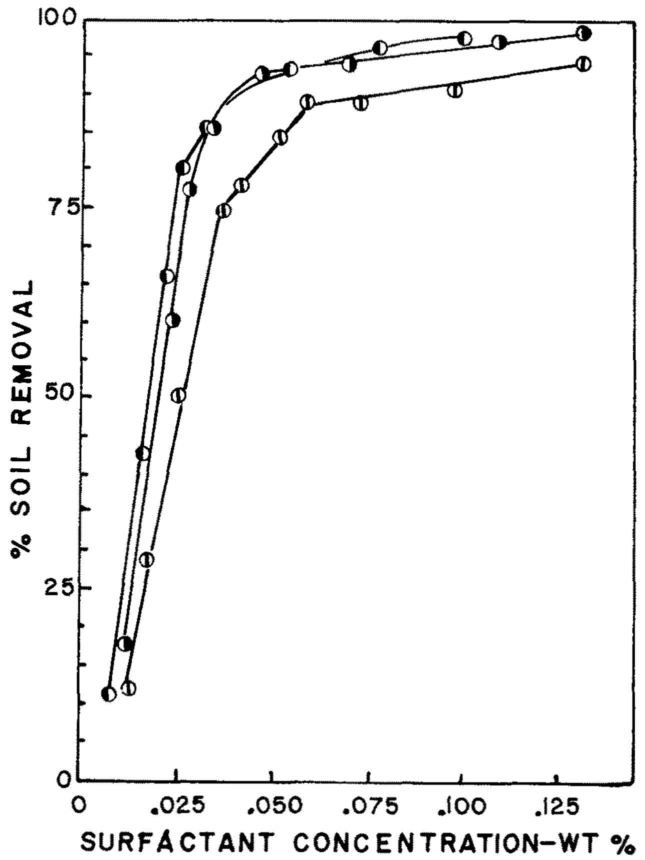

FIG. 3. Detergency of nonylphenol ethoxylates using oleic acid soil. Ethylene oxide units/surfactant molecule: ◑, 30; ◐, 40; ⦶, 50.

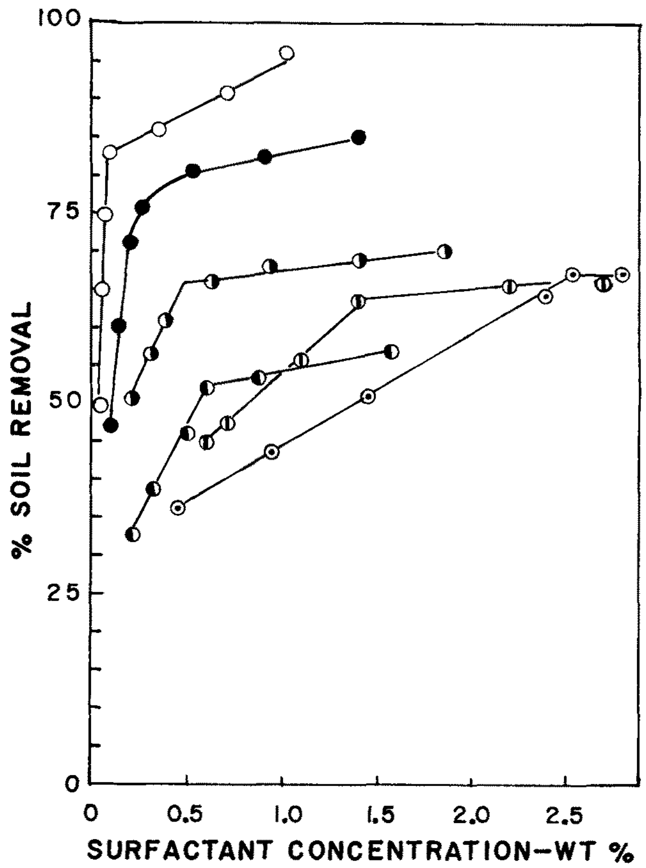

FIG. 5. Detergency of nonylphenol ethoxylates using tetramethylpentadecane soil. Ethylene oxide units/surfactants molecule: ○, 15; ●, 20; ◑, 30; ◐, 40; ⦶, 50; ⊙, 100.

