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**LARGE-SCALE SAMPLES OF SULFONATES FOR LABORATORY STUDIES
IN TERTIARY OIL RECOVERY: PREPARATION AND RELATED STUDIES**

Quarterly Report, August—October 1977

By
Earl W. Malmberg

January 1978
Date Published

Work Performed Under Contract No. EF-77-C-01-2605

Suntech, Inc.
Richardson, Texas

MASTER

U. S. DEPARTMENT OF ENERGY

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Date Published--January 1978

PREPARED FOR THE UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

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I. COVER PAGE

II. OBJECTIVE AND SCOPE OF WORK

The overall objective of this project is to provide samples and information that will contribute to the resolution of current questions/problems in the nature and supply of oil recovery sulfonates. The scope of the work is as follows:

1. To review current refinery and petrochemical operations in order to select candidate feed stocks for the preparation of synthetic and petroleum sulfonates.
2. To study alkylation and sulfonation reactions and their products on a laboratory scale; to survey the properties of these sulfonates in oil recovery systems.
3. To select a suite of samples from the candidates and prepare 50 pounds of each; this quantity will be distributed in laboratory-sized samples to interested organizations; to provide refinery characterization data on all feedstocks used in the preparations.
4. To have all relations with respect to sample distribution, information input and distribution, etc., handled by an independent organization, the New Mexico Petroleum Recovery Research Center, Dr. J. J. Taber.
5. To carry out a preliminary evaluation of these samples with respect to salinity, temperature, and oil recovery.

III. SUMMARY OF PROGRESS TO DATE

- A. Project Time Schedule: - In the Monthly Report for September 1977, the original Milestone/Task Chart was revised to adjust for the date of finalizing the contract and the change of the time period from twelve to fourteen months. This chart, with the subdivision into phases of work, serves as an effective basis for describing the performance and current overall status of the project in this report (Figure 1).
- B. Phase I and II: - The end of the sixth month is the milestone for the end of Phase I, Process Evaluation. The studies on the alkylation reaction and laboratory scale products have defined the nature of the reaction so that the olefin and aromatic starting materials

could be specified and ordered. The alkylates in general have been carried through the sulfonation step; one result is the set of small samples of the sulfonates which were proposed in the original program. Analysis and characterization of these products is one of the important inputs to the choices made for the large-scale samples.

For the alkylation reaction, the needed analytical studies and distillation curves have been completed. Catalyst studies and related work are complete and the large scale alkylation equipment is ready to operate. We were fortunate in being able to share the cost of getting this equipment set up with another project which is using it in a related chemical operation. Some laboratory studies on sulfonation procedures are complete, but the initial large scale work may indicate additional factors to investigate in the laboratory because a rather wide range of hydrocarbon substrates are to be sulfonated.

As mentioned above, characterization and selection of the refinery materials which are to be used has been a primary concern in the process evaluation phase of this project. The candidate sulfonates chosen as final products have as one very important property the molecular weight. Hence backward through the sequence, sulfonation, alkylation, and choice of reactants, the desired final molecular weight and possible degradations during the reactions will dictate the choice of the molecular weight of the reactants.

As discussed in the Monthly Report for September 1977, propylene tetramer has been a standardized industrial product for years. As might be expected from the reaction of preparation, the product is a distribution of molecular weights with the primary product, tetramer, being optimized. Representative distributions were shown in the Quarterly Report for May-July 1977. The "pentamer" has been a co-product for which market demand has never been beyond the level supplied by the co-product from tetramer manufacture.

Mass spectrometry with low ionization voltage is a basic method for analysis of olefins and alkylaromatics. An ASTM procedure is available for propylene tetramer. This MS-computer data processing approach has been extended to C₁₅ oligomers for characterization of the molecular weight distribution and the molecular weight of propylene oligomer fractions from commercial streams. Even in the ASTM procedure for tetramer, certain parts of the mass spectrum are known to be artifacts and are disregarded;

fragmentation of the hydrocarbon produces mass peaks that are known to not be present from, for example, fractional distillation results. As the same analysis is extended to pentamer and higher, the interpretation of the mass spectra becomes more and more difficult. The generally accepted information is the molecular weight distribution in the known boiling range. Despite publication of similar methods for analysis of saturated and alkylaromatic compounds, no agreement on procedures has been reached in cooperative industry programs. For the alkylates, the mass spectrometric analysis has been used for defining the molecular weight distribution of the alkyl benzenes, and for this purpose is accepted. Mass spectrometric data has as well been used as a rough indication of molecular weight of the alkylate, from which the equivalent weight of the sulfonate has been calculated. This calculation requires selection of data and normalization procedures which again can be questionable as attempts are made to apply the method to higher molecular weights. As specific choices of fractional distillation cuts are made for the large-scale starting materials, consideration of other more direct methods for checking the final sulfonate molecular weight are being tested. The first recourse is to methods that are used for sulfonates at present. They are in general rather elaborate and time-consuming procedures. (For example, see the review in the paper by Sandvik, Gale, and Denekas, SPE J 17 184 (1977)). For a procedure which has been in current use, ASTM-D 1216, the committee has voted withdrawal of approval. Other analytical procedures suggest themselves from recent publications on sulfonates; the application to synthetic sulfonates simplifies the problem somewhat. We have developed a preliminary form of a procedure. It has been used in order to help us choose and operate on the valid and most useful part of the mass spectrometric data. The procedure is described later in the report as well as some preliminary results which indicate an appreciably smaller amount of degradation of the propylene oligomer in the alkylation than the overall results from the mass spectrometric results.

