A Comparison of Surfactants Derived from Alcohols Based on Petrochemical and Oleochemical Sources

Brian D. Condon* and **K. Lee Matheson**
Vista Chemical Company, Austin, Texas 78720

Samples of lauryl-range alcohols derived from palm kernel oil, coconut oil and ethylene (Ziegler) were derivatized into alcohol sulfates and alcohol ether sulfates (2 moles of ethylene oxide adduct). Physical properties and performance characteristics for each surfactant were evaluated both individually and in light-duty liquid (LDL) dishwashing formulations. The slight differences observed in the physical and performance properties of the surfactants and their formulations were assignable to slight differences the individual alcohol, alcohol sulfate and alcohol ether sulfate samples employed in this study. The magnitude and type of variation found in the samples resulted from normal production variation and not from any properties inherent to the nature of the alcohol source. We therefore conclude that alcohol sulfates, alcohol ether sulfates and LDLs formulated from them exhibit identical physical property and performance characteristics, regardless of whether the original alcohol was manufactured from petrochemical or oleochemical sources.

KEY WORDS: Alcohol, alcohol ether sulfate, alcohol sulfate, dishwashing, light-duty liquid, oleochemical, petrochemical.

Fatty alcohols are a major feedstock for the surfactants industry and originate from two main sources, petrochemical and oleochemical (1). Three of the more common types of fatty alcohol, Ziegler (petrochemical) and oleochemical palm kernel oil (PKO) and coconut oil (Coco), were selected for this study. These alcohols serve industrially as starting materials for surfactants, such as alcohol sulfates and alcohol ether sulfates (among others). This study examines the physical and performance characteristics of petrochemically and oleochemically derived alcohol sulfates and alcohol ether sulfates. The studies evaluate the surfactants alone and in a light-duty liquid (LDL) formulation and examine properties such as surface tension reduction, response to solution ionic strength, cloud/clear temperatures, viscosity, foaming and manual dishwashing performance.

EXPERIMENTAL PROCEDURES

Surface tension (Gibbs' plots). Gibbs' plots were obtained with spinning drop tensiometers (University of Texas Model 300; Austin, TX). Measurements were taken at 38°C, and solutions were made in 0.01 M sodium sulfate solution.

Flash foam. Flash foam (2) was measured with an in-house-produced foam generator that quickly passes perforated disks through 100 mL of test surfactant solution to produce the foam. An eccentric-drive system varies the speed of the plunger disk such that the disks move quickly through the test solution and slowly through the foam. Tests were carried out at 38°C and 100 ppm hardness as calcium carbonate. Data are reported as the volume of foam, 1 min after agitation was stopped.

Viscosity. Viscosity measurements were obtained from a Brookfield model LVTCP 115/60 viscometer (Brookfield Co., Stoughton, MA) at 25°C and 2 s^{-1} shear rate.

Cloud/clear. Cloud/clear temperatures were measured by slowly cooling 60 g of liquid sample until cloudiness appeared. The cooled sample was then slowly warmed until cloudiness disappeared. The rate of temperature change was controlled to less than 1°F per minute.

Dishwashing. Manual dishwashing performance was evaluated as the LDL formulations at 118°F, 0.05% formula concentration in 6 L water of 100 ppm hardness (as calcium carbonate). The formulations were dissolved into a wash basin, and foam was generated by passing compressed air through a fritted disk submerged in the wash solution. Plates were cleaned of vegetable shortening until the foam could no longer cover the surface of the wash solution.

Alcohol, ethoxylate and ether sulfate samples. The lauryl-range alcohols used in the study were samples of standard commercial-grade material obtained from major commodity alcohol producers.

Chemical analysis. The following analyses were carried out by standardized methods: hydroxyl number and molecular weight (3); iodine value (4); saponification value (5); carbonyl number (6); water (7); active (8); oil (9); sodium sulfate and chloride (10); Klett color (11).

