Influence of Unsulfonated Material and its Sulfone Content on the Physical Properties of Linear Alkylbenzene Sulfonates[1]

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Free oil content (unsulfonated matter) in linear alkylbenzene sulfonates has a considerable influence on the physical properties (viscosity and cloud point) of sulfonate slurries. It has been found that a determining factor in this influence is the sulfone content in free oil. This has been observed in several commercial sulfonic acids and confirmed through laboratory sulfonation tests. In order to better understand the effect of the sulfone content, a high performance liquid chromatography method for its determination was developed.

It is frequently found among different detergent manufacturers and industrial sulfonators that solubility (cloud point) and viscosity of sodium sulfonates of a given linear alkylbenzene (LAB) can show great variations. One possibility is to correlate this with the operating conditions of the sulfonation unit. In fact, it is a normal practice during the operation of sulfonation units to keep a certain free-oil level constant in order to control the quality of the final product. The influence of free oil content on linear alkylbenzene sulfonates' (LAS) characteristics has been reported in past publications (1).

However, more important than the free oil content alone is the sulfone content in this free oil, as this kind of compound is responsible for substantial variations in the physical properties of LAS, even when the free oil content of different sulfonates is the same. The formation of the sulfones is directly correlated to the severity (increasing acidity) of the sulfonation reaction. No effect has been observed when changing the dilution of SO_3 in air. A study has been conducted with commercial sulfonic samples as well as with laboratory samples, and an HPLC analytical method has been developed to determine the sulfones in free oil.

COMMERCIAL SULFONIC ACIDS ANALYSIS

Eight different commercial sulfonic acids, all of them derived from the same LAB (Table 1), were taken from different commercial sulfonation units, all operating with SO_3 as sulfonating agent.

LAB produced via the HF process has a very low tetralin content. Table 2 shows the analysis of the eight sulfonic acids, and it can be observed that all of them reflect normal characteristics with the exception of the free oil content which varies from 0.9 to 2.1. This variation obviously is related to the severity of the sulfonation reaction.

Despite the suspected difference in sulfonation severity, the viscosity of the eight acids is quite constant. This can be observed frequently in sulfonic acids derived from the same LAB, in contrast to viscosities of slurries which are substantially different, as will be noted later on.

TABLE 1

(GC-MS) Analysis of Original Alkylate

	wt %
Phenyl C_{10}	9.5
Phenyl C_{11}	29.9
Phenyl C_{12}	29.9
Phenyl C_{13}	23.8
Phenyl C_{14}	1.1
Branched alkylate	5.04
2-Phenyl alkanes	18.5
Tetralines	0.45
Diphenyl alkanes	0.31
Mol wt	241.2

TABLE 2

Commercial Sulfonic Acids Analysis

Sample	Free sulphuric acid (wt%)	Unsulfonated matter (free oil, wt%)	Active ingredient (wt%)	Water
1	2.0	0.9	95.9	Balance
2	2.5	0.9	96.0	Balance
3	1.9	1.1	95.7	Balance
4	2.7	2.0	94.7	Balance
5	2.3	2.1	94.5	Balance
6	2.8	1.3	95.8	Balance
7	2.1	1.1	96.2	Balance
8	1.7	1.7	95.9	Balance

TABLE 3

Viscosity of Commercial Sulfonic Acids at 30 C

Sample	Centipoises
1	910
2	860
3	960
4	910
5	890
6	920
7	880
8	1,000

Table 3 reflects the viscosity at 30 C of these sulfonic acids, ranging from 860 to 1,000 centipoises. These data are slightly higher than the viscosity of laboratory sulfonic acids, probably because of the effect of the aging step in industrial sulfonation.

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[1] This paper was presented during the XVIII-Jornadas of CED-AID, Barcelona, Spain, in March 1987.