Plans for the preparation of the large samples of sulfonates were sketched briefly in the Monthly Report for September 1977. The initial large scale preparations were to be those with propylene tetramer, for which the characterization data are not in question. Similarly the normal olefin derivatives show no problems. This planning was based on anticipating more difficulty with pentamer, and hence we have some time flexibility to handle these compounds.

- C. Phase III: - Exploratory work in evaluation of the laboratory-produced sulfonates has included middle-phase optimal salinity studies, observations on salinity grids, and oil recovery tests in one-foot sand packs. In view of the product of the number of samples multiplied by the number and the range of variables, the exploratory work has primarily been directed at procedures to contain the proliferation of experimental work.

Initial experimental work had been done on some hydrocarbon phases up to 40 percent aromatic (based on refinery oils used by the Exxon Production Research) because our own work and a certain amount of published work showed a significant proportion of fields involved in tests were 25 percent aromatics and over. As mentioned in the August Monthly Report, the aromatic content can be difficult in some respects; when additional information showed that perhaps only one-tenth of the total candidate reservoirs were in that range, work was restricted to the lower levels of aromatic content.

The work by Dr. Taber and his group at the New Mexico Petroleum Recovery Research Center in evaluation has been primarily in developing capabilities and equipment for the basic operations in surfactant recovery research.

- D. Overall Planning of Program: - Dr. Tabor's primary concern has been soliciting information from groups who are interested in using the sulfonate samples. Their preference as to type of sulfonate, structure of the synthetic sulfonates, and molecular weight have been tabulated and are now available as the final plans are being made for the specific samples. The interest was in general spread over the range of samples we had initially described.

IV. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

The synthetic sulfonate samples to be produced are to be as representative as possible of materials which could be manufactured in large quantities industrially. The design is in a sense tied to existing technology and has limitations in certain areas, as was discussed in the September Monthly Report. At the same time efforts are being made to include materials not now manufactured, but for which it is reasonable to believe that the technology could be developed. The work to be discussed in this part will describe the design

of sample program which will be optimum from this view and from the input from interested groups which has been summarized by Dr. Taber. The first topic in this section will be the description and resolution of the problem of relating the mass spectrometric (M.S.) analysis of alkylates to the equivalent weight of the final sulfonate. This problem is central to the plans for preparation and distillation of the hydrocarbon feed stocks.

A. Phases I and II: Process Evaluation and Preparation of Large Samples

1. Equivalent weight of synthetic sulfonates: - The computer programs which are used in Marcus Hook in the complex data processing of mass spectrometric results includes in its output a value for the "Average Molecular Weight". This output is part of the conventional analyses of samples such as an olefinic or alkylaromatic hydrocarbons with the LIV procedure. This average is sometimes heavily weighted by components which are artifacts of the analysis such as molecular fragmentation particles. Although nominally these components can be eliminated by distillation information on the sample, etc., our problem has been to establish the validity of "editing" MS data in these procedures in which industry standard methods have not been adopted. The complete mass spectrum is printed out in these programs so that, for example, in alkylaromatics the range of molecular weights of the alkylaromatics, $C_n H_{2n-6}$, is presented, and in addition molecular sequences which differ by successive steps of loss of $2H$ by cyclization or aromatization. Thus the sequence of alkylaromatics is followed by $C_n H_{2n-8}$, the naphthenoaromatics, $C_n H_{2n-10}$, the dinaphthenoaromatics, and so forth. This "Average Molecular Weight" thus far has been used to calculate the equivalent weight (same as molecular weight) for the final sulfonates. In many of the alkylations with propylene pentamer, appreciably lower molecular weights in the products than expected has been a serious question. Many of the final sulfonates appear to have equivalent weights which depart appreciably from the planned values.

A method of determining the equivalent weight of sulfonates that is not forbiddingly tedious and time-consuming was suggested by some results of Dr. Larry Smith of our laboratory with petroleum sulfonates. A chromatographic de-oiling and desalting procedure was monitored by thin layer

chromatography for detecting the presence in successive effluent fractions of oil and monosulfonates. In samples where they are present, di- and poly-sulfonates will be separated and follow the monosulfonates. The monosulfonate is isolated by evaporation of the solvent and weighed. Epton titration of the residue will then give the equivalent weight. The procedure and various tests that were applied to ascertain the validity of the run procedure are presented in Appendix I. The equivalent weight data for the sulfonates prepared in the Process Evaluation phase in Marcus Hook are presented in detail in a table in that appendix. For discussion here, the measured values are compared with what are believed to be the best comparison values, as shown in Table I.

The good agreement in the first five samples was gratifying and led us to proceed with the Marcus Hook samples. The "MS results...." column is the calculated weighted average equivalent weight from the alkylaromatic series in the MS results. With this generally good agreement we will adopt the customary procedure of using the data of the alkylaromatic series to describe the molecular weight distribution in the final sulfonate. We will anticipate continued reasonable agreement with an independently measured equivalent weight.

