"Chemometrics" applied to the optimization of the preparation of hydrotropes for detergents starting from BTX fraction of natural gas

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Manufacturers of cleaning products use hydrotropes to increase the solubility of surfactants in concentrated liquid detergents. In contrast to benzenesulfonate, alkylbenzenesulfonates with short chains (*n* < 4) are used as hydrotropes. In this paper, we present the results obtained from the preparation of toluenesulfonic and xylenesulfonic acids by selective sulfonation of toluene and xylenes present in the BTX fraction (benzene, toluene, xylenes) of the Tunisian natural gas MISKAR deposit. Chemometrics were applied to determine the optimal experimental conditions for the selective sulfonation of toluene and xylenes, we use a 2^{6-2}_{IV} fractional factorial design in addition to several analytical methods (GC, HPLC, FTIR...). These conditions were found to be: the use of concentrated sulfuric acid as sulfonating agent, the azeotropic elimination of water during the reaction, a temperature of 110 °C, a duration of 9 hours and a molar ratio of sulfuric acid to toluene plus xylenes of 0.8. The application of all of these experimental conditions gives an aqueous phase with a composition that can be used very effectively as hydrotrope agent in liquid detergents. This conclusion was the outcome from comparing the effect of our product on the clear point of a typical premium formulation of a liquid detergent to that of sodium xylenesulfonates, the most important hydrotrope for light duty liquids.

Introduction

Alkyl benzenesulfonates, particularly when the alkyl radical contains 1 to 4 carbon atoms, are well known and used in concentrated detergents as hydrotropes (substances which increase the solubility of surfactants) [1-3]. Such typical products are sodium toluenesulfonates (STS), xylenesulfonates (SXS) and cumenesulfonates (SCS). Sodium toluenesulfonates, in particular, are extensively used as both hydrotrope and anticaking agent (substances giving free-flowing powder) in spray dried detergents [4].

These products are prepared by reacting the corresponding aromatic hydrocarbons with sulfonating agents such as sulfuric acid, oleum, sulfur trioxide or chlorosulfonic acid, then by neutralizing the corresponding sulfonic acids.

We have intended to prepare hydrotrope agents by sulfonation of the by-product of natural gas commonly known as BTX fraction (Benzene, Toluene, and Xylenes). Unfortunately, sodium benzenesulfonate (SBS) has no hydrotropic power and can lead to cloudy liquid detergent [5]. We have, consequently, tried to determine the experimental conditions permitting to sulfonate selectively the toluene and the xylenes to the detriment of benzene.

The individual behavior of benzene, toluene and xylenes in the presence of sulfonating agents such as sulfuric acid or SO_3 are widely documented. The work of Cerfontain *et al.* [6-12] carried out over many years on sulfonation kinetic and isomer distribution, is still the major reference on this subject. A large body of literature about the methods and processes for the manufacture of aromatic sulfonic acids can be found in the patent literature [4,13-16]. All the data obtained in these cases are useful but there is no experimental information that assures their extrapolability to the mixtures of aromatic hydrocarbons.

Experiments with pairs of these aromatic hydrocarbons have only been conducted with benzene and toluene. The competitive sulfonation of toluene and benzene has been studied by Cerfontain *et al.* [11,12] and El Homsi *et al.* [17,18] using SO_3 as sulfonating agent. These studies were undertaken at low temperatures (–20, +20 °C) in order to find the most selective solvents, as regards the isomer distribution and the relative reactivity of toluene and benzene.

To our knowledge, no information has been published about the behavior of mixtures of benzene, toluene and xylenes in the presence of sulfonating agents.

The purpose of this paper is to determine suitable experimental conditions for selective sulfonation of toluene and xylenes present in the BTX fraction of the natural gas of MISKAR- Tunisia (53 % benzene, 25 % toluene, 10 % xylenes, 1 % ethylbenzene and 11 % non aromatic hydrocarbons). The products obtained are found to be very effective hydrotropes for concentrated liquid detergents.

Methodology

Our search for the best conditions was based on chemometric techniques. This chemical discipline uses statistical methods to select optimal measurement procedures and experiments and to provide maximum chemical information by evaluating analytical data [19].

In this work chemometrics are applied to determine the optimal experimental conditions for the selective sulfonation of toluene and xylenes in an optimal way by carefully planning experiments and using in each case the appropriate analytical methods and measurements.