BANA. BANA stands for boric acid nonalcohol and is a measure of the total nonalcohol content of the alcohol samples. It was developed by Vista Chemical Company (Austin, TX) and consists of running an alcohol sample through a packed-column gas chromatograph. The column is packed with boric acid so that any hydroxy-containing molecules are retained. The nonalcohol components are measured. Dioxane was measured by headspace gas chromatography. Acid value was measured by NaOH titration. The intermediate alcohol ethoxylates were synthesized by NaOH-catalyzed addition of ethylene oxide in a heated autoclave followed by neutralization with acetic acid (12). The alcohol sulfates and alcohol ether sulfates were produced by sulfur trioxide sulfation in a thin-film reactor and neutralization with NaOH (12).

RESULTS AND DISCUSSION

The lauryl-range alcohol feedstocks were analyzed for key characteristics as listed in Table 1. It was suspected that the oleochemical alcohols, being derived from esters, might exhibit a higher carbonyl content than the Ziegler alcohol. However, the Coco-derived alcohol showed a higher carbonyl content, but the PKO-derived alcohol did not. Unexpectedly, though, the Ziegler alcohol revealed slightly higher iodine and BANA values. However, when viewed as a group, the three alcohol samples were quite similar in their chemical characteristics. It appears that no clear-cut distinctions could be made along the lines of petrochemical *vs.* oleochemical alcohols for this set of samples.

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*To whom correspondence should be addressed at 12024 Vista Parke Drive, Austin, Texas 78720.

TABLE 1

Chemical Analysis of Alcohol Samples[a]

Analysis	Ziegler	PKO	Coco
OH#	285.8	284.8	285.3
mw	196.3	196.5	197.8
I_2 value	0.3	0.2	0.1
Acid value	—	0.02	—
Saponification value	<1.0	0.1	0.1
Carbonyl	44 ppm	40 ppm	161 ppm
H_2O (%)	0.04	0.01	0.04
BANA (%)	0.5	0.4	0.3

[a] Abbreviations: PKO, palm kernel oil; Coco, coconut oil; mw, molecular weight; BANA, boric acid nonalcohol.

TABLE 2

Chemical Analysis of Alcohol Sulfates[a]

Analysis	Ziegler	PKO	Coco
Active	20.8	21.3	21.9
Oil	0.80	0.60	0.50
Na_2SO_4	0.63	0.31	0.31
NaCl	<0.1	<0.1	<0.1
Klett	11	30	16

[a] See Table 1 for abbreviations.

TABLE 3

Chemical Analysis of Alcohol Ether Sulfates[a]

Analysis	Ziegler	PKO	Coco
Active	25.8	25.8	24.6
Oil	0.36	0.54	0.51
Na_2SO_4	0.44	0.33	0.48
NaCl	0.35	0.48	0.48
Dioxane	25 ppm	12 ppm	20 ppm

[a] See Table 1 for abbreviations.

Because this study focuses on the surfactants ultimately derived from the three different alcohols, lauryl (surfactant)-range alcohol samples were selected. The carbon chainlength distribution of each alcohol sample is shown in Figure 1. The three samples were quite similar with respect to their homolog distributions. However, the Coco-derived alcohol contained slightly more of the C_{14} and C_{16} homologs at the expense of the C_{12} alcohol, as compared to the Ziegler and PKO-derived alcohol.

Fatty alcohols are often treated with sulfur trioxide or similar reagents to produce alcohol sulfates. These common anionic surfactants are widely used in household and personal-care products, including LDL. Table 2 lists the chemical analysis of each of the alcohol sulfates studied. Efforts were made to sulfate each of the alcohol samples under identical conditions and thus produce a closely matched set of alcohol sulfates. The alcohol sulfate produced from the Ziegler alcohol may have been slightly undersulfated and shows a marginally higher free oil (unsulfated alcohol) and sodium sulfate content, which was paired with lower color.

Another synthetic route leading from fatty alcohols to surfactants is ethoxylation followed by sulfation to produce alcohol ether sulfates. These surfactants find their way into applications similar to those using alcohol sulfates, including LDLs. The ether sulfates examined here contain two moles of ethylene oxide per mole of alcohol. Table 3 gives the chemical analysis of the ether sulfates studied here. The three samples are quite similar to one another.