The generally positive error and the large error for Sample 809 bear out our expectations that persistent and possibly random error will enter in the weight of the residual sulfonate. Contamination with oily material and with column packing material are possible, although a blank run gave a residue of only .2 to .3 percent.

Work Forecast: Work on improving the procedure will continue. Additional measurements of ultraviolet absorption spectra contribute to better control of the chromatographic process. The basic information on equivalent weight of the prototype sulfonates now allows us to finalize procedures for distillation, etc., of the starting materials.

2. Preparation of prototype alkylates and sulfonates: - The sulfonates studied in the preceding Section 1 were prepared in the process studies by the basic

TABLE I
SUMMARY OF EQUIVALENT WEIGHT STUDIES
ON
MARCUS HOOK SYNTHETIC SULFONATES

Base Hydrocarbon	Equiv. Weight, Sodium Sulfonate			Difference %
	Chromatography, Titration	MS Results on Alkylaromatics	Others	
Dodecyl ⁽¹⁾	271		272	0
Exxon Chemical				
(C ₃) ₄ -o-xylene	421		421 ⁽²⁾	0
(C ₃) ₅ -o-xylene	377		381 ⁽²⁾	-1
(C ₃) ₅ -benzene	404,404	400 ⁽³⁾		+1
(C ₃) ₅ -benzene	425	418 ⁽³⁾		+2
(C ₃) ₄ -xylenes 807	387	375		+3
(C ₃) ₄ XTB 809 ⁽⁴⁾	470	388		+21
(C ₃) ₅ toluene 815	424	412		+3
(C ₃) ₅ xylenes 837	445	418		+6
(C ₃) ₅ toluene 851	400	390		+3
(C ₃) ₅ toluene 871	420	410	375 ⁽⁵⁾	+2
(C ₃) ₅ toluene 873	410	404	404 ⁽⁵⁾	+1
MC ₁₇ -xylenes 887	422	431		-2

(1) Pure recrystallized sample.

(2) From manufacturer's "Physical Characteristics", as determined by ASTM D 1216.

(3) Made from commercial alkylate.

(4) XTB: xylene tower bottoms, C₉ alkyl benzene

(5) Based on molecular weight of alkylate as determined by vapor pressure osmometry.

procedures which are described in Appendix II. Further information on preparation of the alkylates was developed in a set of experiments shown in Table II.

TABLE II

EFFECT OF CATALYST RATIO ON
ALKYLATION REACTION: TOLUENE + $(C_3)_5$

Run No.	Catalyst Level gm/100gm	Alkylate Yield %
865	1.2	12
863	2.3	30
869	3.5	47
879	4.7	47
881	5.8	56

It must be realized that with such a wide structural range for the olefins and aromatics in this program there is no way to work towards optimum reaction conditions for high yields. This study was needed because catalyst preparation may require appreciable effort and hence should be minimized if possible.

Work Forecast: The alkylation procedures now are ready for large-scale work. As the sulfonation reaction is applied on larger scale, laboratory studies may be necessary to define the reaction conditions for some of the hydrocarbon substrates. Some with higher substitution, etc., will be more difficult to sulfonate in good yield.

3. Preparation of large-scale samples: - Preparation of equipment for alkylation is complete and the required feed stocks are on hand. Large-scale preparation has been started.

Work Forecast: The work is planned in accord with the general approach already mentioned. It is best described with respect to the classes of alkylate.

- a. Propylene Tetramer: Alkylates from $(C_3)_4$ will be prepared first since the feed stock requires less preparation and the reaction proceeds more cleanly. Since these alkylates are a better raw material situation and are not as complex as the $(C_3)_5$ products, they will be used in the initial runs for large-scale sulfonation.
- b. Propylene Pentamer: Preparation of the pentamer alkylates in large scale can now proceed. The molecular weights of the sulfonates will be at the planned level. The samples involving the wide boiling range pentamer will be watched as closely as possible to note any exceptional properties.
- c. n-paraffin alkylates: The preparation of alkylates from Chevron alpha olefins is a good clean reaction which proceeds in good yield. The lowest cost potential industrial product in the C_{15} - C_{18} range is the random olefin, and hence we hoped to randomize the alpha olefin if necessary (the alkylation catalyst probably will not randomize enough before alkylation occurs; the possibility is to be checked). The recommended catalyst for randomization involves a hazard in large-scale use. Hence at this stage we plan to make only one of the linear n-paraffin alkylates.

B. Phase III: Sample Evaluation.

The sulfonate prototype samples have been used for exploratory studies on characterization. During the past several months studies on salinity grids up to five percent sodium chloride and 500 ppm. of Ca^{++} have been made. The various sulfonates have sorted out into groups as might be expected from their related structures. The use of the Exxon refinery products, the Heavy Aromatic Naphtha and Isopar M, are still useful and of interest, but are lower in molecular weight than is desirable for generality. However, other commercially available hydrocarbons are either of the same low molecular weight or

else of very high viscosity. We have not found a generally available material with which the full range of most crude oils can be simulated.

Work Forecast: As the large-scale samples become available, the salinity grids and sand pack recovery runs will be used in at least the initial stages of the study.