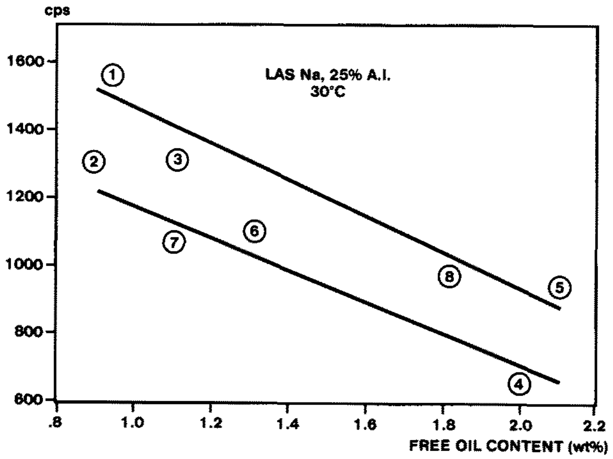


FIG. 1. Commercial sulfonic acids, slurries viscosity.

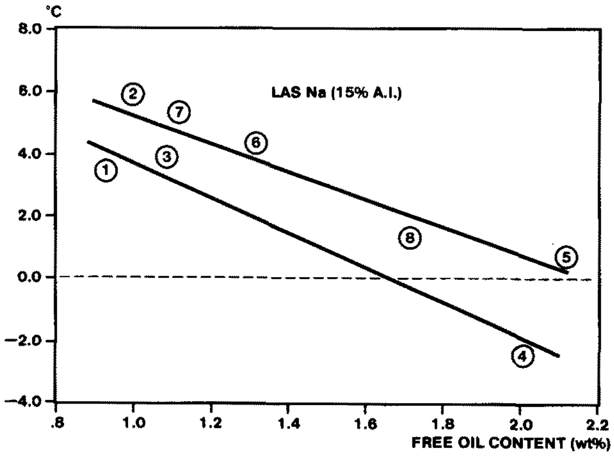


FIG. 2. Commercial sulfonic acids, slurries solubility (cloud point).

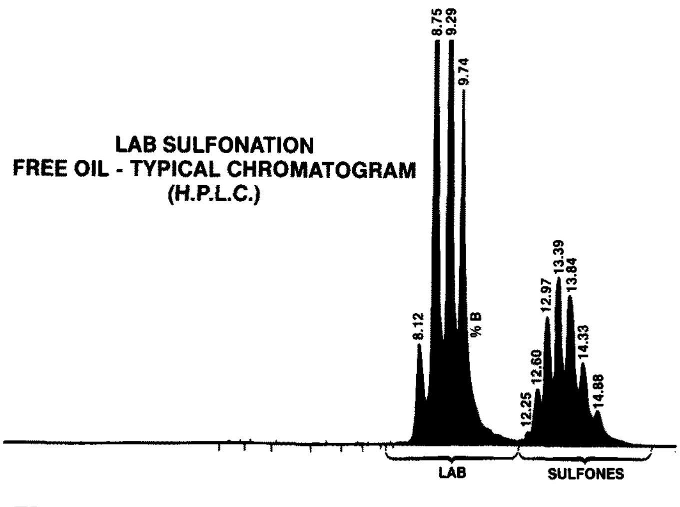


FIG. 3. LAB sulfonation, free oil, typical chromatogram (HPLC).

Once the acids were neutralized with caustic soda, a viscosity and solubility (cloud point) determination was carried out on the corresponding sodium sulfonate derivatives. Figure 1 shows the viscosity vs the free oil content for the sulfonate solutions of 25% active ingredient concentration.

Free oil was extracted from either the sulfonic acid or the sodium sulfonate with petroleum ether or hexane. As expected, the higher the free oil the lower the viscosity value was. The lowest viscosity was around 600 centipoises and the highest around 1,600.

The solubility data (as cloud point) indicating a higher solubility for a higher unsulfonated matter content are depicted in Figure 2. A difference up to 8 C in favor of the sulfonate with the highest free oil content can be seen.

This free oil content effect was noted in previous works, but no consideration was given to its chemical composition so as to better understand this effect.