The ability of each of these surfactants to reduce the surface tension of water was measured. For the purposes of comparison between surfactants derived from the various alcohol sources, surface tension data were collected under conditions of swamping electrolyte at elevated temperature. As a result, the values observed for the critical micelle concentration (CMC) and the surface tension at the CMC were both numerically lower than data, reported elsewhere in the literature, taken in distilled

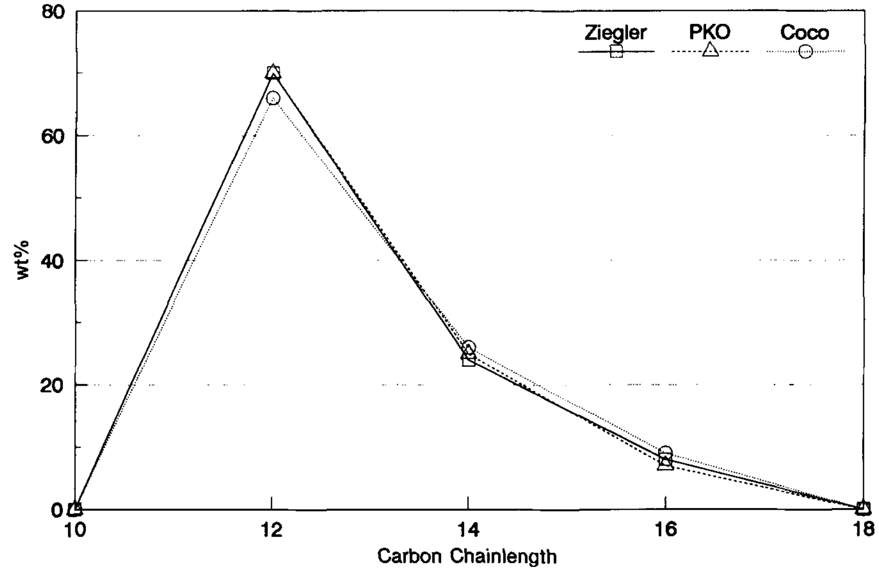

FIG. 1. Alcohol carbon chainlengths. PKO, palm kernel oil; Coco, coconut oil.

water at room temperature (13). Table 4 shows the surface tension reducing ability of the three alcohol sulfates to be similar, with the Coco-derived alcohol sulfate showing a slightly lower surface tension. Likewise, the ether sulfate derived from Coco-type alcohol exhibited surface chemical attributes slightly different from its Ziegler and PKO counterparts. One possible reason for this difference lies with the slightly longer average carbon chainlength of the Coco-derived alcohol upon which the surfactants were based.

With this relatively small irregularity in mind, we next studied the viscosity response of the ether sulfates to added ionic strength. This property, commonly known as salt thickening, plays an important role in formulating many liquid home-use products, like LDLs (14). Figure 2 shows the increasing viscosity with increasing sodium chloride concentration for 10% (w/w) aqueous solutions of each of the ether sulfates tested. The Ziegler and PKO-based ether sulfates showed nearly identical behavior of increasing viscosity with higher concentrations of sodium chloride. The Coco-based ether sulfate, however, did show significantly greater salt thickening response. One possible explanation may lie in the slightly skewed carbon chainlength distribution (toward the higher homologs) observed for the Coco-based alcohol sample. It is known that the salt thickening response of ether sulfates is quite sensitive to the carbon chainlength of the hydrophobic portion of the molecule (15). The carbon chainlength distribution of the various commercially available fatty alcohols depends almost entirely upon distillation capability at the production site and little upon the original source of the crude alcohol.

The relative solubilities of the surfactants derived from petrochemical and oleochemical alcohols were examined through their cloud/clear temperatures (Fig. 3). The data for the alcohol sulfates show a large difference between the cloud and clear temperatures relative to the ether sulfates. This results from the higher crystallinity of alcohol sulfates. However, within each surfactant group, the source of alcohol employed to produce these surfactants did not influence their solubility characteristics.

TABLE 4

Surface Chemistry of Petrochemical and Oleochemical Surfactants[a]

	Ziegler		PKO		Coco	
	CMC (mg/L)	Surface tension at CMC	CMC	Surface tension at CMC	CMC	Surface tension at CMC
Alcohol sulfate	107	21.6	111	21.5	107	20.9
Alcohol ether sulfate	48	31.7	42	31.8	46	28.7

[a]See Table 1 for abbreviations. CMC, critical micelle concentration.