C. Overall Planning of the Program:

So far in this report information on studies of the reactions and the products has been discussed, and the implications for the preparation of the large-scale samples have been mentioned where they are pertinent. The work is proceeding rather close to the overall program as it was originally proposed. Dr. Taber has summarized the response to his questionnaires regarding the needs and desires of groups interested in the samples. The results have been summarized in Table III. The input from this source is essentially in agreement with the work now planned. Several early requests were for sulfonates of higher equivalent weight. Suitable alkylates for agents of this type are under study and are kept in mind as distillation of various alkylates may yield products of higher molecular weight.

V. CONCLUSIONS

- A. In exploring and evaluating feed stocks and reaction conditions, about fifteen synthetic sulfonates have been prepared. The group is an expanded prototype of the sulfonates to be made as large-scale samples.
- B. These prototype samples have been used to evaluate methods of formulating and characterizing the sulfonates as oil recovery agents.
- C. A method of determining the equivalent weight of sulfonates has been developed with this group of prototype samples. A problem in interpreting and applying mass spectrometric analyses of alkylates has been resolved with this procedure.
- D. The feedstocks for the preparation of alkylate are on hand. The resolution of the equivalent weight question has confirmed the original estimates of distillation ranges, etc.

TABLE III
Synthetic and Petroleum Sulfonate
Samples Requested by Research Workers

Reported to and summarized by Dr. J. J. Taber

Sample No.	Number of Researchers Requesting Each Sample					Apparent Preference (1=1st ch.)
	Total Requests	1st. Choice	2nd Choice	3rd Choice	Total 1st, 2nd & 3rd choice	
I	6	2	1	0	3	4
II	8	2	2	2	6	1
III	5	2	0	0	2	7
IV	7	2	3	0	5	2
V	6	1	1	3	5	3
VI	5	1	1	1	3	5
VII	6	0	2	1	3	6
VIII	5	0	1	0	1	9
IX	6	0	1	0	1	8
X-P.S.	4	2	0	1	3	10
No prefer- ence	4	-	-	-	-	10

<u>SAMPLE CODE</u>	<u>Mol.Wt.</u>	<u>AROMATIC</u>	<u>OLEFIN OLIGOMER</u>
I	288	Mixed Xylenes	Narrow Range (C ₃) ₄
II	316	Mixed Xylenes	Narrow Range (C ₃) ₅
III	288	Toluene	C ₁₄ Normal Random Olefin
IV	316	Toluene	C ₁₆ Normal Random Olefin
V	302	Toluene	Narrow Range (C ₃) ₅
VI	302	Toluene	Broad Range (C ₃) ₅
VII	309	BTF (C ₆ -C ₉)	Broad Range (C ₃) ₅
VIII	309	BTF (C ₆ -C ₉)	Narrow Range (C ₃) ₅
IX	288	XTB (C ₉)	Narrow Range (C ₃) ₄

APPENDIX I

The determination of the equivalent weight of petroleum and synthetic sulfonates is a history of the extreme difficulty of removing oil and salt completely from the crude industrial products in order to obtain a pure weighable sample of the desired sulfonate. It is somewhat simplified for synthetic sulfonates which by thin layer chromatography (TLC) can be shown to be free of di- and poly-sulfonates. The synthetics will in general include a narrow range of molecular weight of the monosulfonate. Earlier work with a chromatographic method by Dr. Larry Smith, of the Richardson Laboratory, on petroleum sulfonates was interesting because TLC was used to monitor the presence of the oil and various sulfonates as they appeared in the effluent.

The procedure in its current form is described in separate pages at the end of this section. The results of the application of this method to a number of synthetic sulfonates are given in detail in Table A-I. The results were discussed with a shortened form of the table in the text of this report. Additional discussion is given immediately following on various tests on the reliability and validity of the results.

Tests on Procedure for Determination of Sulfonate Molecular Weight

1. Sulfonates of known confirmed equivalent weight: Six of the first eight determinations in Table I-A are on known compounds. The pentadecylbenzene samples included in this group were those for which acceptable MS molecular weight results were available. The only set of duplicates run for this method were in this group, as shown in the table. In all ways the agreement is excellent.
2. TLC for detection of oil in the isolated sulfonate: Procedures used by Dr. Smith for separating components of crude sulfonates were used to detect oil in the weighed sulfonate residue. Seven samples chosen at random from Table I-A were all negative. Sample 809 was chosen as one of the samples because the high measured value indicated that non-sulfonate material might be present. Detection of possible oil zones was done with a standard charring procedure; the procedure will detect at least as low as 5 percent oil in the residue, and probably as low as 2 percent.

