

## Determination of Sulfonation Conditions of HAB as a By-product of Linear Alkylbenzene Production

Amir Naser Ahmadi<sup>1\*</sup>, Ali Mehdizadeh<sup>1</sup>, and Amir Hossein Jalili<sup>2</sup>

<sup>1</sup> Chemical Science and Technology Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

<sup>2</sup> Development of Gas Processing and Transportation Technology Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

### ABSTRACT

Heavy alkylated benzene (HAB), which is a by-product in linear alkylbenzene (LAB) production by UOP process, is separated by distillation from LAB and consists of a range of components such as polyalkylbenzenes, diphenylalkanes, alkyl tetralins, and alkylindans. The products of sulfonation of HAB or its distillation cuts are of wide industrial applications such as emulsifiers, dispersants in lubricating oils, anionic surfactants, and aqueous phase stable waterflooding.

The sulfonation of the HAB mixture using oleum as the sulfonating agent has been carried out and optimum reaction conditions have been defined based on the highest degree of sulfonation. Some light, average, and heavy distillation cuts were then sulfonated under optimum conditions. The degree of sulfonation of the fractions was found to be dependent on the composition of the mixture. <sup>1</sup>HNMR spectroscopy was used to investigate the relationship between the ratio of aliphatic to aromatic protons of the compounds and the trend in sulfonation.

**Keywords:** Heavy Alkylated Benzene, Sulfonation, Oleum, Alkylbenzene, Tetralin, Indan, Diphenylalkane

### INTRODUCTION

Heavy alkylated benzene (HAB) usually refers to arylalkyl compounds with aliphatic branches containing over 18 carbons. However, HAB may also consist of a series of by-products in linear alkyl benzene (LAB) production by UOP process including dialkylbenzenes, diphenylalkanes, 1,4-dialkyltetralins, and 1,3-dialkylindanes [1]. These by-products consist of a wide range of compounds differing in their alkyl chain length (C<sub>10</sub>-C<sub>13</sub>) and comprise 10% of the UOP process for LAB production. During the process, the dehydrogenation

of normal paraffins leads to alpha olefins subsequently used to alkylate benzene in the presence of a catalyst. They may also be formed, if the linear alkyl benzene production process does not proceed to completion.

One of the most important applications of HAB is related to the sulfonation products of HAB or its distillation cuts, which yield products vastly used in industry. They are mostly applied as emulsifiers [2-3], dispersants in lubricating oils [4], anionic surfactants [5-8], detergents [9], and aqueous phase stable waterflooding [10].

#### \*Corresponding author

Amir Nasser Ahmadi  
Email: ahmadian@ripi.ir  
Tel: +98 21 4473 9753  
Fax: +98 21 4473 9713

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HAB sulfonating agents previously reported include sulfuric acid ( $H_2SO_4$ ),  $SO_3$  gas, and oleum ( $SO_3.H_2SO_4$ ). The source of the gas may be either liquid  $SO_3$  or  $SO_3$  produced by burning sulfur. For example, a mixture of monoalkylbenzene, dialkylbenzene, and diphenylalkane has been sulfonated using  $SO_3$  gas with the sulfonation yield varying from 54.6 to 56.52% [10].

Furthermore, the sulfonation of a mixture of diphenylalkanes (10-25%), tetralin (5-18%), dialkylbenzenes (40-70%), and naphthalene and indan (4-12%) and that of a mixture composed of alkylbenzenes (0.5-30%), dialkylbenzenes (25-90%), diphenylalkanes (0-70%), and tetralin and indan (<25%) has been carried out using oleum to give 81-88% sulfonated products [4].

In addition, postdodecylbenzene containing alkylbenzenes (30%), *m*-dialkylbenzenes (49%), and *p*-dialkylbenzenes (21%) has been sulfonated using oleum to yield 87% sulfonated products [11]. Some more recent works regarding HAB sulfonation include a process to obtain a highly soluble linear alkylbenzene sulfonate surfactant with 9-20 carbon atoms [9] and the sulfonation of linear olefins with 20-24 carbon atoms having a relatively high aryl ring attached to positions 1 or 2 or the linear alkyl chains [12].

The application of oleum and  $H_2SO_4$  as sulfonating agents has some disadvantages, e.g. the formation of water as a by-product in both cases can cause the hydrolysis of the product giving rise to the reversibility of the reaction. Undesirable sludge formation during work-up, especially in the case of  $H_2SO_4$ , is yet another drawback of  $H_2SO_4$  and oleum. In comparison with  $H_2SO_4$ , oleum gives fewer side reactions, occurs at lower temperatures, and since the viscosity of the reaction mixture drops as a result of excess  $H_2SO_4$ , the sulfonation reaction takes place more smoothly using oleum. Oleum sulfonation also does not require complicated equipment and the whole reaction and work-up processes can be carried out in one batch reactor.