SULFONE DETERMINATION IN FREE OIL

A gas chromatogram of an isolated free oil sample will tell us only that it is basically unsulfonated LAB. The composition of the unsulfonated matter was therefore determined by an HPLC technique using the following procedure: Free oil was extracted from either the sulfonic acid or the sodium sulfonate with petroleum ether or hexane. The extract was concentrated to one ml after solvent evaporation. This concentrated free oil sample subsequently was injected into an HPLC equipment (HP-1084 B or similar). Operating conditions were: Column type, RP-8 or RP-18 (5-10 μm); length, 23 cm; i.d., 4.6 mm; solvents, acetonitrile-water; flow rate, 2 ml/min; gradient, 0 time: 50% acetonitrile, and 10 min; 90% acetonitrile; temperatures, acetonitrile, 45 C; water, 80 C; oven, 50 C; detector, UV wave length, 254 μm.

The corresponding chromatogram (Fig. 3) shows two clearly differentiated groups of peaks. The first one corresponds to the nonsulfonated alkylbenzene, while the second one consists of sulfones.

However, the integration of both groups of peaks is not quantitative because the sulfones have a higher absorption coefficient at 254 μm than LAB, and it is therefore necessary to conduct a previous calibration using a standard sulfone. This calibration was done in our case using diphenylsulfone (Aldrich-Chemie) and LAB by preparing the following LAB:sulfone combinations; 100:0, 80:20, 60:40, 40:60, 20:80 and 0:100.

In addition to the above described method, the sulfones present in the free oil of commercial sulfonic acids were identified by mass spectrometry and quantified by SO_2 fluorometry after a combustion step.

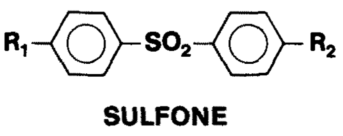
As can be observed in the chromatogram in Figure 3, the group of sulfones consists of a total of seven peaks. This is the maximum number of sulfone combinations with a C_{10}-C_{13} alkyl chain LAB, as can be observed in Figure 4.

The sulfone content in the eight commercial sulfonic acids was analyzed using the HPLC method described, and the results are summarized in Table 4. The correlation between the sulfone content in free oil and the viscosity of the sodium sulfonates is shown in Figure 5. It can be observed that the higher the sulfone content

TABLE 4

Sulfone/Alkylate Relationship in Free Oil (unsulfonated material)

Sample	Unsulfonated matter (wt%)	Sulfones (wt%)	Alkylate (wt%)	Sulfone: alkylate ratio
1	0.9	60	40	1.50
2	0.9	60	40	1.50
3	1.1	56	44	1.27
4	2.0	42	58	0.72
5	2.1	43	57	0.75
6	1.3	46	54	0.85
7	1.1	48	52	0.92
8	1.7	52	48	1.08



$R_1 + R_2$	20	21	22*		23*		24*		25	26
R_1	10	10	10	11	10	11	11	12	12	13
R_2	10	11	12	11	13	12	13	12	13	13

* DOUBLE PEAKS IN CHROMATOGRAPHY

FIG. 4. Sulfone.