3. Sulfonate material balance: A sulfonate of uniform equivalent weight can be retrieved from the chromatogram in any yield without compromising the result. However, the greater the range, the more important it is that different molecular weights which may come off the column at different times be recovered quantitatively. Some of the determinations were made before more care was exercised in this regard, but there is no indication among the results that any problem was encountered.
4. Blanks on procedure: Blanks on the weight of residue and on the Epton titer of the residue were measured for the standard procedure. They were both of the order of .3 percent or less. In some samples which required isopropyl alcohol for preparation of the sample solution, the residue showed 2-3 mg. of residue, presumably from the column packing. The alcohol was used on samples such as the dodecyl sulfonate.
5. Molecular weight measurements on alkylates: The molecular weight of two alkylates, for 871 and 873 were measured by vapor pressure osmometry. As shown, 873 gave agreement, this 871 was low. This latter sample is one of the wide boiling range C₁₅ alkylates; in general studies will be continued on these samples. This measurement is being applied to a wide range of samples.
6. Ultraviolet spectroscopy: The sulfonates show ultraviolet absorbance in about the same region as the oils. Hence, the use of the Epton end point indicator. The absorbance is a more sensitive measure, however, and is preferable. Measurements and characterization in this area continue so that this measurement can be exploited for this application and for others.
7. Chromatographic procedure: The ratio of samples size to amount of adsorbent may be satisfactory for samples in which the separation is basically a fractional elution but it is not good chromatographic practice. Preliminary experiments with a better ratio on samples of broad C₁₅ alkylate showed that care must be exercised to detect and avoid weighable residues which had no Epton titer.

Evaluation of Mass Spectrometric Data

In Table I-A, the printed out "MS Average" equivalent weight of the sulfonate is obtained by taking the computer print-out for

the alkylate and adding 102 for conversion to the sodium sulfonate. This column, by comparison to the nominal equivalent weight as calculated from the formula name, indicates the basic difference we have been concerned with. In this section examples of some of the MS spectral data will be given; the best interpretation and utilization of these data we have arrived at will be presented in a number of examples.

Propylene tetramer:

Sulfonate 807 - Alkylate 797 - Fractions IV and V

MS Alkylaromatics

	Reported	Normalized	
C ₁₉	10.7	13.0	
C ₂₀	67.1	81.6	
C ₂₁	3.9	4.7	Average carbon number = 19.9
C ₂₂	0.5	0.6	
	<hr/> 82.2	<hr/> 100.0	

Sulfonate 809 - Alkylate 799 - Fractions V and VI

C ₁₉	2.0	2.6	
C ₂₀	14.2	18.3	
C ₂₁	54.9	70.6	Average carbon number = 20.9
C ₂₂	6.1	7.8	
C ₂₃	0.6	0.8	
	<hr/> 77.8	<hr/> 100.1	

Propylene pentamer:

Sulfonate 815 - Alkylate 793 - Fractions VIII, IX, and X

C ₂₁	5.9	9.9	Average carbon number = 22.6
C ₂₂	24.2	40.8	
C ₂₃	18.2	30.7	
C ₂₄	8.1	13.7	
C ₂₅	2.9	4.9	
	<hr/> 59.3	<hr/> 100.0	

Sulfonate 851 - Alkylate 847 - Fraction V

C ₂₀	20.9	33.3	Average carbon number = 21.0
C ₂₁	26.7	42.6	
C ₂₂	12.2	19.5	
C ₂₃	2.2	3.5	
C ₂₄	0.5	0.8	
C ₂₅	.2	.3	
	<hr/> 62.7	<hr/> 100.0	

Sulfonate 837 - Alkylate 827 - Fractions VIII, IX, and X

C ₂₂	8.3	15.2	Average carbon number = 23.0
C ₂₃	36.8	67.6	
C ₂₄	8.8	16.1	
C ₂₅	0.6	1.1	
	<hr/> 54.5	<hr/> 100.0	

n-alpha olefin - nominal C₁₅ - C₁₈

Sulfonate 887 - Alkylate 885

C ₂₁	1.4	1.7
C ₂₂	20.9	25.8
C ₂₃	22.2	27.4
C ₂₄	23.7	29.2
C ₂₅	11.7	14.4
C ₂₆	1.2	1.5
	<hr/>	<hr/>
	81.1	100.0

In the propylene tetramers and pentamers, the indanes and tetralins will peak at the same carbon number as for the alkyl benzenes. They will be present at about 4-6 percent level and dinaphthenoaromatics at 2-4 percent. Any fragmentation will amount to 10 percent or less. In the pentamers, the distribution of indanes and tetralins for sulfonate 837 is as follows:

C ₂₂	1.5%
C ₂₃	23.1
C ₂₄	1.5

Here again the distribution has its peak at the same carbon number as the alkylbenzene, and is correspondingly sharp. The total of analyzed species is lower and presumably a greater degree of fragmentation occurs for the more complex pentamer. There is reason to think the cyclized compounds are real and not artifacts. With, for example, the xylenes, it should be noted that four rather than three of the benzene carbons are substituted and therefore sulfonation may be more difficult.

The alkylate 885 made from the Chevron alpha olefin has been regarded as forming a rather clean alkylate in that the alkylbenzenes, for example in alkylate 885, forms 80-85 percent of the total mass spectrum. This compound has a special feature in the spectrum in that the only other series is the C_nH_{n-14}, molecules which contain two separate benzene rings. The content in this analysis is:

C ₂₉	3.5
C ₃₀	3.6
C ₃₁	3.0
C ₃₂	1.1

Note also the fact that the carbon number is seven above the corresponding grouping in the alkylbenzenes. For now, this circumstance will only be noted, with an admonition to be concerned about disulfonates in sulfonate 887 and similar compounds.