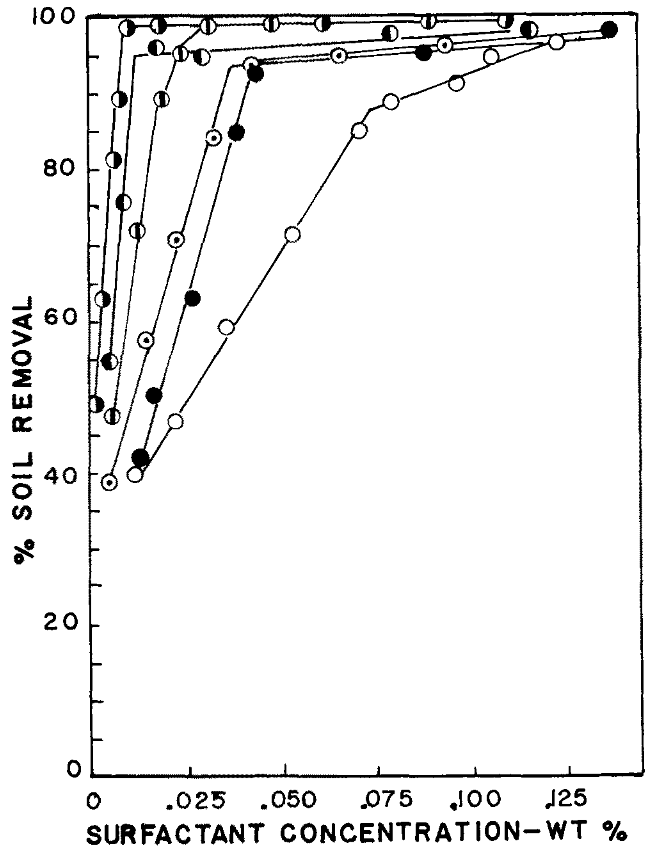

FIG. 6. Detergency of nonylphenol ethoxylates using lauryl alcohol soil. Ethylene oxide units/surfactant molecule: ○, 15; ●, 20; ◑, 30; ◐, 40; ⦶, 50; ⊙, 100.

surfactants were used. These were 100% active materials of the following classes: (A) ethoxylates of tridecanol $C_{13}H_{27}(OCH_2CH_2)_nOH$ and (B) ethoxylates of nonylphenol C_9H_{19}–C_6H_4–$(OCH_2CH_2)_nOH$. These surfactants are described further in Table I.

The three soils used in this investigation were from the group previously studied at this laboratory: oleic acid, USP, 93%; lauryl alcohol, 98%; and 2, 6, 10, 14 tetramethylpentadecane, 98%+.

Detergency Tests

The method used for determining detergency values was essentially the one developed by Mankowich (8). Test panels for use as the substrate were cut 2-½ x 2-½ in. from 1020, 18-20 gauge, cold-rolled steel. A 1/4 in. hole was placed near one corner of each panel. The test panels were polished in one direction with coarse emery cloth, then washed with acetone, wiped with paper toweling, dipped in absolute ethyl alcohol, allowed to air dry, and weighed. The cleaned test panel, suspended on a wire hook passing through the 1/4 in. hole was dipped into the liquid soil at 80 F, removed, and allowed to drain at the same temperature for 15 min. At the end of the draining period, the soiled panel was weighed and the amount of adhering soil determined.

The soiled panel then was immersed for 2 min by means of a wire hook in 1600 ml distilled water solution of the surfactant at 180 F. Immediately after removal, the panel was given two 6 sec rinses by immersion, with a 4 sec drain between rinses. Each rinse consisted of 800 ml distilled water at 80 F in a 1 liter beaker. Neither the surfactant solution nor the rinses were agitated during test. After rinsing, the panel was dried at 130 F for 1/2 hr, allowed to come to room temperature, and weighed. The panel then was cleaned with a suitable solvent (acetone, benzene, etc.), wiped with paper toweling, dipped in absolute ethyl alcohol, and air-dried. The panel was weighed and the weight of residual soil determined by difference.