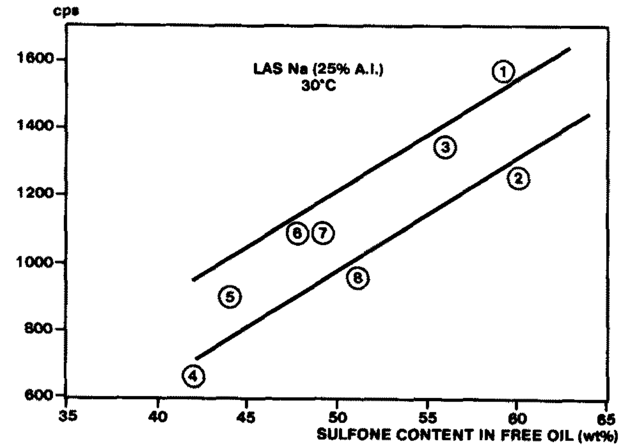
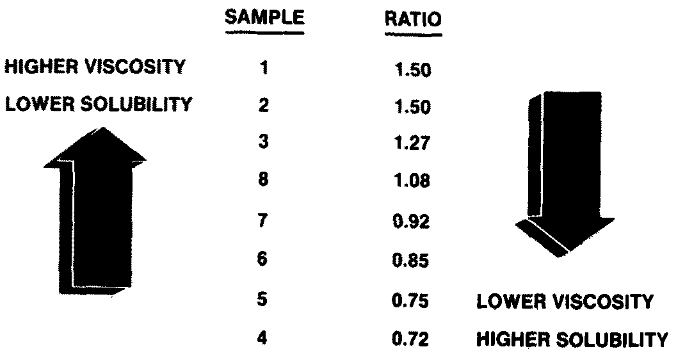
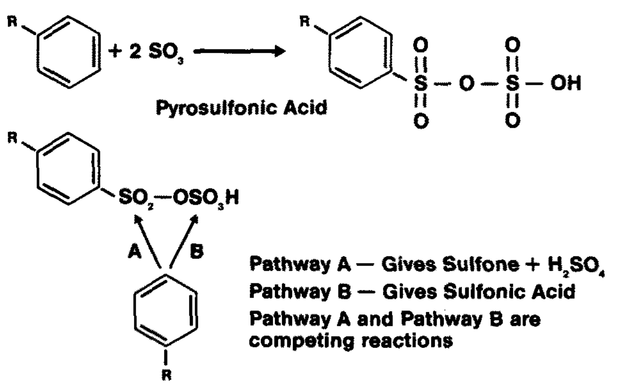


FIG. 5. Commercial sulfonic acids, slurries viscosity vs sulfone content in F.O.



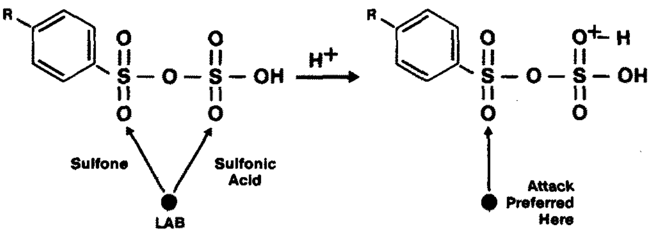
SAMPLE	RATIO
1	1.50
2	1.50
3	1.27
8	1.08
7	0.92
6	0.85
5	0.75
4	0.72

FIG. 6. Sulfone/LAB.



Pathway A — Gives Sulfone + H_2SO_4
Pathway B — Gives Sulfonic Acid
Pathway A and Pathway B are competing reactions

FIG. 7. Mechanism of sulfone formation.



Theory : Increasing Acidity Increases Sulfone Formation

FIG. 8. Acidity argument.

the higher the viscosity for a given active ingredient concentration.

Summarizing all these sulfone determinations in the eight commercial sulfonic acids (Table 4), we will observe that the lower the free oil content the higher the sulfone content (or the lower the unsulfonated LAB in free oil). Table 4 also reflects the ratio of sulfones/LAB in free oil ranging from 0.72 to 1.50. We think this ratio is even more important than the sulfone content as such; in fact, when ordering the eight samples according to this ratio (Fig. 6), we will observe that this ranking coincides exactly with increasing solubility (decreasing viscosity) and vice versa.

Therefore, it has been observed and explained that a high sulfone content will have a negative effect on the solubility behaviors of sodium sulfonate solutions. How is this sulfone content controlled? The first thing we need is to understand the mechanism of the sulfone formation. In Figures 7 and 8 we reflected a commonly accepted mechanism (private communication with Vista Chemicals) which indicates that the sulfones formation is favored by an increasing acidity. At the end of the sulfonation process, the SO_3/alkylate ratio is substantially higher than at the beginning, because of the excess of SO_3 normally used. Therefore, a careful control of the final aging step in commercial plants is very important in order to minimize sulfone formation.

