Studies in Detergency Correlation

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Abstract

In alkaline cleaning solutions of ca. pH 12 containing either a primary alcohol sulphate, a straight chain alkyl aryl sulphonate, or a fatty acid soap, detergent efficiency is increased synergistically by the addition of nonionic agents the HLB values of which lie within certain ranges. Those cleaners containing the anionic surfactant with the highest HLB exhibit the most synergism. In such cleaners, increasing detergency is directly related to increasing surface tension and critical micelle concentration of the unbuilt anionic surfactant, and to increasing surface tension of the nonionic surfactant. Asphalt soil removal, judged the resultant of the combined properties of penetrability, peptization, and wetting, was used to indicate detergent synergism in the aqueous alkaline cleaners studied.

Introduction

THE USUAL THEORIES of detergency postulate that the mechanism consists, in whole or part, of preferential adsorption of surfactant by the basis material, lowering of the boundary surface free energy, emulsification, capillary penetration, peptization, and micellar solubilization. An alternative process has recently been proposed (1) which suggests that detergency is due to the forces originating in the van der Waal attractions between the hydrocarbon chains of fatty soil and surfactant. This theory states that in a surfactant/water/soil system, soil is penetrated even at room temperature by aqueous surfactant solution with the formation of a liquid-crystalline phase from the close-packed soil and surfactant hydrocarbon chains. Some investigators (2), believing there is a connection between detergency and the liquid-crystalline phase containing soil, have further suggested that detersive efficiency depends on the presence of liquid crystals (anisotropy) in the aqueous cleaning solution. This hypothesis goes on to say that, since anisotropy is due to close-packed lamellar micelles, good detergency should result from combinations of anionic and nonionic surfactants which tend to form such aggregates. The latter are mixed micelles in which the hydrocarbon chains of the nonionic molecules have penetrated between those of the anionic molecules of the outer micellar layers, with the hydrophilic groups of the former lying in the ionic portion of the outer layer (3,4). There is support for the belief that nonionic additives containing highly hydrophilic polar groups are to be avoided because they tend to form isotropic solutions (2). The hydrophilicity of the polar part of a nonionic compound is related to the hydrophile-lipophile balance, HLB, of the latter. The preceding hypothesis, therefore, can be reduced to the question as to whether high or low HLB nonionic additives to anionic syndets tend to improve detergency.

This paper reports the results of attempts to resolve this question of detergency-HLB correlation, as well as the degree of correlation between detergency and the factors of surface tension and anionic CMC (critical micelle concentration). Previous work at this Laboratory has indicated that surfactant HLB is only one of several parameters determining soil removal efficiency (5).

Experimental

Procedures

Detergency was determined essentially as described in Federal Specification P-C-436a, "Cleaning Compound, Alkali Type," with 1,600 ml of a boiling, 7.5% distilled water solution of the test compound contained in a 2-liter beaker. Test panels of SAE 1010, 18–20 gauge, cold-rolled steel, 2½ × 2½ inches in size, were subjected to standardized polishing, cleaning, soil application, and aging. SAE 30 mineral oil and petroleum asphalt were used as soils. Mineral oil panels were evaluated for cleanliness after a 3 min cycle by the "residue-pattern" method (6), which carries the sensitive water break test thru a confirmatory step involving only the drying and examination of the panel for residual stains. Asphalt detergency was evaluated by the gravimetric method.

Surface tensions were determined by a du Nouy tensiometer at 25–26C with test solutions aged one hr.

Test Compositions

The soil removal studies were made in 7.5% solutions containing the amounts of builders prescribed for the Federal Specification P-C-436a standard comparison compound. The latter consists of the following:

sodium metasilicate pentahydrate	34.5%
primary sodium phosphate monohydrate	12.0%
trisodium phosphate dodecahydrate	33.5%
alkyl aryl sulphonate (40% active)	14.8%
ethylene oxide adduct of alkyl phenol	5.2%

Thus, 20% by weight of the test compounds consisted of surfactants or surfactants plus neutral builder, sodium sulphate. The test solutions had pH values ca. 12, and were suitable for use on both ferrous and nonferrous materials. Soak tank cleaners of the P-C-436a type exceed conventional heavy duty alkaline cleaners in detersive ability because of the synergism of their surfactant combination (8). The practical significance of the asphalt test for an aqueous-based detergent is that it provides a rapid and simple indication of the surface-active characteristics of penetrability, peptizing power, and wetting.

