By the surface tension depression method, the same conditions resulted in an increase from 4.2 to 13.9 μmoles per liter. This is in contrast to the data obtained by Schick (16) and by Ginn and co-workers (18). They reported that CMC values of oxyethylated alkanols and alkyl phenols, in general, decreased with increasing temperature.

After this investigation had been completed, it was reported (19) that the CMC's of Pluronic polyols L62, L64 and F68 were 2.40, 2.20 and 0.1 g/dl, respectively. We are unable to account for the discrepancy in the data.

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T. Kalis and G. Kabalka prepared solutions; R. Seaton carried out the detergency measurements.

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Neutral Oil in Linear Alkyl Benzene Sulfonate Slurries: Determination and Composition

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Abstract

A method of improved accuracy and acceptable precision for the determination of neutral oil in detergent slurries is described. The increase in accuracy results from minimizing loss of highly volatile constituents of the neutral oil.

The composition of the neutral oil in linear alkyl benzene slurries has been determined utilizing infrared and mass spectrometry techniques.

Highly branched, saturated aliphatic hydrocarbons constitute the principal portion of the neutral oil. Traces of aromatic hydrocarbons are also present. The balance of the neutral oil comprises dialkylsulfones together with trace quantities of unidentified sulfur containing components.

Analogies are drawn between the composition of neutral oil from linear alkyl benzene sulfonates and branched alkyl benzene sulfonates.

Introduction

IN A STUDY OF THE COMPOSITION of neutral oil from linear alkyl benzene sulfonate detergent slurries, it was necessary to isolate a large quantity of the neutral oil without loss of components. An attempt was made to isolate it by scaling up AOCS Tentative Method Dd 4-60 (1). Low recoveries of neutral oil indicated that highly volatile materials are present and lost by volatilization during evaporation of the petroleum ether extract. Weeks et al. (2) describe the determination of unsulfonated oil [1] by distillation of neutralized sulfonate (slurry) with ethylene glycol. The distillation operation is quite rapid, requiring approximately 10 min, and there is no loss of volatile materials. In their opinion the primary properties influencing the quality of alkyl benzene sulfonates are: (a) the amount of unsulfonated oils and (b) product color. For this reason they are not particularly interested in the sulfone content of the neutralized sulfonates except to note that sulfones can be recovered from the still residue by extraction of the latter with petroleum ether. However, in our view, the amount of sulfone present in slurries designated for detergent formulation is considered significant since it exerts a deleterious effect on the performance of formulated products.

Part I of this paper presents evidence that the method of Weeks et al. (2) for the determination of neutral oil when performed in two operations (distillation and extraction) yields results of the same degree of precision but of vastly improved accuracy over the results obtained by use of AOCS Tentative Method Dd 4-60. Part II incorporates a discussion of the composition of neutral oil isolated from typical commercial linear alkyl benzene sulfonate slurries.

Part I—Determination of Neutral Oil

AOCS Tentative Method Dd 4-60 yields results for neutral oil which include such sulfones as may be present. However, inadvertent losses of neutral oil are occasioned in the performance of this method during the operation of evaporation to constant weight. It will be shown in Part II of the present paper that some of the constituents of neutral oil are highly volatile and evaporate spontaneously at room temperature. By determining the volatile constituents of the neutral oil by distillation with ethylene glycol and determining the sulfones and other nonvolatile organic constituents by petroleum ether extraction of the residue in the distillation flask as described by Weeks et al. (2) and combining the two quantities, a result can be obtained for neutral oil which is independent of the variable loss of highly volatile con-

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[1] Unsulfonated oil is frequently confused with neutral oil and free oil. The term unsulfonated oil is specific but all three have been used interchangeably. In this paper neutral oil refers to material which may consist of unsulfonated oil, sulfones and other concomitant organic constituents in admixture.

TABLE I

Comparison of Results for Determination of Neutral Oil Content of Detergent Slurry by Three Methods

Method	Weight of sample, g	Ethylene glycol distillation, %	Petroleum ether extraction, %	Total neutral oil, %
I	52.61	0.41	0.37	0.78
	28.02	0.43	0.37	0.80
	32.09	0.41	0.37	0.78
II	4.13			0.40
	5.52			0.45
	4.54			0.50
III	32.49			0.63
	31.86			0.63
	37.18			0.63
	39.16			0.62

Method I: Method of Weeks et al. (2); combined distillation-extraction.
II: Neutral Oil by AOCS Tentative Method Dd 4–60.
III: Neutral oil by evaporation of petroleum ether extract at room temperature.

stituents resulting from evaporation to constant weight.