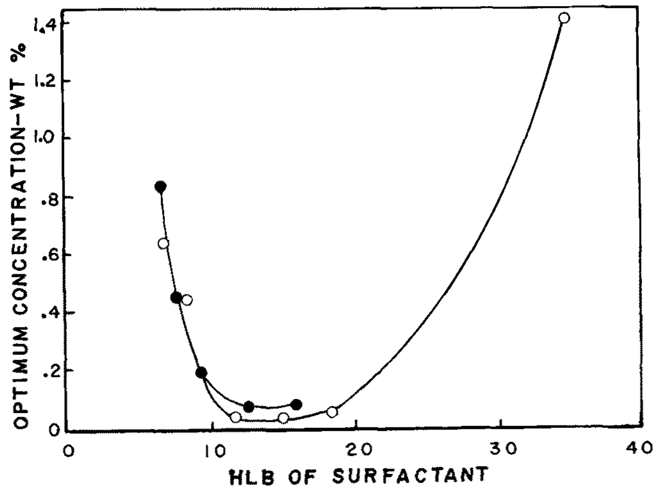

FIG. 7. Optimum surfactant concentrations for oleic acid soil: ○, nonylphenol ethyoxylates; ●, tridecanol ethoxylates. HLB = hydrophile-lipophile balance.

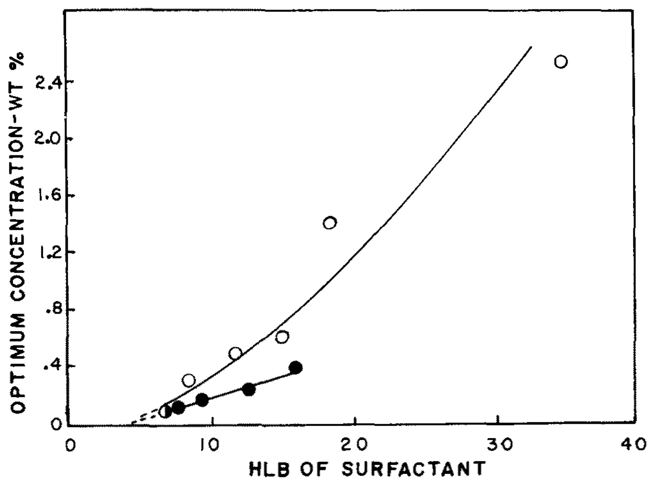

FIG. 8. Optimum surfactant concentrations for tetramethylpentadecane soil: ○, nonylphenol ethoxylates; ●, tridecanol ethoxylates. ◑, = both, nonylphenol and tridecanol ethoxylates.

DISCUSSION

Figures 1-6 show detergencies expressed as percent soil removal for a range of concentrations from near zero through the practical range for this study. Portions of some of these curves were reported earlier (9) but were not sufficiently complete to permit some important comparisons between surfactant-soil systems. It can be seen from these curves that detergency increases ca. linearly with increases in concentration until a concentration is reached where there is a sharp change in slope. After this change in slope, detergency may either increase at a lower rate or it may decrease. This concentration where the slope changes abruptly can be labeled the optimum concentration for the given surfactant-soil system, since a further increase in concentration results in, at best, a small increase in detergency. This optimum concentration, together with the corresponding value of detergency, can be used for comparing the effectiveness of different surfactants for a given soil. As will be seen later, within a given homologous series, the surfactant having the lowest optimum concentration also shows maximum soil removal and is, therefore, the most efficient surfactant for the given soil.

Optimum concentration, as defined above, is plotted against surfactant HLB in Figures 7-9. The HLB values were calculated from group numbers (Table II) using the equation:

$$HLB = \Sigma \text{ hydrophilic groups} - \Sigma \text{ lipophilic groups} + 7$$

These groups numbers and the equation were developed for use in the selection of emulsifiers (10).