INFLUENCE OF SO_3/LAS MOLAR RATIO AND SO_3/AIR DILUTION RATIO ON THE PHYSICAL PROPERTIES OF LAS

SO_3/LAB Molar Ratio. Some bibliographic references indicate (2) that sulfone formation is not related to the SO_3/LAB ratio. These conclusions were based, however, on a very narrow SO_3/LAB range and, in fact, our findings proved that sulfone formation is very dependent on the SO_3/LAB ratio, because the higher the SO_3/LAB ratio, the higher the acidity in the reaction media, and therefore the higher the sulfone formation.

The practical work was carried out using three different alkylbenzenes whose compositions are indicated in Table 5. Alkylate A is derived from the HF process and alkylate B from the $AlCl_3$ process. Alkylate C is also derived from the HF process, but it has been doped with pure 2-phenyl alkanes up to the same level as the $AlCl_3$ process derivative.

These alkylbenzenes were all sulfonated with SO_3 in a semicontinuous laboratory unit, varying the SO_3/LAB molar ratio from 0.9 to 1.5. Free sulphuric acid and unsulfonated matter contents (free oil) of the corresponding sulfonic acids are reflected in Figures 9 and 10. We should point our that laboratory data (semicontinuous) may not coincide with industrial (continuous) results for a given molar ratio, although the qualitative trend is valid.

In Figures 9 and 10 a minimum in free oil formation, for molar ratios around 1.1/1.2, can be seen. These SO_3/LAB molar ratios would correspond to approximately 1.0/1.1 on a commercial unit. When the molar ratio increases, the free oil level increases again, probably as a consequence of dealkylation reactions and/or oxidative pyrolysis (3). This effect is especially noticed on alkylates A and C and slightly less remarkable in alkylate B.

Viscosities of sulfonic acids and LAS slurries. Viscosity vs the SO_3/LAB molar ratio of both sulfonic acids and LAS slurries is represented in Figures 11 and 12.

The three alkylates give very similar sulfonic acid viscosities up to a molar ratio around 1.2. This value corresponds with a minimum in the free oil formation (see previous figures). When increasing the SO_3/LAB molar ratio the viscosity decreases (Fig. 11).

LAS slurries, however, show a different behavior, as can be observed in Figure 12. Low tetraline content alkylates (A and C) show an increasing viscosity with an increasing SO_3LAB ratio, but alkylate B (high in tetralin content) lead to a LAS with a slow viscosity change. The explanation of this effect is in the viscosity depressing effect caused by tetralin sulfonates.

TABLE 5

GC-MS Analysis of Laboratory LAB Samples

	Wt %		
	A	B	C
Phenyl C_{10}	9.5	9.8	9.7
Phenyl C_{11}	29.9	27.2	28.4
Phenyl C_{12}	29.9	29.1	28.8
Phenyl C_{13}	23.8	16.3	24.3
Phenyl C_{14}	1.1	0.5	1.9
Branched alkylate	4.9	2.9	5.9
2-Phenyl alkanes	18.5	29.6	29.0
Tetralines	0.45	13.9	0.4
Diphenyl alkanes	0.45	0.3	0.6
Mol wt	241.2	240.0	241.8