Surfactants (Table I)

Three types of anionics were studied, an alcohol sulphate (SDS), a straight chain alkyl aryl sulphonate

TABLE I
Surfactants

Anionic	Symbol	HLB
Sodium dodecyl sulphate, U.S.P.	SDS	40.0
Sodium alkyl (C_{10}—C_{20} straight chain) benzene sulphonate, 40% active	SKBS	11.7
Sodium oleate	....	18.0
NONIONIC: ethylene oxide adducts of,		
Nonyphenol		
15 mole ratio	NPPGE	15.00
30 " "	NPTGE	17.20
50 " "	NP50E	18.18
100 " "	NP100E	19.05
Decynediol[a]		
10 mole ratio	D-10	13.21
15 " "	D-15	14.90
30 " "	D-30	17.08
Octylphenol		
9–10 mole ratio	OPE9-10	13.40

[a] Structure:

$$\mathrm{CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_2{-}\underset{\underset{HO(C_2H_4O)m}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}C{\equiv}C{-}\underset{\underset{(OC_2H_4)nOH}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}CH_2{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

TABLE II

Detergent Solutions and HLB Characteristics

Cleaner	Nonionic		Anionic		Surfactant Mixture	
	Weight %	HLB	Weight %	HLB	Net HLB	Mol % Nonionic
23—SCC	5.2% OPE9-10	13.40	14.8% SKBS	11.70	12.50	36.3
1	5.2% D-30	17.08	14.8% "	11.70	14.22	18.7
40	5.2% NPTGE	17.20	14.8% "	11.70	14.28	18.8
37	5.2% NP100E	19.05	14.8% "	11.70	15.14	7.2
32	5.2% OPE9-10	13.40	5.9% sodium oleate	18.0	15.80	30.1
33	5.2% NPPGE	15.00	5.9% " "	18.0	16.60	23.4
31	5.2% D-30	17.08	5.9% " "	18.0	17.57	14.8
34	5.2% NPTGE	17.20	5.9% " "	18.0	17.63	14.8
38	5.2% NP50E	18.18	5.9% " "	18.0	18.09	10.0
35	5.2% NP100E	19.05	5.9% " "	18.0	18.49	5.5
24	5.2% OPE9-10	13.40	5.9% SDS	40.0	27.54	28.9
28	5.2% D-10	13.21	5.9% "	40.0	27.45	27.6
30	5.2% D-15	14.90	5.9% "	40.0	28.24	22.3
21	5.2% D-30	17.08	5.9% "	40.0	29.26	14.1
39	5.2% NPTGE	17.20	5.9% "	40.0	29.32	14.2
36	5.2% NP100E	19.05	5.9% "	40.0	30.19	5.2
2-A	5.2% NP100E	19.05	None		19.05	100
54	5.2% NP50E	18.18	"		18.18	100
2	5.2% D-30	17.08	"		17.08	100
57	5.2% OPE9-10	13.40	"		13.40	100
56	5.2% D-10	13.21	"		13.21	100
51	None		14.8% SKBS	11.70	11.70	None
53	"		5.9% sodium oleate	18.0	18.0	None
52	"		5.9% SDS	40.0	40.0	None

TABLE III

Detersive Efficiency and Surface Tension on Table II Cleaners

Detergency		Cleaner	Surface tension[a]
Mineral oil	Asphalt (min for removal)		
Good	12	23—SCC	30.1
Good	9–9	1	40.1
Good	16	40	36.5
Unsatisfactory	21	37	40.3
Good	21	32	32.0
	13–10	33	35.6
	10–10	31	41.1
Good	9–7	34	38.6
Unsatisfactory	10	38	39.5
Unsatisfactory	18–15	35	40.1
	8	24	31.5
Good	5–6	28	41.5
	9–7	30	41.8
Good	7–6	21	42.2
Good	19	39	38.9
Good	21	36	41.4
Good	Poor	2-A	
Good	Poor	54	
Good	Poor	2	
Good	Poor	57	
Poor rinsability	Poor	56	
Good	Poor	51	
Unsatisfactory	Poor	53	
Good	Poor	52	

[a] Surface tension, dynes per cm, at 25–26C, of 0.05% solutions aged 1 hr.

(SKBS), and sodium oleate soap.

The nonionics were commercial products, homologous series of ethylene oxide condensates of nonyl phenol and tetramethyldecynediol, and also the 9–10 mole ratio adduct of octylphenol.

The HLB values of the nonionic surfactants were computed by Griffin's method for polyethenoxy adducts (7), and the values for the anionic syndets were taken from the literature (7). Table I gives the surfactants, their symbols, and HLB numbers.

Results and Discussion

Detergency vs. HLB in Built Cleaners Containing Anionic-Nonionic Mixtures. Tables II and III show the effect of the HLB of the nonionic additive on the detergency of built alkaline cleaners of the type just described.