To this end, several analytical methods as HPLC, GC and, FTIR have been performed to identify and to measure quantitatively the components of the reaction products; this is achieved using a designed experiment to study the sulfonation reactions. The fractional factorial designs are among the most widely used types of designs for product and process improvement [14-20]. Thus, a two-level fractional factorial design 2^{6-2}_{IV} was applied to determine the direct influence of six experimental variables as well as their possible interaction effects on the selectivity of the sulfonation reaction. The experimental results obtained were treated by the computer program NEMROD [25]. The following paragraph is devoted to briefly remind some principles governing the construction and analysis of this experimental design.

Basic definitions

In a two level factorial design 2^k, all possible combinations of the levels of k factors are investigated. This permits to determine the influence of the variation of each factor and the effects of all their mutual interactions on the response. In a fractional factorial design, we assume that interaction effects between three or more factors are negligible; useful information on the main effects and low order interactions may be obtained, thus, by running only a fraction of the complete factorial design.

In a 2^{6-2} fractional factorial design, six variables (factors) are studied each at two levels. The effects of two variables (extra variables) are confounded with two high order interactions between the four other variables (basic variables).

In this work, the 2^{6-2} fractional factorial design is obtained by writing down the complete 2^4 factorial as the basic design (with the four variables X_1, X_2, X_3 and X_4) and then equating factors X_5 and X_6 to the $X_1X_2X_4$ and $X_2X_3X_4$ interactions respectively.

Effects and aliases

The last conditions allow us to identify the independent generators (1) and the corresponding complete defining relation (2) which is the set of all columns that correspond to the identity column I:

$$\mathrm{I} = 1245 = 2346 \tag{1}$$

$$\mathrm{I} = 1245 = 2346 = 1356 \tag{2}$$

From this set of generators, it is possible to develop the complete alias structure for this design and to select fifteen effects and their aliases which may be estimated from the experimental data as shown in table I (the four factor and higher interactions are neglected). Consequently, the design is of resolution IV because every main effect is aliased with a three-factor interaction and every two-factor interaction is aliased with at least another two-factor interaction. We can reasonably assume that three-factor interactions are negligible and would expect this design to provide excellent information concerning the main effects.

Table I. Effects and their aliases.

$l_1 = b_1 + b_{245} + b_{356}$
$l_2 = b_2 + b_{145} + b_{346}$
$l_3 = b_3 + b_{246} + b_{156}$
$l_4 = b_4 + b_{125} + b_{236}$
$l_5 = b_5 + b_{124} + b_{136}$
$l_6 = b_6 + b_{234} + b_{135}$
$l_{12} = b_{12} + b_{45}$
$l_{13} = b_{13} + b_{56}$
$l_{14} = b_{14} + b_{25}$
$l_{23} = b_{23} + b_{46}$
$l_{24} = b_{24} + b_{15} + b_{36}$
$l_{34} = b_{34} + b_{26}$
$l_{16} = b_{16} + b_{35}$
$l_{123} = b_{123} + b_{345} + b_{146} + b_{256}$
$l_{134} = b_{134} + b_{235} + b_{126} + b_{456}$

Estimates and significance of the effects of the factors

To simplify the calculations, coded variables X_j are used instead of natural variables u_j. The range of variation of each u_j is transformed into a variation of X_j between –1 and +1 [20-22].

The main effect b_j of a factor X_j and the interaction effect b_{jk} of a two factor interaction X_jX_k are calculated using equations (3) and (4) [20-24]:

$$b_j = \frac{\sum_i y_i X_{ij}}{16} \tag{3}$$

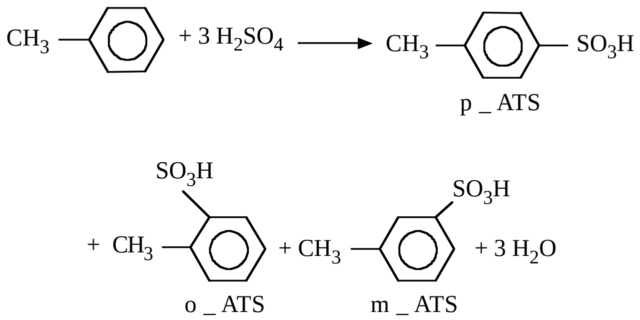
$$b_{jk} = \frac{\sum_i y_i X_{ij} X_{ik}}{16} \tag{4}$$

where y_i and X_{ij} represent respectively the response of interest and the reduced value of the level of the factor j in the run i.