A surfactant's foaming ability often determines its viable end-use applications. LDLs require high foaming potential and resistance to the adverse effects of soils on cleaning and foaming performance. Because anionic surfactants exhibit these characteristics, alcohol sulfates and ether sulfates are often chosen when formulating LDLs. For this reason, the agitation foam volumes were assessed for all six surfactants. Figure 4 shows some differences in foaming behavior between the various samples.

The enhanced foaming by the ether sulfates over the alcohol sulfates under the hardness conditions of the test is not unusual. For the alcohol sulfates, however, the Coco-derived sample showed moderately reduced performance. It is well known that sensitivity to water hardness, already high for alcohol sulfates, increases rapidly with increasing molecular weight (16). The slightly higher carbon chainlength of the Coco-derived alcohol sulfate explains at least a portion of why that alcohol sulfate foamed less than the other two.

The ether sulfates show nearly the opposite phenomenon: The Coco-derived sample foamed more than the other two samples. The slightly longer hydrophobe of the Coco

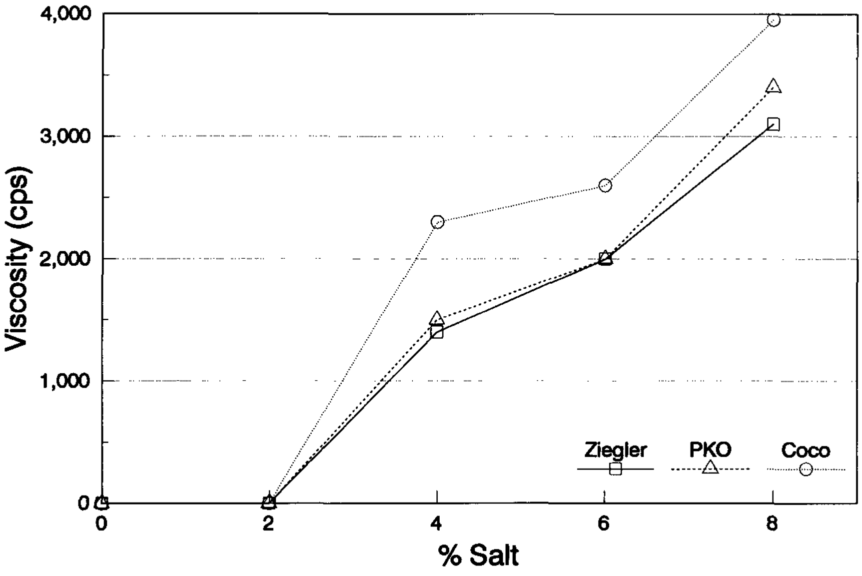

FIG. 2. Salt thickening of alcohol ether sulfates derived from petrochemical and oleochemical alcohols. Abbreviations as in Figure 1.

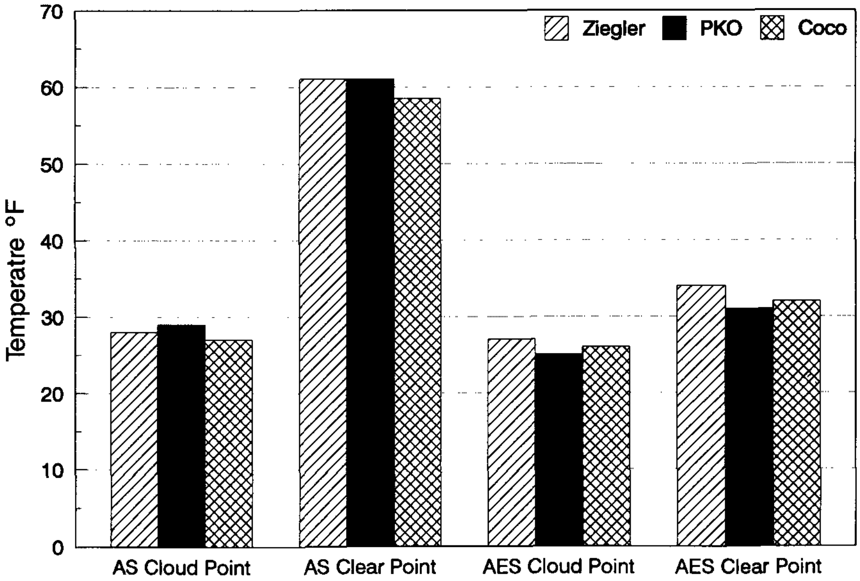

FIG. 3. Cloud/clear temperatures for alcohol sulfates (AS) and alcohol ether sulfates (AES) as 1% solutions in water. Abbreviations as in Figure 1.