The data indicate that conventional alkaline cleaners (those containing only one syndet, anionic or nonionic) in solutions of ca. pH 12 can deterge SAE 30 mineral oil (sodium oleate soap is an exception). It is to be noted that none of the cleaners containing only one surfactant can remove asphalt soil.

Nonionic surfactants with HLB values of 13.2–17.1 impart excellent asphalt detergency to solutions containing sodium dodecyl sulphate, SDS (5–9 min cleaning) and impart good asphalt detergency to solutions with the alkyl aryl sulphonate, SKBS (9–12 min cleaning). For both SDS and SKBS systems (containing nonionic additives), there is no significant variation of asphalt detergency with increase of nonionic HLB in this range. In cleaning solutions containing sodium oleate soap as the anionic surfactant, asphalt detergency improves from possably fair (21 min cleaning) with a 13.4 HLB nonionic additive to excellent (7–10 min cleaning) in the 15.0–18.18 nonionic HLB range. With all three systems, asphalt detergency then falls off sharply with further increase in nonionic HLB value to 19.05. The data further indicate that the anionic with the highest HLB, sodium dodecyl sulphate (40.0 HLB), forms the most synergistic detergent mixtures with nonionic additives in the 13.2–17.1 HLB range. It must be noted that the 17.1 nonionic HLB point seems to be a characteristic one for sys-

TABLE IV

Nonionic Concentration, HLB, and Detergency

Cleaner	% Active content in cleaner	Nonionic		Anionic		Surfact. mixture		Asphalt detergency min for removal
		Weight %	HLB	Weight %	HLB	Net HLB	Nonionic mole fraction	
27	7.3	5.2% D-10	13.21	5.2% SKBS	11.70	12.78	0.60	31 mg residue[a]
29	7.3	5.2% D-15	14.90	5.2% SKBS	11.70	13.99	0.53	14–17–21
3	7.3	5.2% D-30	17.08	5.2% SKBS	11.70	15.54	0.40	10–10
1	11.7	5.2% D-30	17.08	14.8% SKBS	11.70	14.22	0.19	9–9
4	6.8	5.2% D-30	17.08	3.9% SKBS	11.70	15.84	0.47	18–18
5	6.2	5.2% D-30	17.08	2.6% SKBS	11.70	16.18	0.57	30 mg residue[a]
6	4.2	2.6% D-30	17.08	3.9% SKBS	11.70	15.06	0.30	12–12
7	3.2	1.6% D-30	17.08	3.9% SKBS	11.70	14.42	0.21	12–12
8	2.6	1.0% D-30	17.08	3.9% SKBS	11.70	13.80	0.14	15–15
9	2.1	0.5% D-30	17.08	3.9% SKBS	11.70	13.01	0.08	2 mg residue[a]
10	2.6	0.5% D-30	17.08	5.2% SKBS	11.70	12.74	0.06	21–18
42	8.5	2.6% NPTGE	17.2	5.9% SDS	40.0	29.32	0.08	11–11
39	11.1	5.2% NPTGE	17.2	5.9% SDS	40.0	29.32	0.14	19
41	20.0	14.1% NPTGE	17.2	5.9% SDS	40.0	29.32	0.31	13–12

[a] Asphalt residues after 21 min cleaning.

TABLE V

Anionic Surface Tension vs. Asphalt Detergency

Anionic	Anionic surface tension, dynes/cm at 25C	Nonionic agent and asphalt detergency (min for removal)			
		OPE9-10 (HLB = 13.4)	D-30 (HLB = 17.08)	NPTGE (HLB = 17.20)	NP100E (HLB = 19.05)
Sodium oleate	27.0	21	10–10	9–7	18–15
SKBS	30.5	12	9–9	16	21
SDS	37.8	8	7–6	19	21

Surface tension of pure anionic agents at concentration of 0.44 g per 100 ml (Table II concentrations):

Sodium oleate	reference 9
SKBS	reference 10
SDS	reference 9

tems containing sulphonate or sulphate anionics, a point beyond which further increase in the HLB of the nonionic additive causes a decrease in surface-active properties as judged by asphalt detergency. Of interest is the fact that mineral oil detergency is good throughout the nonionic HLB range of 13.2–19.05 for the sodium dodecyl sulphate mixtures; while for the soap and alkyl aryl sulphonate systems, it is good only in the nonionic HLB range of 13.4–17.2. Table III shows no general correlation between asphalt detergency and either nonionic mole fraction in the surfactant mixture or net HLB of the latter.