The estimate of the influence of each variable on the systematic variation has a probability distribution due to the experimental error. In many cases a useful estimate of the experimental error (with sufficient degrees of freedom) is not available. In such cases, the significance of the estimated parameters can be assessed from a normal probability plot [20-22,25,26].

The procedure is to construct a normal probability plot of the effects, which is a graph of the cumulative distribution of the ordered effects on a normal probability paper. All of the effects that lie along the line are negligible, whereas, the large effects are far from the line.

In this work, both an analysis of variance and a normal probability plot assess the significance of the estimated parameters.



Experimental section

Apparatus and reaction conditions

The sulfonation of aromatic compounds is a process that presents very interesting theoretical characteristics and practical difficulties. For example, the sulfonation of toluene leads to the three isomers ortho, para and meta-toluenesulfonic acids (the m-isomer is formed in very low amount). The global equation can be written as follows:

The sulfonation reaction of the “BTX mixture” of the natural gas – MISKAR – Tunisia, was carried out in a batch reactor of 1000 mL placed in an oil bath and equipped with an agitator and a thermometer. One neck of the reactor was fitted to a 500 mL graduated separatory funnel for addition of the sulfonating agent (H_2SO_4 97 % or oleum 10 % SO_3) at a known rate. A second neck of the reactor was fitted with a condenser for refluxing vapours or with a Dean and Stark apparatus filled with “BTX mixture” to azeotropically remove the water produced. The reaction was conducted by adding the sulfonating agent to the mixture, which had previously been brought to the reaction temperature. Vigorous agitation was used throughout the reaction, while the temperature was maintained constant at ± 0,5 °C. At the end of the reaction time, the resulting mixture was treated with a fixed volume of water to facilitate the separation of organic phase (the upper layer) and sulfuric phase (the lower layer). The recovery of organic and inorganic material was quantitative.

Analytical methods

Analyses of the BTX mixture

Analyses of the raw material (BTX fraction of natural gas) were carried out by gas chromatography on a Shimadzu GC-9A apparatus equipped with a flame ionization detector. Quantitative analyses of benzene, toluene and xylenes were performed with external standard procedure. Calibration factors were determined by using six standards mixtures of these three aromatic hydrocarbons. The use of the internal standard method has been attempted unsuccessfully particularly with diethylether, isopropanol or ethanol as internal standard.

The external standard method was also applied to analyze the BTX mixture of the Dean and Stark apparatus after reaction.

Analyses of the organic phase

After separation and weighing, the organic phase was also analysed by gas chromatography in order to determine the quantities of the unreacted reagents.

Analyses of the aqueous phase

Analyses of the aqueous phase were performed to determine the proportions of benzenesulfonic acid (BSA), toluenesulfonic acids (TSA), xylenesulfonic acids (XSA) and unreacted sulfuric acid (SA).

Ion exchange high performance liquid chromatography was used to determine the amounts of BSA, TSA and XSA after neutralization. Chromatograms were obtained with a Shimadzu HIC chromatograph equipped with an UV detector. Calibrations were achieved with the standard addition method and the internal standard method using sodium phthalate as standard. All calibration curves had a correlation coefficient of 0.99.

The amount of unreacted sulfuric acid was measured as free sulfates by volumetric titration in a water-ketone medium using a lead solution as titrating agent and dithizone as indicator.

Qualitative analyses of the neutralized and dried aqueous phase were performed by FTIR spectroscopy.

Results and discussion

Although the sulfonation procedure was simple, evaluation of the results obtained from preliminary experiments carried out on synthetic mixtures of benzene and toluene, indicated that several variables could influence the yield and the selectivity of the sulfonation reaction. Some of these variables were previously found [6-12,14-18,27-29] to have a significant effect on the sulfonation of toluene alone or benzene alone.

Table II. Variables and experimental domain.

Variables	*Level (-)*	*Level (+)*
X_1: Reaction time (***D***).	5^H	9^H
X_2: Sulfonating agent (***C***).	97 % H_2SO_4	Oleum (10 % SO_3)
X_3: Temperature of the oil bath (***T***).	95 °C	110 °C
X_4: Azeotropic elimination of water (***E***).	Without elimination	With elimination
X_5: Time over which the sulfonating agent is added (***t***).	10 min	30 min
X_6: Molar ratio of sulfuric acid to (toluene + xylenes) (***R***)	0.8	1.2

In this work, the purpose is to indicate which variables have a significant effect on the selectivity of the sulfonation reaction of the BTX fraction of the natural gas. Six variables were investigated and a fractional factorial design was applied. The variables and the range of their variations are given in table II. These ranges are chosen taking into account the yields of the sulfonation reaction obtained with the synthetic mixtures of toluene and benzene.