Experimental

Weigh 25 to 50 g ± 0.5 mg of the sample slurry by difference into a 2-liter distillation flask and follow the procedure described by Weeks et al. (2) for the distillation step.

The specific gravity of the ethylene distillate must be determined for use as a factor in converting the volume of distillate to a weight basis. In our work a micropicnometer possessing a water value of 0.08978 ml at 23C was employed. The specific gravity of the distillate usually approximates the value of 0.856 at 23C/23C.

After cooling to room temperature, transfer the still residue to a 1-liter extraction cylinder. Wash the flask with several successive volumes of a 1:1 water-alcohol mixture and add the washings to the still residue in the extraction cylinder. Finally bring the contents of the extraction cylinder to a volume of 600 ml by addition of the required volume of 1:1 water-alcohol.

Add 300 ml of petroleum ether to the contents of the extraction cylinder and shake vigorously for several minutes. Allow the extraction cylinder to stand until the layers separate. If an emulsion forms it can be broken by the addition of a few granules of anhydrous sodium sulfate.

Siphon the ether layer into a tared 500-ml Erlenmeyer flask. Evaporate the solvent on a steam plate using a stream of clean dry air to facilitate the evaporation.

Repeat the extraction an additional five times. The extracts should be clear and free of suspended matter. Branched alkyl benzene sulfonates usually yield clear extracts; linear alkyl benzene sulfonates, on the contrary, often require filtration. This appears to be a characteristic of the extracts obtained from linear alkyl benzene sulfonates. If filtration is necessary, filter through a Whatman No. 42 paper and wash the paper thoroughly with additional volumes of petroleum ether.

Add the successive extracts to the Erlenmeyer flask and evaporate to dryness. Finally heat the residue in an oven at 105C for 3 to 5 min.

TABLE II

Neutral Oil Content of Three Sulfonates Prepared from Typical Commercial Linear Alkylates

Alkylate No.	Ethylene glycol distillation, %	Petroleum ether extraction, %	Total neutral oil, %
1	0.13	0.25[a]	0.38
2	0.43	0.36[a]	0.79
	0.39	0.40	0.79
3	0.20	0.32	0.52

[a] Petroleum ether extract required filtration.

Calculate the amount of neutral oil present as follows:

$$\frac{\text{Ml distillate} \times 0.856 \times 100}{\text{Weight of sample}} = \%\ \text{Volatile neutral oil}$$

$$\frac{\text{Weight of extract} \times 100}{\text{Weight of sample}} = \%\ \text{Nonvolatile neutral oil}$$

$$\%\ \text{Volatile neutral oil} + \%\ \text{nonvolatile neutral oil} = \%\ \text{Total neutral oil}$$

Discussion

Table I presents a comparison of results for the determination of the neutral oil content of a commercial sodium alkyl benzene sulfonate by the method of Weeks et al. (2) and AOCS Tentative Method Dd 4-60. Results by a third method in which the extracted neutral oil was permitted to come to constant weight by spontaneous evaporation at room temperature are included in the table.

It is apparent from an inspection of the results that the AOCS method yields low results as a result of evaporation of the petroleum ether extract of neutral oil to constant weight on a water bath. The neutral oil results obtained by combined distillation-extraction are appreciably higher due to avoidance of the losses occasioned by heating to constant weight, and the third method yields results that are intermediate. In the latter case it is believed that the extract finally attains static equilibrium during spontaneous evaporation of the more highly volatile constituents.

Seven replicate determinations of the neutral oil content of a typical detergent slurry by one analyst yielded a high of 0.660 and a low of 0.605% neutral oil by the distillation-extraction technique.

The standard deviation of these results is 0.018, an estimate of the same relative order of magnitude as the precision of the current AOCS Tentative method; however, the results are inherently more accurate since there are no losses of volatile neutral oil in bringing the petroleum ether extract to constant weight.

Part II—Composition of Neutral Oils from Linear Alkyl Benzene Sulfonate Slurries

A number of studies, undertaken to elucidate the composition of neutral oil, have been reported (3,4). The work described to date has been concerned mainly with branched alkyl benzene sulfonate slurries and a corresponding paucity of information exists in respect to the composition of the neutral oil from linear alkyl benzene sulfonates.