Table IV shows principally that good asphalt detergency can be imparted to cleaners containing a very low percentage (1.6% active material) of the alkyl aryl sulphonate, SKBS, by a wide concentration range of the D-30 nonionic (1.0–5.2%). The upper limit is an economic cut-off point. Within the family of ethylene oxide adducts of decynediol, direct correlation exists between increasing asphalt detergency and nonionic HLB in the 13.2–17.1 range, for cleaners containing the SKBS anionic. Because of the increasing molecular size of the decynediol adducts in this HLB range, there is also direct correlation between increasing asphalt detergency and decreasing nonionic mole fraction in the surfactant mixture. However, there is no correlation between asphalt detergency and the nonionic mole fraction of the NPTGE-SDS surfactant mixture, in which the change in mole fraction is accomplished by varying the amount of NPTGE nonionic in the cleaner. Detergency is fair to good in cleaners containing the NPTGE-SDS combination.

Surface Tension, Asphalt Detergency, and HLB

Table V shows that in the built alkaline cleaners described herein (Table II) anionic syndets vary in the synergism they produce when combined with nonionic agents. With nonionics of 17.1 HLB maximum, the order of increasing synergism is sodium oleate, SKBS, and SDS, while for nonionics of greater HLB (to 19.05), this order is reversed. It is important to note that the order of soap, straight chain alkyl aryl sulphonate, and primary alkyl sulphate is that of increasing surface tension of the pure anionic syndets. Table VI reveals: 1) that increasing HLB of the nonionic additives correlates in general with increasing surface tension of their 0.39% solutions (their concentrations in the Table II cleaners); 2) the effectiveness of nonionic surfactants in improving asphalt detergency increases with increasing values of nonionic solution surface tension until a nonionic HLB of 17.1 is reached, with further increase of nonionic surface tension reversing this trend.

TABLE VI

Surface Tensions of 0.39% Solutions of Various Nonionic Agents[a]

Nonionic	Surface tension, dynes/cm	Temp C	HLB
OPE9-10	30.0	25.8	13.40
D-10	30.5	25.8	13.21
NPPGE	35.3	25.6	15.00
D-15	33.6	25.3	14.90
D-30	36.1	25.4	17.08
NPTGE	42.4	25.6	17.20
NP50E	45.1	25.5	18.18
NP100E	45.0	25.8	19.05

[a] Concentration of the nonionic additives in the 7.5% cleaning solutions of Table II, all formulations of which contain 5.2% nonionic by weight, dry basis.

TABLE VII

Detergency vs. CMC (See Table V)

Anionic surfactant	CMC (molarity)	Reference
Sodium oleate	.0007	(3)
SKBS[a]	.0015	(11)
SDS	.0081	(12)

[a] For a 12 carbon straight chain alkyl benzene sodium sulphonate.

Critical Micelle Concentration and HLB

It is significant that the order of increasing synergism of surface-active properties of cleaners containing anionic-nonionic mixtures is also that of increasing critical micelle concentration (CMC) of the pure anionic surfactants. Table VII shows this correlation. This means that the higher the anionic CMC, the greater the asphalt detergency imparted to the cleaner by a nonionic additive in the 13.4–17.1 HLB range. Harkins (3) related the lowering of anionic CMC by nonionic additives to the formation of mixed micelles thru polar-nonpolar solubilization, in which the hydrocarbon chains of the nonionics penetrate between those of the anionic molecules in the outer micellar layers with the hydrophilic groups of the nonionic lying in the ionic portions of the outer layers. The amount of such CMC lowering has been connected with improved foam stability of alkaline detergent solutions containing anionic-nonionic mixtures (10).

It is suggested that the drop in asphalt detergency (i.e., in surface-active characteristics) a) in cleaners containing sulphonate or sulphate anionics when the nonionic HLB exceeds 17.1, and b) in cleaners containing sodium oleate soap when the nonionic HLB is greater than 18.18, is due to the following sequence of events:

The increased hydrophilicity of the nonionic additive (resulting from the longer ethylene oxide chains) causes a change, or partial change, in the type of its solubilization by the anionic syndet, perhaps from oriented polar-nonpolar to adsorption solubilization in which there is no penetration of the anionic micelle by the nonionic; this change in type of micellar interaction could influence the size, shape and charge density of the mixed micelle, with consequent effect on the combination of surface-active properties of capillary penetration, peptization, and wetting as indicated by asphalt detergency.