On the other hand,  $SO_3$  gas is usually diluted using different proportions of dry air because of the exothermic reaction. This dilution is somewhat favorable, because it enhances mixing and prevents the local increased heat. The drawback associated with  $SO_3$  is side reactions such as the formation of anhydrides and sulfones, polysulfonation, and rearrangements.

By the comparison of the three sulfonating agents, oleum was chosen because of the simplicity of reaction conditions and accessibility.

In the present work, sulfonation conditions using oleum have been optimized for a HAB mixture, a by-product in linear alkylbenzene (LAB) production by UOP process in a LAB plant (Isfahan), which is separated by distillation from LAB, and three low-boiling ( $b_p=350-360$  °C), average-boiling ( $b_p=390-400$  °C), and high-boiling ( $b_p=440-450$ °C) cuts from HAB fractional distillation, resulting in 66-70% sulfonated products.

## EXPERIMENTAL PROCEDURES

### Materials

Heavy alkylated benzene with an average molecular weight of 310 is a by-product in LAB production in Isfahan LAB Plant. Oleum was obtained from the Iranian Defense Ministry Chemical Industry.  $^1H$ NMR spectra were recorded on a Bruker AVANCE 500 MHz instrument. HAB cuts were obtained by the distillation of HAB at a pressure of 1 mmHg, each cut differing from the previous one by 10 °C. The initial and final boiling points were 350°C and 450°C respectively (Table 1) [9].

**Table 1: HAB distillation data**

Cut Number	Cutting Range (°C) AET	Cutting Range (°C) ACT	Cut wt. %	Cum wt. %
1	IBP* -350	IBP**-152	1.61	1.61
2	350-360	152-160	7.16	8.77
3	360-370	160-168	8.39	17.16
4	370-380	168-175.7	10.17	27.23
5	380-390	175.7-184	10.17	37.40
6	390-400	184-192	11.45	48.85
7	400-410	192-200	8.11	56.96
8	410-420	200-208	11.32	68.28
9	420-430	208-216.2	7.92	76.20
10	430-440	216.2-224.4	5.82	82.01
11	440-450	224.4-232.6	4.44	86.45
12	RES>450	RES>232.6	13.50	100.00

AET= Atmospheric equivalent temperature, ACT = Actual temperature at 1 mmHg, IBP\* = 326.7°C, IBP\*\* = 134°C

### General Procedure for Sulfonation

a) HAB: HAB (310 g) was placed in a 1-liter glass reactor equipped with a reflux condenser, a mechanical stirrer, a thermometer, and an addition funnel. A 20% solution of oleum in H<sub>2</sub>SO<sub>4</sub> (325-340 gr) was gradually added to HAB over a period of 1 hour at ambient temperature after which the temperature was raised to 50-60 °C and the reaction mixture was vigorously stirred at this temperature for 4-5 hours. Sulfonation yields were obtained using standard procedures for the determination of sulfonic acid [15], free oil [16], and inorganic acid contents [18].

b) HAB cuts: The optimal sulfonation conditions obtained for the sulfonation of HAB were used in the sulfonation of three low-boiling ( $b_p=350-360$  °C), average-boiling ( $b_p=390-400$  °C), and high-boiling ( $b_p=440-450$  °C) HAB cuts. Sulfonation yields were obtained using the same standard procedures.

### RESULTS AND DISCUSSION

The wide range of HAB components including alkylbenzenes, diphenylalkanes, alkyltetralins,

and alkylindans and different reaction conditions required for the sulfonation of each component make the choice of reaction conditions somewhat difficult. The problem arises because mild sulfonation conditions will result in lower degrees of sulfonation and undesirable reactions such as polysulfonation will occur under harsher reaction conditions, on the other hand. In other words, mono and dialkylbenzenes as well as diphenylalkanes are expected to be sulfonated under mild conditions and severe conditions will give disulfonated products [13], whereas compounds such as tetralins and indans can only be sulfonated under harsh reaction conditions [14]. Thus the objective of this work was to determine the optimum conditions for the sulfonation of a HAB mixture.

Table 2 illustrates the results obtained in HAB sulfonation by varying weight ratios of reactants, reaction times, and temperatures. The percentage of free acid remaining is inversely proportional to the degree of sulfonation. Hence this percentage was taken as an indication of the sulfonation yield.

**Table 2: HAB sulfonation reaction conditions and percentage of free acid**

Entry	Gram of oleum/ 100 grams of HAB	Time (hr)	T (°C)	Free acid (%)
1	100	4	40	28
2	100	4	45-50	22
3	140	3	50-60	22.2
4	140	4	50-60	20.1
5	140	4.5	50-60	20
6	120	5	50-60	16.4
7	110	5	50-60	14
8	105	5	50-60	12.7

The lowest amount of free acid was obtained in entries 7-8, which means that, comparatively, higher sulfonation yields are obtained under these conditions. The products of these two reactions were further analyzed using standard procedures. The specifications of the products

obtained under these conditions are listed in Table 3.