The current availability and interest in linear alkylates prompted an investigation of the neutral oil isolated from detergent slurries produced by the oleum sulfonation of three commercial linear alkylates. The linear alkylates were selected to cover the range of material presently available on the market and are representative of production by three different suppliers of alkylate.

Experimental

Preliminary work indicated that the neutral oil contained highly volatile fractions. The method of Weeks et al. (2) is ideally suited to avoid losses by volatilization, and it was, therefore, employed to isolate a sufficiently large quantity of the neutral oil to permit a study of composition.

Detergent slurries in the form of sodium salts of the respective sulfonates of three different commercial linear alkylates resulting from plant production sul-

TABLE III

Mass Spectrometric Data on Ethylene Glycol Distillates of Sulfonates Prepared from Three Typical Commercial Linear Alkylates

Alkylate No.	1		2		3	
	Neutral Oil	Standard[a]	Neutral Oil	Standard[a]	Neutral Oil	Standard[a]
Mol. Wt.[b]	247.79	254.23	259.23	256.12	239.33	236.88
Distribution[b]						
Mass 176 C-7	3.3	0.6	1.2	0.5	0.8	0.4
190 C-8	6.8	0.8	1.6	0.7	1.1	0.6
204 C-9	3.8	0.7	1.5	0.6	1.1	0.3
218 C-10	3.9	0.5	0.7	0.5	5.9	10.2
232 C-11	8.1	7.2	2.3	3.2	42.3	51.2
246 C-12	22.6	37.1	23.8	31.7	37.6	29.6
260 C-13	24.4	34.1	44.3	47.8	9.5	6.7
274 C-14	25.3	18.7	17.3	14.2	1.5	1.0
288 C-15	1.5	0.2	1.8	0.3	0.3	0.02
302 C-16	0.3		1.8	0.1	0.04	
316 C-17			1.7	0.1	0.03	
330 C-18			1.1	0.1		
344 C-19			0.5	0.04		
358 C-20			0.5	0.09		
Unsaturates[c]	41.97	5.89	5.75	5.93	3.28	3.80
Phenyl Positions:						
2-phenyl	7.4	29.17	6.8	32.99	17.7	35.98
3-phenyl	18.1	17.61	13.8	17.98	30.5	20.07
4-phenyl	20.2	15.28	17.9	14.37	14.9	12.93
5-phenyl	24.9	19.98	28.7	18.12	20.9	16.53
6-phenyl	29.3	17.94	32.9	16.54	16.0	14.49
Diphenylalkanes	Absent	Absent	Present	Present	Absent	Absent
Dialkylbenzenes	Absent	Absent	Present	Present	Present	Absent

[a] The standard is alkylate obtained by desulfonation of the detergent slurry from which the neutral oil was isolated.

[b] Molar mol. wt. and distribution of normal alkylbenzenes.

[c] The per cent unsaturates is relative to the alkylbenzenes.

fonation were selected for study. The neutral oil was isolated utilizing the distillation-extraction procedure. Parallel quantitative determinations run on smaller quantities of the identical samples yielded results for the neutral oil content shown in Table II.

The physical characteristics of the distillates varied widely. The distilled oil from the alkylate designated as No. 1 (Table II) was colorless and possessed an odor similar to that of paraffin wax. The distillate from the second sample was pale yellow in color with the typical odor usually associated with neutral oil. Sample No. 3 yielded a colorless and almost odorless distillate. In all cases the petroleum ether extract of the still residue after evaporation was odorless.

Composition of Neutral Oil

The distillate from No. 1 (characterized as containing the smallest amount of neutral oil of the three samples examined) was found to consist of linear mono-alkyl benzenes, a trace of linear p-dialkyl benzenes and aliphatic linear hydrocarbons. The extent of branching of the aliphatic hydrocarbon chains is very low. An infrared spectrum of this material is shown in Figure 1,A.

Mass spectrometric examination of the distillate from No. 1 disclosed large yields of unsaturated species (approximately 42%) compared to normal alkyl benzenes (cf. Table III). The unsaturated species possess a chain length of C_9 to C_{10} carbon atoms. Branching is apparent. Practically no high molecular weight materials are to be found above the normal C_{15} alkylate. The excessive amount of unsaturates is unexplainable, but it is evident that these entities are preferentially concentrated in the neutral oil. While alkylates from sulfonation-desulfonation processes are essentially unaltered, possible structural changes, disproportions, or branched species may be concentrated in the neutral oil and thus become greatly magnified compared to the total sample.