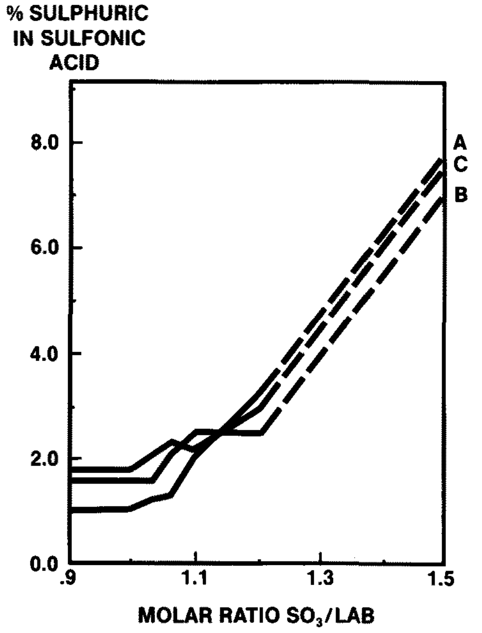


FIG. 9. Sulphuric vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

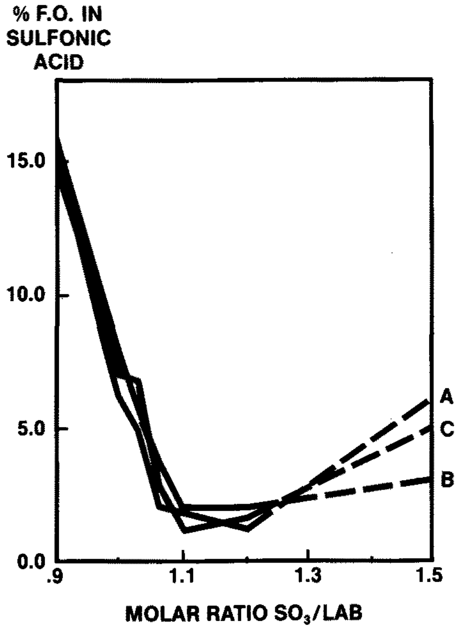


FIG. 10. Free oil vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

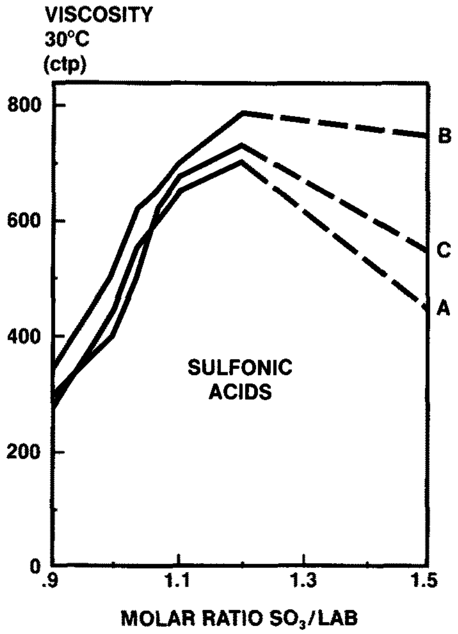


FIG. 11. Viscosity vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

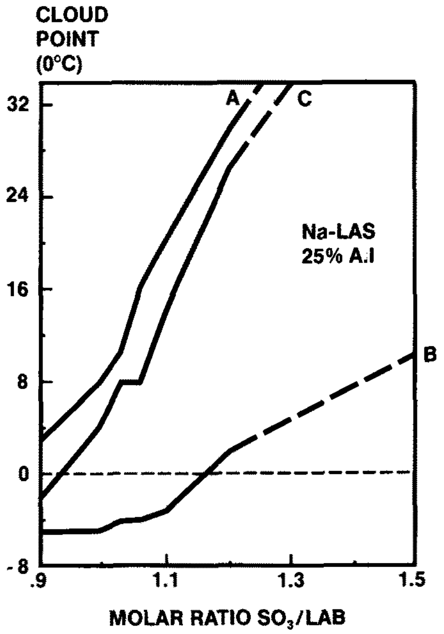


FIG. 13. Solubility vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

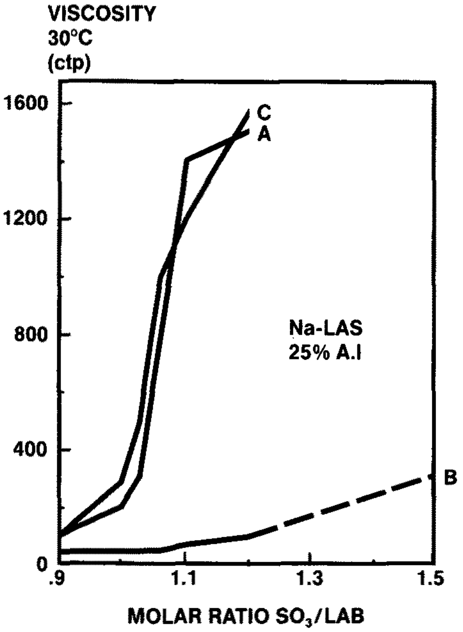


FIG. 12. Viscosity vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

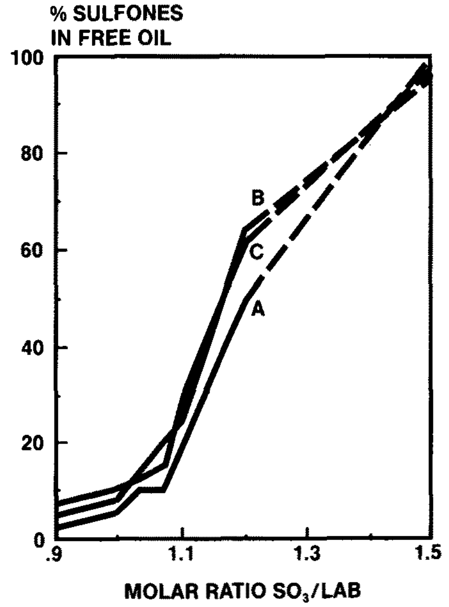


FIG. 14. Sulfones vs molar ratio, LAB laboratory sulfonation. A, HF process; B, $AlCl_3$ process; C, HF process (30% 2-phenyl).

Solubility (cloud point). It is already well known in the detergent industry that LAB derived from the $AlCl_3$ alkylation process gives slurries with higher solubility than LAB derived from the HF process, as can be observed in Figure 13. This effect has been explained historically as a function only of the higher 2-phenyl alkane isomer content of the $AlCl_3$ derivative. Although the external isomers, (2, 