**Table 3: Specifications of the products obtained under optimal conditions (7&8)**

Entry	Sulfonic acid <sup>a</sup> (%)	H <sub>2</sub> SO <sub>4</sub> <sup>a</sup> (%)	Free oil <sup>b</sup> (%)	Acidity <sup>c</sup> (mg KOH/g)
7	54.34	11.64	34.02	686
8	70.66	10.89	18.45	584

a) ASTM D4711 [15], b) ASTM D500 [16], c) ASTM D664 [17]

As can be observed in Table 3, the best sulfonation yield (70.66%) is obtained in the optimal conditions for HAB sulfonation including gram of oleum/100 gram of HAB=105, reaction time=5 hrs, and reaction temperature=50-60°C (entry 8).

The optimal sulfonation conditions thus obtained were subsequently used for the sulfonation of HAB cuts (Table 1). Three low-boiling ( $b_p=350-360$  °C), average-boiling ( $b_p=390-400$  °C), and high-boiling ( $b_p=440-450$  °C) cuts were selected and sulfonated under these conditions. The results are tabulated in Table 4.

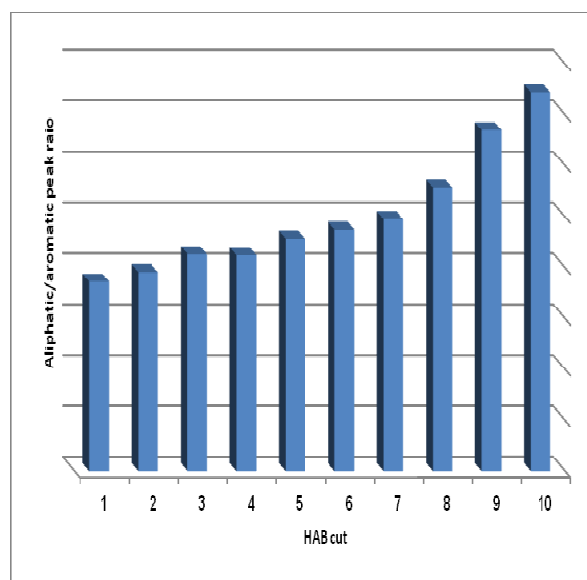
**Table 4: Sulfonation of HAB fractions**

Entry	Boiling point Range (°C)	Sulfonic acid (%)	H <sub>2</sub> SO <sub>4</sub> (%)	Free oil (%)	Acidity (mg KOH/g)
1	350-360	63.22	15.91	20.77	467
2	390-400	52.08	13.59	34.33	444
3	440-450	26.4	11.49	62.11	532

As can be inferred from Table 4, the initial cut, having a boiling range of 350-360 °C, shows the greatest degree of sulfonation. This is probably

due to the presence of components requiring milder sulfonation conditions. However, the final cut, which probably contains components been sulfonated under more severe conditions such as indan and tetralin, gives a lower degree of sulfonation.

<sup>1</sup>HNMR studies of HAB cuts reinforce the above results. As shown in Table 5 and the Figure1, the ratio of peak areas of aliphatic to aromatic protons increases as the average molecular weight of the cuts increases. This means that the initial cuts contain more LAB and diphenylalkanes. Furthermore, dialkylbenzenes are more predominant in the middle and final cuts and consist of dialkyltetralins, indans, and cyclic and straight chain aliphatics. The final cuts possess the minimum amounts of aromatics and the maximum amounts of aliphatics.



**Figure 1: Aliphatic/aromatic peak area ratio for different HAB cuts**

**Table 5: <sup>1</sup>H NMR data of HAB**

HAB Cut	1	2	3	4	5	6	7	8	9	10	Mixture
Aliphatic/aromatic peak area ratio	7.46	7.83	8.53	8.50	9.15	9.50	9.91	11.17	13.40	14.90	10.26

## CONCLUSIONS

HAB mixtures have been sulfonated using 20% oleum under the optimum conditions of weight percent, temperature, and time to yield 70.66% sulfonated products. Various HAB cuts have also been separated and sulfonated under optimum conditions.

In the sulfonation of HAB cuts, the highest degrees of sulfonation (the lowest percentage of free acid) were obtained in the case of lighter cuts ( $b_p=350-360^\circ\text{C}$ ) (63.22%) and ( $b_p=390-400^\circ\text{C}$ ) (52.08%). This observation is due to the fact that these cuts are more easily sulfonated, because they contain more LAB and diphenylalkanes. However, heavier cuts are least sulfonated (the highest percentage of free acid). The latter cuts contain components such as indan and tetralin, which are not easily sulfonated.

The trend in the degree of the sulfonation of HAB cuts is supported by the increased ratio of peak areas of aliphatic to aromatic protons in  $^1\text{H}$ NMR spectra as the average molecular weight of cuts increases.

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