The first of these figures, Figure 7, shows the curve for both the tridecanol ethoxylates and the nonylphenol ethoxylates using oleic acid (HLB = 1.0) as soil. These two curves exhibit an optimum concentration minimum and thereby demonstrate that, for this soil, the surfactant HLB can be either too high or too low. For each curve, a surfactant HLB of ca. 12 corresponds to the minimum optimum concentration. This HLB value of 12 is one of the points where maximum detergency occurs. For oleic acid soil, then, the most effective surfactant from either class has an HLB of ca. 12, whether considering soil removal or surfactant concentration.

Figure 8 shows the relationship between surfactant HLB and optimum concentration for the two surfactant series using tetramethylpentadecane as soil (HLB = 2.0). The curves have no minimum, but each one extrapolated toward the X-axis indicates that a surfactant, having an HLB value of ca. 4, would have the lowest optimum concentration. This surfactant HLB of 4 corresponds to the value of maximum soil removal. These curves for Figures 7 and 8 show that, for a given soil, the HLB corresponding to the lowest optimum concentration does not change from one surfactant series to the other.

The third soil studied was lauryl alcohol (HLB = 3.2). Since the first two soils showed each surfactant series to have the same most effective HLB for a given soil, it was considered redundant to evaluate both series with the third soil. Therefore, only the ethoxylated nonylphenol series was tested with lauryl alcohol. Figure 9 shows the relationship between surfactant HLB and optimum concentration for this soil. The minimum optimum concentration corresponds to an HLB of ca. 12, the same as for oleic acid soil. This HLB value of 12 is also in the range of maximum detergency for optimum concentrations.

The above figures show that the most effective surfactant of a given homologous series for deterging a given soil varies with the type of soil. That is, a relationship is indicated between the molecular structure of the soil and the molecular structure of the most effective surfactant. Since the HLB of the most effective surfactant decreases in going from the polar soils (oleic acid and lauryl alcohol) to the nonpolar soil (tetramethylpentadecane), it is suggested that the HLB of the most effective surfactant is related to the HLB of the soil. The data reported here indicate that the HLB for the most effective surfactant is constant for higher HLB soils. But for lower HLB soils the HLB for the

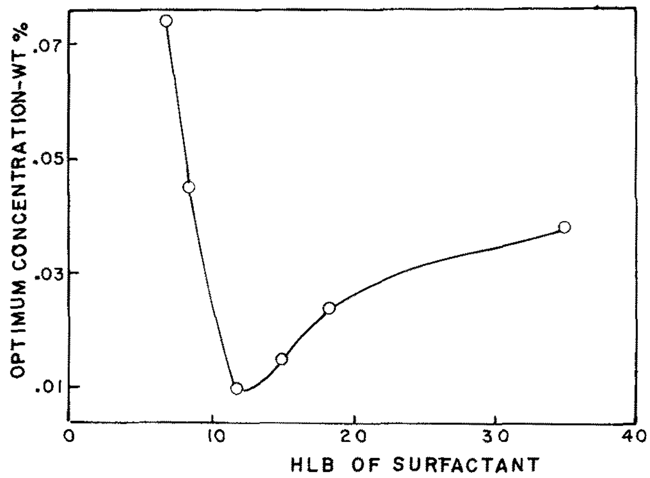

FIG. 9. Optimum concentrations for nonylphenol ethoxylates using lauryl alcohol soil.

most effective surfactant decreases with a decrease in soil HLB. This relationship for lower HLB soils is especially significant since the liquid soils most difficult to remove are in the lower HLB range. In general agreement with the present study, Arai (11) found that, for anionic surfactants, the most effective surfactant HLB decreases with a decrease in the polarity of the soil.

Further investigations are needed to establish firmly the above relationships of soil HLB to surfactant HLB and to extend the soil HLB range. Also, an investigation is needed to determine whether, for a given soil, the optimum HLB is the same for anionic and nonionic surfactants.

ACKNOWLEDGMENTS

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