These examples will suffice to illustrate, (1) the nature of the MS data as obtained on higher alkylates and (2) the accepted practices in the use of this data to help characterize the final sulfonates. With the help of a new Hewlett-Packard quadrupole GC-MS, we may be able to unravel some of this chemistry in the coming months.

TABLE A-I

COMPARISON OF MS AND CHROMATOGRAPHIC-TITRATION DETERMINATIONS
OF THE EQUIVALENT WEIGHTS OF SYNTHETIC SULFONATES

Sample Description All as Sodium Salt	Meg. of Sulfonate		% of Total Sample Rec.	Equivalent Weight Data: All Sources			
	In Sample	Eluted		This Exper.	M.S. Average	Alkylate ⁽¹⁾ Alkylarom.	Formula Other
Dodecylsulfonate, pure standard	0.1397	0.1274	91	271			272
Exxon Chemical Pentadecyl-o-xylene Sulfonate	0.1512	0.1508	100	421			418 421 ⁽²⁾
Dodecyl-o-xylene Sulfonate	.1715	.127	74	377			376 381 ⁽²⁾
A-I-7 Pentadecylbenzene Sulfonates, in chronological order	.1757	.1766	100	392			390
	.152	.158	104	375			390
	duplicate	.2385	96	404		400	390
	pair	.2508	101	404		400	390
		.1627	81	425	361	418	390
Dodecylxylene Sulfonate, 807	0.261	0.249	95	387	353	375	376
Dodecyl XTB Sulfonate, 809	.130	.121	93	470	373	388	390

TABLE A-I (continued)

Pentadecyltoluene Sulfonate, 815	.2538	.2408	95	424	369	412	404	
Pentadecylxylene Sulfonate, 837	.2418	.2067	85	445	378	418	418	
Pentadecyltoluene Sulfonate, 851	.300	.289	96	400	350	390	404	
Pentadecyltoluene Sulfonate, 871	.1517	.1173	77	420	363	410	404	375 ⁽³⁾
Pentadecyltoluene Sulfonate, 873	.1128	.1038	92	410	359	404	404	404 ⁽³⁾
n-hexadecylxylene Sulfonate, 887	.247	.231	94	422	431	431	---	

(1) This equivalent weight calculated from the distribution of alkylaromatics in the mass spectrum.

(2) Determined by ASTM D 1216. (in sample description)

(3) Determined by vapor pressure osmometry on alkylate and conversion to sodium sulfonate.

THE EXPERIMENTAL DETERMINATION OF THE
EQUIVALENT WEIGHT OF A SYNTHETIC SULFONATE

A. Chromatographic Separation of the Sulfonate (De-oiling and De-salting).

Procedure

A chromatographic column (Note 1) with reservoir is prepared by first placing a Pyrex glass wool plug in the bottom of the column and then packing with a slurry of 15 grams $\pm$ 0.5g. of 60/100 mesh A Florisil (Note 2) in approximately 100 ml of chloroform. The chloroform filtrate may be re-used to maintain the consistency of the slurry. When the packing has reached a level of approximately 3/4-1 inch from the bottom of the reservoir, a 1/4-1/2 inch layer of glass beads (0.2 mm average diameter) is added to prevent erosion of the packing material (i.e., when sample is added). The packed column is then washed with approximately 60-75 ml of Reagent Grade chloroform (Note 3).

Following the chloroform washing, the sulfonate sample is introduced. It is prepared by weighing to the nearest 0.1 mg. the amount of sulfonate sample which is estimated to contain 60-100 mg. of sulfonate and dissolving it in 5 ml of chloroform (inorganic salts may not dissolve) (Note 4). The dissolved sulfonate is then added quantitatively to the column by rinsing with approximately two 10 ml portions of chloroform.

The sample is allowed to flow through the column at a convenient rate and then 175-200 ml of chloroform is added to elute the aromatic hydrocarbon (oil) contents (Note 5). Because of the large differences in absorptive strengths of the oil and sulfonate, this procedure is a selective elution of the two components and not a chromatographic developing procedure.

Once the oil has been eluted off the column, 150 ml of a 1:2 (volume) solvent of methanol in chloroform is added to elute the sulfonates (Note 6).

B. Drying and Weighing of the Residue.

Procedure

Following separation, the oil and sulfonate fractions are evaporated under a stream of nitrogen and then placed in a 60°C vacuum oven for drying to constant weight. Upon cooling in a desiccator, the sulfonate and oil residues are then weighed to the nearest 0.1 mg. (Note 7).

C. Epton Titration for Number of Equivalents of Anionic Surfactant.

Procedure

A two-phased dye-transfer titration of a sulfonate aliquot is carried out as described by Epton and modified by Smith and Malmberg (Note 8). This titrimetric analysis gives the sulfonate concentration (meq/ml) in the aliquot, from which the sulfonate's equivalent weight may be determined.