sample may also be the causative factor here. Not counting the effects of water hardness, lauryl-range anionic surfactants exhibit greater foam volumes at higher carbon chainlengths. Ether sulfates are much less sensitive to the deleterious effects of water hardness, the Coco-derived ether sulfate performed marginally better for the same reason that the Coco-derived alcohol sulfate performed marginally poorer, a slightly longer hydrophobe (16).

The next step in the investigation was to determine if the small differences observed between each of the surfactants, when tested individually, would remain apparent when the surfactants were formulated into an LDL. Table 5 lists the LDL formulation tested. The active surfactants consist of the alcohol sulfates and ether sulfates previously discussed. For each LDL, both anionic surfactants used were of the same source type; Ziegler, PKO or Coco. Additionally, components were included that are traditionally used in LDL formulations, such as lauryl monoethanolamide, various sodium salts and hydrotrope.

The first comparison made among the three formulated LDLs was viscosity. Figure 5 illustrates that there were no significant viscosity differences among the LDLs,

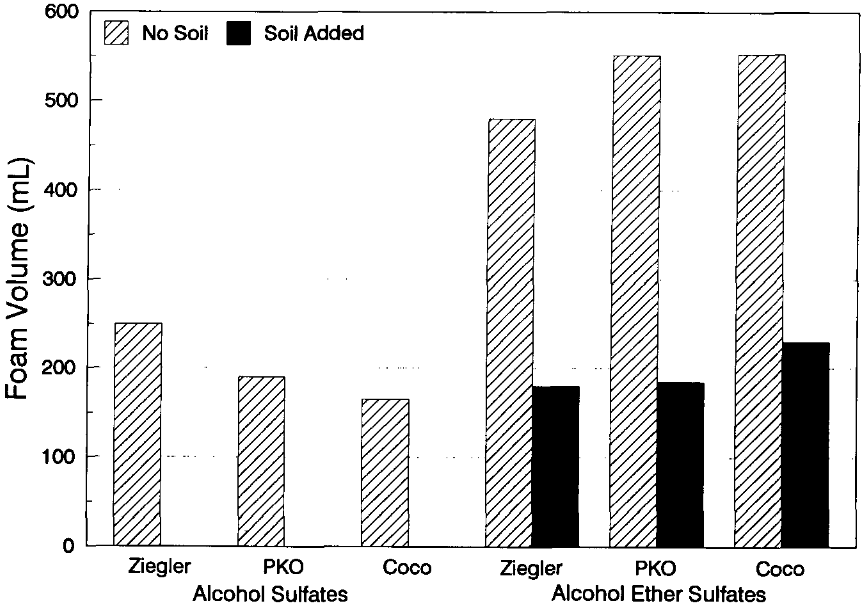

FIG. 4. Agitation foam volume and soil tolerance for alcohol sulfates and alcohol ether sulfates. Abbreviations as in Figure 1.