Sixteen experiments were run to determine how the six variables influenced the following responses:

- y_B: the percentage of benzene sulfonation;
- y_T: the percentage of toluene sulfonation;
- y_X: the percentage of xylenes sulfonation;
- $S = y_{(T+X)/B}$: the ratio of the percentage of toluene and xylenes sulfonation to the percentage of benzene sulfonation. This response is used to study the selectivity of the reaction.

General remarks

The product of the sulfonation reaction of the BTX fraction separates, at room temperature, in two phases; the aqueous phase, the heaviest, is a viscous liquid with a clear brown color, the organic phase, on the other hand, is characterised by a pale yellow colour.

Gas chromatograms of the organic phase and ion exchange chromatograms of the aqueous phase provide an adequate resolution to allow accurate quantitative analyses.

Gas chromatogram of the organic phase compared to that of BTX, the raw material (Fig. 1) proved that this phase contains mainly residual BTX mixture.

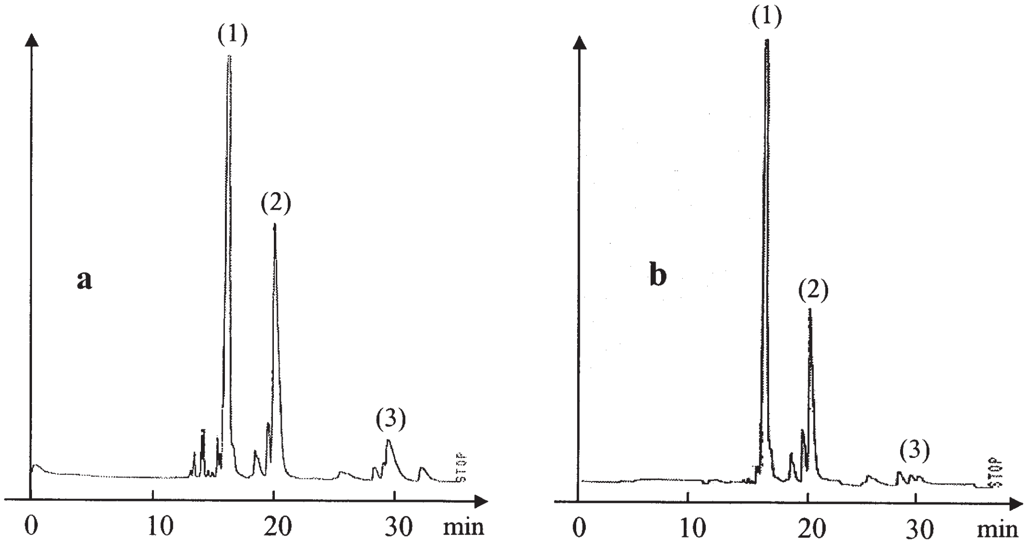


Figure 1. Gas chromatograms of (a) BTX fraction of natural gas; (b) residual organic phase.

Apparatus: Shimadzu, Column: bonded phase CBP1 (non-polar), L = 50 m; Temperature: 100 °C; Detector: FID; Injection of 0.5 µl. (1) Benzene, (2) Toluene, (3) Xylenes.

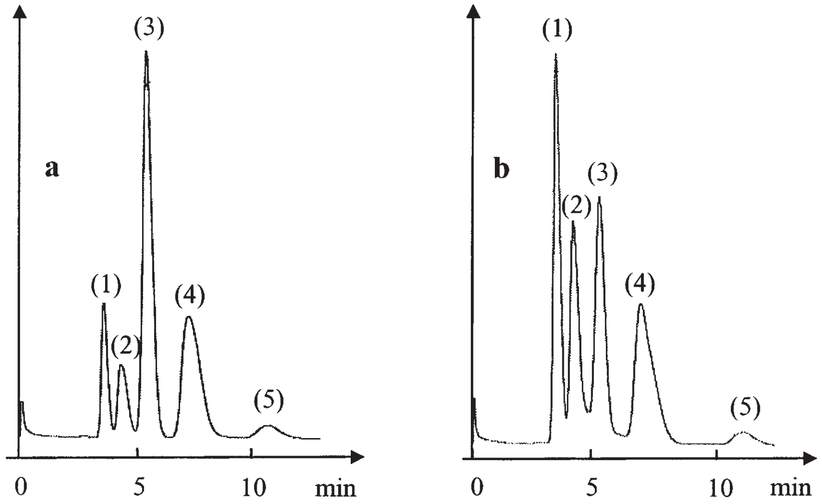


Figure 2. Ion exchange chromatograms of (a) neutralized aqueous phase; (b) reference solution.