The distillate from sample No. 2 was determined to consist of linear mono-alkyl benzenes, appreciable quantities of p-dialkyl benzenes and aliphatic linear hydrocarbons. The extent of branching is again low but higher than found in Sample No. 1. Figure 1,B shows the infrared spectrum obtained with this material.

Mass spectrometric examination of the distillate from this second sample disclosed it to be definitely branched and rich in alkylate content (cf. Table III). Essentially normal amounts of unsaturates were found. A possible explanation for this would be a lower degree of sulfonation, resulting in a higher neutral oil content and possibly maintenance of the ratio of unsaturates to normal alkylates. This distillate shows twice as much light ends and approximately a tenfold increase in the heavy ends, compared to its standard.

The distillate from the third sample possessed a fairly high mono-alkyl benzene content and showed appreciable branching of the alkyl chain. Di-alkyl benzene was not detected. The amount of aliphatic hydrocarbons is very low. The infrared spectrum of this material is shown in Figure 1,C.

Mass spectrometric examination of the distillate from sample No. 3 revealed high amounts of the customary alkylbenzenes together with dialkylbenzenes (small) and moderate amounts of paraffin. An unidentified component of mol wt 326 was detected. The extent of branching is greater than normal.

The corresponding petroleum ether extracts of the still residue for all three alkylates were found to be nearly identical in character and gave infrared spectra typical of di-(p-linear alkyl aryl) sulfones. Examination of the petroleum ether isolate from the third sample disclosed fairly appreciable alkyl branch-

TABLE IV

Summary of the Composition of Neutral Oil Present in Branched and Linear Sodium Alkyl Benzene Sulfonates

Branched alkyl benzene sulfonate[a]	*Linear alkyl benzene sulfonate*[a]
Neutral oil: Ethylene glycol	*Neutral oil: ethylene glycol*
Distillation fraction	*Distillation fraction*
Extremely complex, highly branched hydrocarbons exhibiting t-butyl groupings.	Paraffins, cycloparaffins or olefins. Marked branching present in some samples.
Mono- and dialkyl benzenes, C_8 to C_9.	Linear monoalkyl benzenes.
	Linear dialkyl benzenes.
Conjugated diolefins.	Indane, indene types may be present with tetralinics.
Carbonyl compounds (Ketones).	
Neutral oil: extraction fraction after distillation	*Neutral oil: extraction fraction after distillation*
Di(p-alkyl aryl) sulfones.	Di(p-linear alkyl aryl) sulfones.
Trace amounts of carbonyl compounds.	Small to trace quantities of carbonyl compounds.
	Traces of unidentified sulfur containing materials.

[a] Components are listed in order of decreasing amounts in each fraction. The table embodies results of both infrared and mass spectrometric examination.

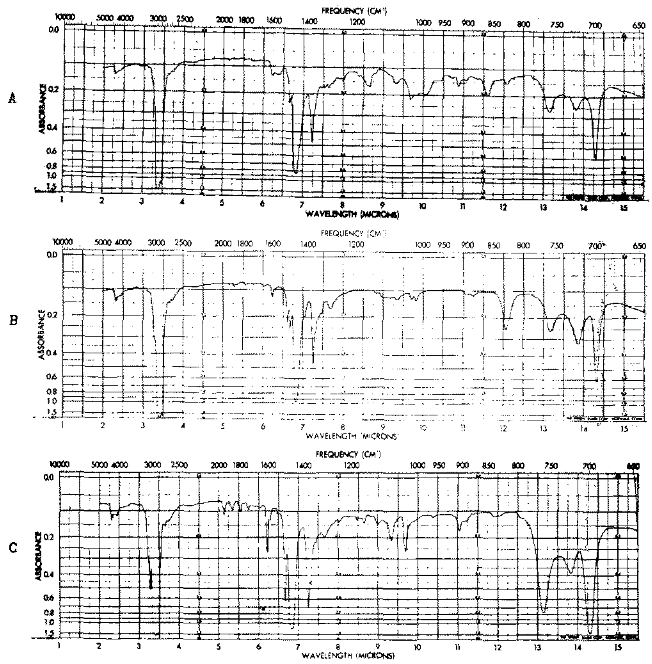

FIG. 1. Infrared spectra of ethylene glycol distillate from sulfonated alkylates A, B and C for alkylates 1, 2 and 3, respectively with 0.020 mm spacer.

ing in the side chain. Infrared spectra of all three petroleum ether extracts are shown in Figure 2.