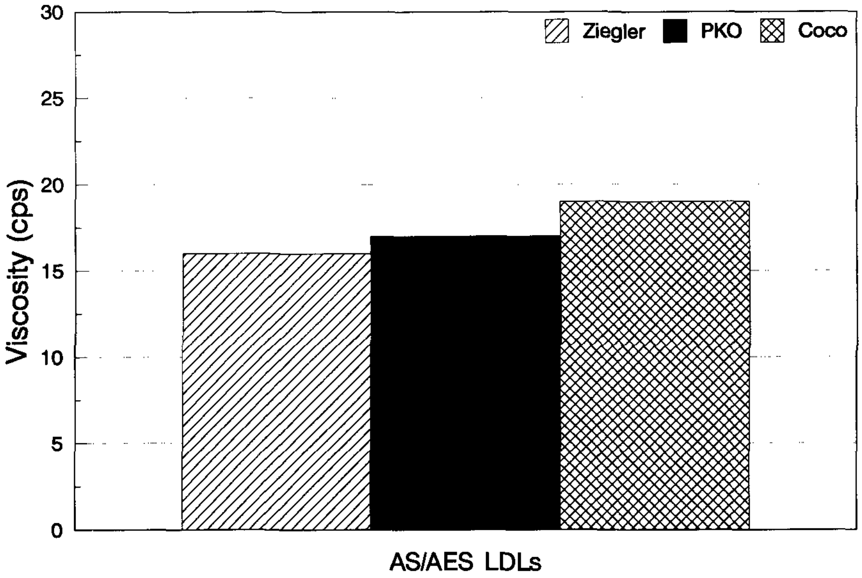

FIG. 5. Viscosity of formulated light-duty liquids (LDLs) at 25°C and 150 s^{-1}. Abbreviations as in Figure 3.

TABLE 5

Light-Duty Liquid Formulation

Light-duty liquid	Content (%)
Alcohol ether sulfate	11
Alcohol sulfate	9
Ethanolamide	0.5
Na_2SO_4	0.5
Na_2CO_3	1.4
NaCl	2.0
Sodium xylene sulfonate	2.8
Ethanol	4.4
H_2O	to 100

regardless of the original alcohol source from which the surfactants were derived. One might have suspected that the Coco-based formulation would have displayed a higher viscosity because the ether sulfate alone did provide greater viscosity at 4% NaCl (see Fig. 2). Apparently, the viscosity differences observed among the single surfactant systems did not manifest themselves within the test formulation, which included 7.2% hydrotrope.

The next physical property measurements taken on the formulated LDLs were their cloud and clear temperatures. Figure 6 shows that, within experimental error (+2 F), there were no differences between the various LDLs with respect to their response to temperature changes.

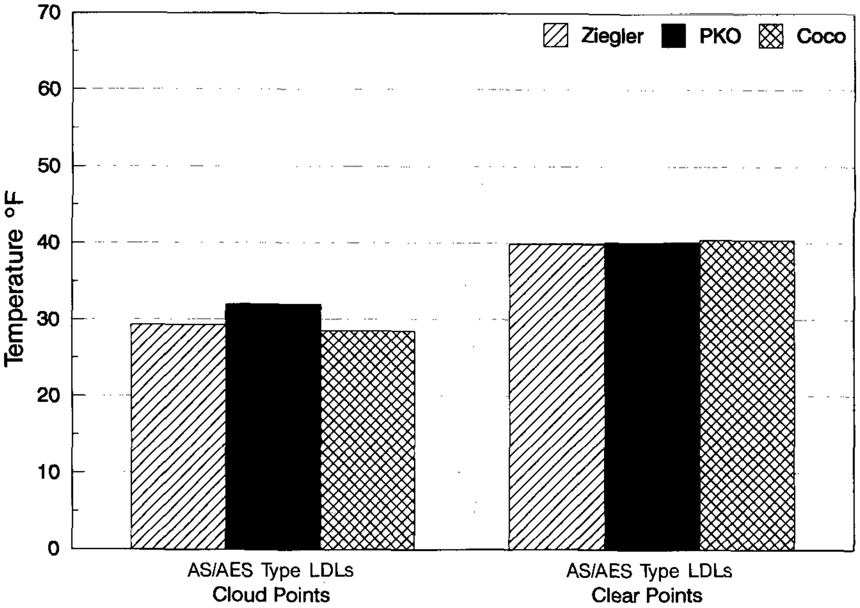

FIG. 6. Cloud/clear temperatures for formulated LDLs. Abbreviations as in Figure 3.