3-phenyl) of a given homolog have a different solubility than the internal ones (4,5,6-phenyl), the reason why $AlCl_3$ derivatives give lower cloud points than the HF ones is also related to the higher tetralin content of the former. This fact can be observed by comparing graphs A, B and C in Figure 13.

At the same time we can also state that the higher the sulfonation severity the poorer the solubility. This general trend will be explained as a consequence of the sulfone formation.

Sulfones formation. The three alkylates considered in this study behave in the same way. The higher the sulfonation severity, the higher the sulfone content (Fig. 14) and the poorer the solubility. The relationship between these factors is, therefore, quite remarkable, although each alkylate should be considered separately

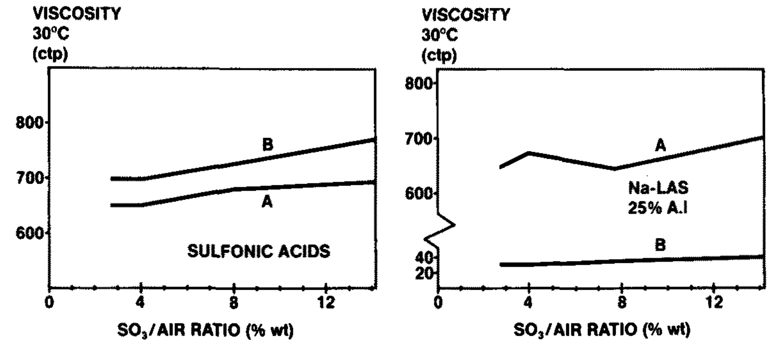


FIG. 15. Viscosity vs SO_3/air ratio, LAB laboratory sulfonation. SO_3/LAB mol ratio, 1.07; A, HF process; B, $AlCl_3$ process.

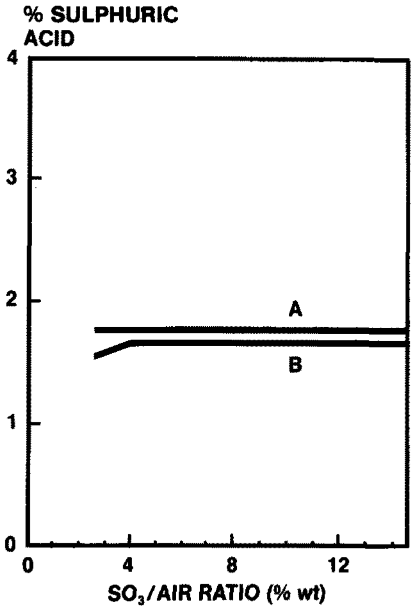


FIG. 16. Sulphuric vs SO_3/air ratio, LAB laboratory sulfonation. SO_3/LAB mol ratio, 1.07; A, HF process; B, $AlCl_3$ process.