Discussion

Complete mass spectrometric data for the three samples studied are shown in Table III. Methods for the derivation of molar distributions (5,6) and phenyl position computation (7) have been published elsewhere. In each case the standard employed consisted of desulfonated alkylate obtained from the detergent slurry from which the neutral oil was isolated. The sulfonates were reduced to the original alkylates by desulfonation with phosphoric acid (8,9).

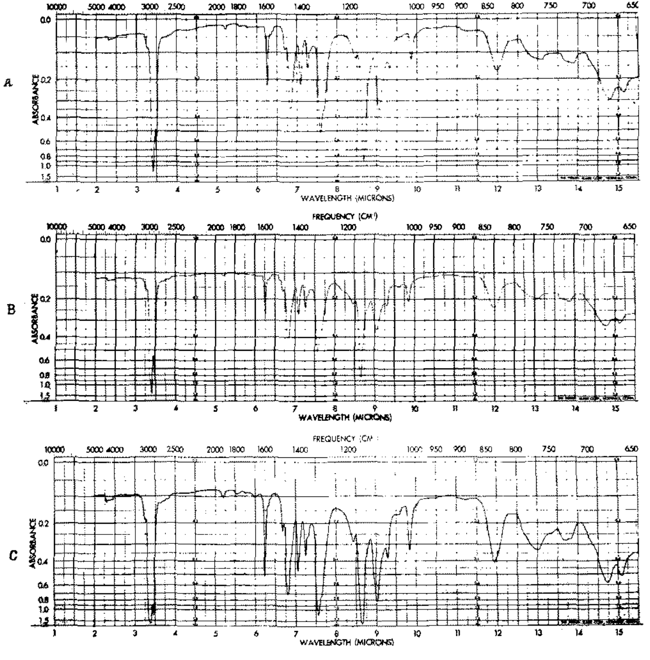

FIG. 2. Infrared spectra of petroleum ether extract of still residues from sulfonated alkylates A, B and C for alkylates 1, 2 and 3, respectively.

A general observation can be made relative to the composition of the alkyl benzenes obtained by ethylene glycol distillation. In each instance it appears that the principal chains are shifting to increased chain lengths. In addition, light and/or heavy ends are becoming more evident. This conclusion is apparent from examination of the data presented in Table III.

A further significant fact is that all of these distillates show an obvious drop in the 2-phenyl content. This alteration is quite striking but no explanation is available at this time. The third sample shows a marked excess of 3-phenyls which suggests that a greater degree of branching is present than normally encountered in linear alkylbenzenes.

Table IV presents a summary of the volatile and non-volatile components found in neutral oil isolated from linear sodium alkyl benzene sulfonates respectively by combined distillation over ethylene glycol at 185C and extraction of the still residue. The composition of neutral oil from a typical branched alkyl benzene sulfonate, previously examined, is included for comparison.

In evaluating the infrared and mass spectrometric results, particularly the latter, for the composition of the neutral oil isolated from branched versus linear alkyl benzene sulfonates, an obvious difference is apparent between the chaotic mixture of components present in neutral oil from branched alkyl benzene sulfonate compared to the fewer and less complex components that constitute and distinguish the neutral oil in linear alkylate sulfonates.

Attention is called to the small or trace quantities of carbonyl compounds found in that portion of the neutral oil obtained by petroleum ether extraction of the still residue remaining after the ethylene glycol distillation of linear alkyl benzene sulfonates. It has been observed that in separating the inorganic salts from a linear sodium alkyl benzene sulfonate slurry by extraction with alcohol, the carbonyl content of the alcohol soluble material (active ingredient) increases proportionately with length of time required to dry the alcohol soluble material, eventually reaching a relatively high concentration as the length of time of heating at 105C increases. This is readily observable when infrared spectra of the organic alcohol soluble material are run at successive intervals of drying time and later compared. An hypothesis to explain this observation is that the secondary hydrogen on the α-carbon to the phenyl ring readily oxidizes to a hydroperoxide alcohol which in turn oxidizes to a ketone. Since this oxidation proceeds readily in linear sodium alkyl benzene sulfonates it may be of importance in the evaluation of spray dried detergent formulations. The exact nature of the carbonyl compound is unknown. Infrared spectra also indicate the possible presence of an acid carbonyl.

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