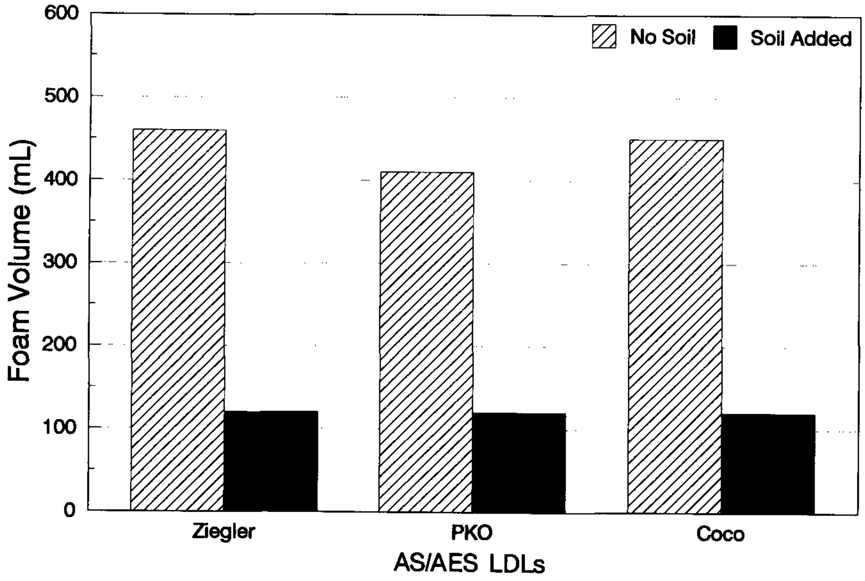

FIG. 7. Agitation foam volume and soil tolerance for formulated LDLs. Abbreviations as in Figure 3.

The agitation foam volume performance was also assessed (Fig. 7) for the three formulated LDLs, as well as the ability of the generated foam to resist the defoaming action of soil (Wesson cooking oil). The lower foam volume observed for the LDL formulated with the PKO-derived surfactants is not statistically significant for this test (95% confidence limit, ±5% of measurement). Upon addition of Wesson cooking oil, all foam volumes dropped to nearly the same value. From these experiments, we conclude that there are no significant differences among these LDLs formulated with surfactants originating from Ziegler alcohol, PKO-derived alcohol or Coco-derived alcohol.

All of the results reported up to this point do shed light on the remarkable similarity between petrochemically and oleochemically derived alcohol sulfates and ether sulfates and LDLs formulated from them. However, no performance characteristic is more important to LDLs than their ability to wash dishes. With this in mind, Figure 8 reveals no significant differences among the three LDLs (95% confidence limit, ±1 plate) with respect to their plate-washing capacity.

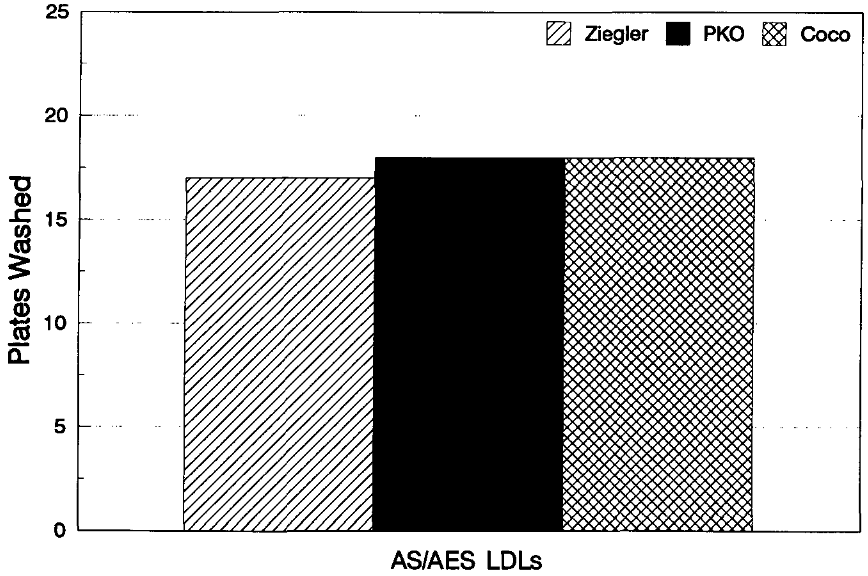

FIG. 8. Manual plate washing of formulated light-duty liquids (LDLs). Abbreviations as in Figure 3.

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