The analysis is performed by first dissolving the weighed sulfonate residue in 10-20 ml of chloroform (small volumes of isopropyl alcohol may be added to aid solubilization) and then quantitatively transferring to a 100 ml volumetric flask by rinsing with several 5-10 ml portions of chloroform. The flask is then filled to the mark with chloroform and the solution's concentration is calculated in mg./ml. Next, 15 ml of corrected chloroform, 25 ml of methylene blue solution and an aliquot (Note 9) of the sulfonate solution are pipeted and added to a 25 x 200 mm capped culture tube along with the volume of distilled water necessary to obtain a total volume of 60 ml. This aliquot is then titrated with a standardized Hyamine (Note 10) solution until the end point (equal color density in both phases) is reached. The concentration in meq/ml of the sulfonate solution is then determined (Equation 1) and also the total number of milliequivalents of sulfonate. Finally, the sulfonate's equivalent weight is calculated (Equation 2).

Notes

1. The chromatographic column was 31 cm. in length with an outside diameter of 1.2 cm. It had a Teflon stopcock and a 100 ml reservoir.
2. Silica Gel (100-200 Mesh) was also studied as a packing material and found to be a stronger absorbent than Florisil. However, Florisil was determined to be more convenient since it required less volume of solvent to develop the two sample components and because the packing did not craze or expand as greatly when methanol was added.
3. The column was washed with chloroform until the effluent chloroform stream measured essentially zero absorbance at a wavelength of 262 nm. on a Beckman Model 24 Spectrophotometer.
4. Some sulfonates are quite insoluble in chloroform. These samples can be dissolved in hot isopropyl alcohol and diluted with two parts of chloroform. For example, 70 mg. of a pure sodium dodecylbenzene sulfonate in 40 ml of the mixed solvent; no sulfonate was detected in the effluent with the usual chloroform developer. However, the isopropyl alcohol may greatly decrease the flow rate and a slight pressure of nitrogen gas may have to be applied to regain the desired flow rate.

5. Spectrophotometric techniques were used to detect the aromatic hydrocarbon content of the effluent stream and to determine completion. Absorption measurements at 240 nm. and 262 nm. Wavelengths (maximum absorption) were utilized on a double beam spectrophotometer with chloroform as the reference.
6. An Epton end point check was used to detect the initiation and completion of the sulfonate elution. The procedure was to add 3-5 drops of the effluent stream to a 13 x 100 mm capped culture tube containing 1 ml of corrected chloroform and 1.5 ml of methylene blue solution and shaking vigorously. By comparing the color density of the two phases against a blank it was possible to determine the presence or absence of any sulfonates.
7. Tare weights of the evaporation containers (200 ml beakers) were taken (to the nearest 0.1 mg.) before the fraction was added for evaporation and drying.
8. The Smith and Malmberg modified procedure is concerned mainly with using chloroform adjusted with anionic surfactant to achieve a zero end point blank (Smith, L., et al, SPE Paper Number 5369, April 1975).
9. The sulfonate solution aliquot volume was chosen to contain approximately 0.008 to 0.015 milliequivalents of sulfonate.
10. The titrant used was a 4.088×10^{-3} N Hyamine 1622 solution. The Hyamine 1622 was manufactured by Rohm and Haas.
11. The sensitivity of the Epton end point check (note 6, page 3) was tested by observing test results of various dilutions of a known sulfonate solution. The concentration of the known sulfonate solution was 2.23×10^{-3} meq/ml. The dilutions prepared (known sulfonate solution plus CHCl_3) were 4.46×10^{-5} meq/ml, 2.97×10^{-5} meq/ml, and 2.23×10^{-5} meq/ml.

The dilution containing 2.23×10^{-5} meq/ml gave a negative test for sulfonate (test consists of one ml diluted sulfonate solution and 1.5 ml methylene blue. No corrected CHCl_3 was added so that the volume of sulfonate solution added could be increased to equal the total volume of CHCl_3 necessary). The remaining dilutions were both positive for sulfonate. Therefore, the maximum sensitivity of the Epton check test is 2.97×10^{-5} meq/ml. In view of these results, the amount of effluent stream used for the test could be increased up to a total of one milliliter (this one ml to replace the one ml of corrected CHCl_3 originally used for the test), thereby increasing the sensitivity of the check test.

Calculation

1. $N_{\text{sulfonate}} = 1/V_{\text{sample}} \times V_{\text{Hyamine}} \times N_{\text{Hyamine}}$, where V_{sample} is the volume (ml) of the sulfonate solution aliquot used and $N_{\text{sulfonate}}$

represents the normality (meq/ml) of the sulfonate solution. To calculate the total number of milliequivalents in the sulfonate solution, multiply the concentration (N) by the total volume of the solution (i.e., 100 ml).

2. Equivalent Weight of Sulfonate - Weight of sulfonate (mg.) divided by the total number of milliequivalents of sulfonate.

Chemicals

A. Chromatographic Separation

1. Chloroform, Reagent Grade
2. Methanol, Absolute
3. Florisil (Trade Mark), 60/100 Mesh A, manufactured by Floridan Co.

B. Epton Titration

1. Chloroform, Reagent Grade
2. Hyamine 1622, manufactured by Rohm and Haas
3. Distilled water
4. Ultrawet, manufactured by ARCO Chem. Co. anionic surfactant used to adjust chloroform
5. Isopropyl alcohol
6. Sulfuric Acid, Concentrated
7. Methylene Blue, used as the Epton indicator
8. Sodium Sulfate, anhydrous

This procedure was developed and tested by J. W. Anderton and E. W. Malmberg. It was based on earlier studies on equivalent weight of sulfonates by Larry Smith and Sara Fowler.