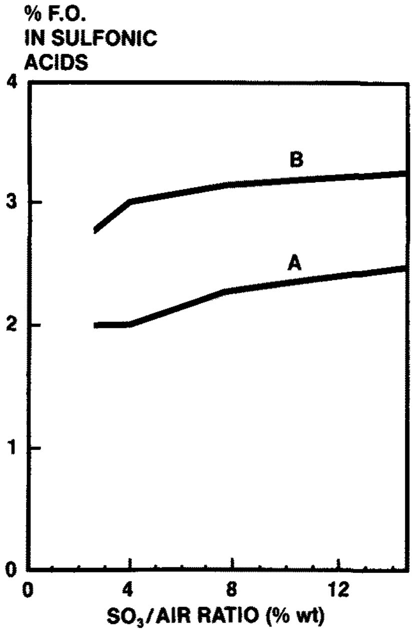


FIG. 17. Free oil vs SO_3/air ratio, LAB laboratory sulfonation. SO_3/LAB mol ratio, 1.07; A, HF process; B, $AlCl_3$ process.

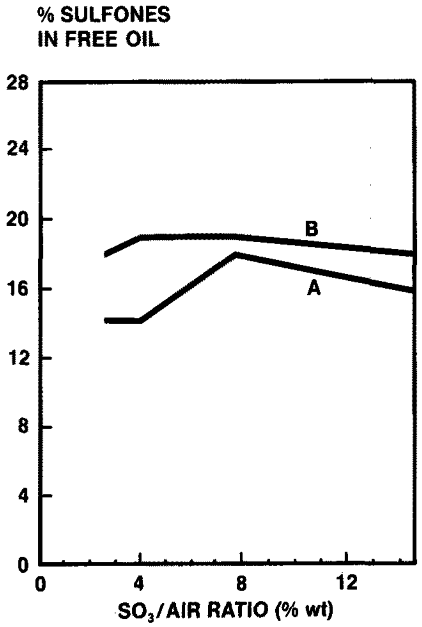


FIG. 18. Sulfones vs SO_3/air ratio, LAB laboratory sulfonation. SO_3/LAB mol ratio, 1.07; A, HF process; B, $AlCl_3$ process.

due to the additional effect of the tetralin content of the $AlCl_3$ derivatives.

SO_3/Air ratio. Another variable considered in our work was the SO_3/air ratio for a given SO_3/LAB molar ratio. The laboratory work was conducted keeping the SO_3/LAB molar ratio constant at 1.07. The dilution of SO_3 in air was now the variable from 4 wt% to 12 wt%. According to the laboratory data, this variable was not very important to the sulfone formation effect although on a commercial sulfonation scale it might have some effect due to other factors, among them diffusion and reactor geometry.

Figures 15 to 18 reflect the different parameters considered (free oil, solubility, sulfones content, etc), and it can be observed that the SO_3/air ratio has no influence on any of those variables. As a consequence, we believe the SO_3/LAB molar ratio is the driving factor in the final slurry characteristics. This is even more important in the commercial sulfonation process due to the aging step which can produce very high instantaneous SO_3/LAB ratios. It is therefore very important to control the SO_3/LAB ratio on commercial sulfonations in order to obtain the desired quality of the final product.

REFERENCES

1. Moreno, A., M. Alamany and A. Mompeón, Proceedings of IV Jornadas del CED, Barcelona, Spain, 1973.
2. Shoji, Hiroshi, and Kanji Majima, *J. Am. Oil Chem. Soc. 40*:179 (1963).
3. Gilbert, E.E., in *Sulfonation and Related Reactions,* edited by G.A. Olah, Robert E. Krieger Publishing Co., Huntington, NY, 1977, pp. 427–434.

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