Discussion

This investigation has indicated that in alkaline cleaning solutions of ca. pH 12 containing either a primary alcohol sulphate, a straight chain alkyl aryl sulphonate, or a fatty acid soap, detergent efficiency is increased synergistically by the addition of nonionic agents the HLB values of which lie within certain ranges. In such cleaners those containing the anionic surfactant with the highest HLB possess the most synergism. Also, in these cleaners when the HLB values of the nonionic agents are within the above-mentioned ranges, increasing detergency is directly related to increasing surface tension and critical micelle concentration of the unbuilt anionic surfactant and to increasing surface tension of the nonionic surfactant.

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Nutritional Effects of Dihydroxystearic Acid in Rats[1,2]

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Abstract

Two matching groups of weanling male albino rats were fed a purified diet containing 5% dihydroxystearic acid. All animals survived until they were killed; the first group was sacrificed at age 150 days and the second at 305 days. Fecal fat analyses showed that at least 80% of the ingested dihydroxystearic acid was not excreted. Growth was depressed during the first four weeks; this was followed by a period of rapid weight increase. The weight of the epididymal fat pads indicated depression of neutral fat deposition. Livers and adrenals were relatively heavy in the group killed earlier and essentially normal in those killed later. This and the eventual weight increase showed that the rats adapted themselves to the intake of the material. Gas liquid chromatography carried out on the methyl ethers of the epididymal fat did not reveal the presence of dihydroxystearic acid. The fatty acid composition of the lipids of serum, kidney, liver and epididymal fat was determined on the methyl esters of the lipid extracts.

Introduction

BIOLOGICAL WORK with oxidized fats has often been hindered by the inability of investigators to use pure materials. Furthermore, in many biological studies, the main attention has been given to polymerized fractions. In view of this fact, we decided to carry out a study on rats fed dihydroxystearic acid. This material is available in quantities sufficient for feeding studies and occurs in oxidized fats, probably in concentrations of a few tenths of one per cent (1).

Dihydroxystearic acid has been used previously in nutritional studies (2,3). Harris et al. found that feeding of this material was associated with an increase in the acetyl value of the carcass fat, suggesting deposition of the material in the tissues. However, the question of whether the material is actually deposited has not been answered satisfactorily.

Experimental

The 9,10-dihydroxystearic acid used in this experiment was prepared from oleic acid according to the method of Greenspan (4). The melting point of the material was 92–94C, which is close to values previously observed. The dihydroxystearic acid was fed together with saturated triglycerides of C_{10-18} acids with the following composition: C_{10}....5%; C_{12}....45%; C_{14}....25%; C_{16}....8%; C_{18}....16%. The latter triglyceride mixture was obtained from coconut oil by fractionation of the split fatty acids and their random reconstitution into triglycerides (5). This material is well absorbed and it was hoped that it would aid in the absorption of the high melting dihydroxystearic acid with little danger of oxidative interaction between the two.

Five per cent each of dihydroxystearic acid and saturated triglycerides were included in a diet containing 30% alcohol-extracted casein, 54% destrose, 2.5% USP XIII salt mixture, 0.5% calcium carbonate, 2% cellulose, 2% of a 75% linoleic acid concentration, and adequate amounts of all vitamins. The diet was fed to two matching groups of eight weanling male rats of the Columbia-Sherman strain. Their mothers had been given, during the later stages of pregnancy and during lactation, a low fat diet prepared by the replacement of the triglycerides, the dihydroxystearic acid, and the linoleic acid concentrate in the above diet by dextrose. One per cent of a safflower oil concentrate containing at least 98% linoleic acid was added.

One group of rats was killed with chloroform at age 150 days. Blood was drawn from the heart, the organs were weighed, sections were taken for histological studies, and the rest was frozen for lipid analyses. The serum liver, kidneys, and epididymal fat pads were extracted with 2:1 chloroform:methanol, for determinations of fatty acid composition of their lipids. Methyl esters were prepared for gas-liquid chromatography by transesterification. Chromatography was carried out on a Barber-Coleman instrument having a 6 ft × 1/8 in. i.d. glass column packed with ethylene glycol succinate on Chromosorb W. The column was operated at 200C with argon at 40 psi. A sample of the dihydroxystearic acid used in these studies and a sample of the lipid extract of the epididymal fat were converted to methyl ethers because this has been found to increase the volatility of hydroxy compounds (6). The ethers were chromatographed on a 4 ft × 1/8 in. i.d. glass packed column with neopentyl sebacate on Chromosorb W operated at 225C with argon at 40 psi. The standard dihydroxystearic ether emerged after 20 min. In order to determine the approximate amount detectable in the lipid extract, 0.2% of dihydroxystearic acid was added to the depot fat and the methyl-ethers of the mixture were chromatographed. A peak of ca. 2 mm in height appeared 20 min after the injection of the material corresponding to the peak obtained on the standard run with pure

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