APPENDIX II

Procedures used in the study of the alkylation and sulfonation reactions and for the preparation of the prototype laboratory samples of the sulfonates. Dr. D. F. Rugen and T. J. Schaefer, Marcus Hook.

ALKYLATION OF MIXED XYLENES WITH PROPYLENE TETRAMERS

1. Procedure

In a 2.0 liter round bottom three-necked flask fitted with mechanical stirrer, gas inlet tube, and addition funnel, is placed 316 g. (3.0 mole) of dry mixed xylenes. Hydrogen chloride gas is then bubbled through the xylenes for ten minutes. 7.0 g (0.053 mole) of anhydrous AlCl₃ in pseudocumene (Note 1) is added to the xylenes. A mixture of 316 g (3.0 mole) of mixed xylenes and 225 g. (1.34 mole) of propylene tetramer is added dropwise from the addition funnel with vigorous agitation. The reaction flask is cooled if necessary to maintain the flask contents at 22-25°C.

Following addition of the tetramer, the reaction mixture is poured into 1000 ml. of water and allowed to separate into two phases. The aqueous layer is discarded and 100 ml of 1.0 N NaOH solution is added to the aromatic layer with gentle stirring. The aqueous layer is again discarded and the aromatic layer is transferred to a 2.0 liter flask for distillation.

The excess mixed xylenes are removed by atmospheric distillation followed by vacuum distillation of unreacted tetramer and desired alkylate product. Yield of alkylate product, b.p. 140-160°C at 2.0 mm, is 274.4 g. (74.7%) (Note 2).

-2-

2. Notes

1. Catalyst solution is prepared by adding 125 g. (0.94 mole) of anhydrous AlCl_3 to 365 g. (3.0 mole) of dry pseudocumene and passing in hydrogen chloride gas until the solid AlCl_3 dissolves. The mixture is transferred to a moisture-proof separatory funnel. The lower layer is deep red and contains the AlCl_3 in solution.
2. Four distillation cuts of alkylate product contained 52.6, 62.9, 63.0, and 54.4% respectively of C_{20} component as determined by mass spectrometry analysis. The average molecular weight of all four cuts is 249.

SULFONATION OF XYLENE - C₁₂ ALKYLATE

m.w.	249	80.1	329.1	351
wt.	60 g.	26.3 g.	79.0 g.	84.2 g.
	0.24 mole	0.33 mole	0.24 mole	0.24 mole

1. Procedure

A solution of 60 g (0.24 mole) of xylene -C₁₂ alkylate (Note 1) in 60 g. of ethylene dichloride is placed in a 500 ml. three-necked flask equipped with magnetic stirring bar, gas inlet tube, and reflux condenser. A second 500 ml. three-necked flask containing 26.3 g (0.33 moles) of liquid SO₃ is connected to the first flask inlet tube by means of a 1/4" I.D. Teflon tube. Dry nitrogen gas is swept through the flask containing SO₃ and into the alkylate solution. The SO₃ flask is heated to 50-60°C in an oil bath and the alkylate flask is kept at 22-25°C. by means of an ice bath.

The introduction of the SO₃ requires about 2 hours during which time the alkylate solutions turn black. Following addition of the SO₃, the ethylene dichloride is removed by heating on a steam bath with an air stream to constant weight.

The sulfonic acid mixture is neutralized to pH 9.0 with 39.2 ml. of 10.0 N. NaOH solution. Final weight of the neutral sulfonate is 136 g. The neutral sulfonate mixture is then analyzed for Epton activity, water, salt, and oil content.

2. Notes

1. Alkylate average molecular weight determined by mass spectrometry is 249.

ANALYSIS OF SULFONATE

1. Procedure

A. Sulfonate activity

A two-phased dye-transfer titration of 16 mg. of neutral sulfonate is carried out as described by Epton and modified by Smith and Malmberg (Note 1). This titrimetric analysis gives % activity, i.e., milliequivalents of sulfonate per milliequivalent of sample.

B. Water content

A 50 g. sample of neutral sulfonate is analyzed for % water content by ASTM D-95-70 using 500 ml of toluene as the water-immiscible solvent. The volume of water collected in the Dean-Stark tube is measured and divided by the weight of the sulfonate sample.

C. Salt content

The toluene solution from the water analysis is filtered through a 60 ml sintered glass filter funnel containing 1/2 inch of packed Celite analytical filter aid. The sintered glass funnel with celite has been previously heated at 100°C for 1-hour and weighed. 50 ml of toluene is used to wash the flask and put through the filter.

The filter is then heated in an oven at 100°C for 1-hour and weighed. The difference in weight (final minus original) is taken as weight of salt. % salt content is then weight of salt divided by weight of sample.

D. Oil content

The oil content is calculated as the difference between the sum of the % sulfonate activity, % water, % salt and 100.0.

2. Notes

1. The Smith & Malmberg modified procedure is concerned mainly with using chloroform adjusted with added anionic surfactant to achieve a zero end point blank (Smith, L., et al, SPE Paper Number 5369, April 1975).