Apparatus: Shimadzu HIC, Column: Shim pack IC A1 (quaternary ammonium resin), *L* = 10 cm, ID 4.6 mm; Temperature: 40 °C; Mobile phase: $NaClO_4$ 6 mM in phosphate buffer NaH_2PO_4/Na_2HPO_4, Flow rate: 0.6 mL/min; Detection: UV, λ = 254 nm; injection of 20 µL. (1) Standard: Sodium phthalate, (2) SBS, (3 and 5) STS and (4) SXS.

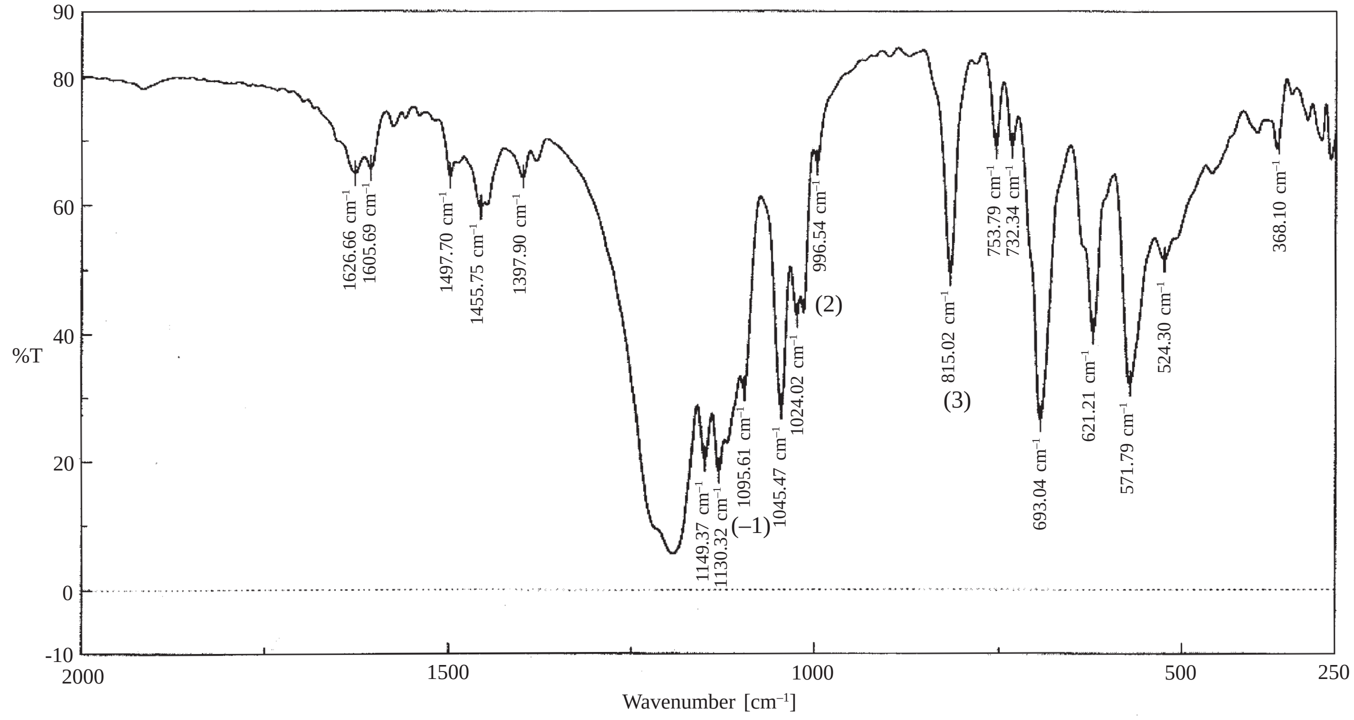


Figure 3. FTIR spectrum in KBr of a dried neutralized sample of BTXS 14.

(1) SXS, (2) SBS, (3) SXS and STS

Figure 2 illustrates a typical ion exchange chromatogram of the neutralised and dried aqueous phase. It indicates that this phase contains SBS, STS and, SXS.

In addition, we show that FTIR spectrometry is a useful method to qualitatively analyse the reaction product. Figure 3 shows an infrared spectrum of a dried neutralised sample of the aqueous phase. The vibration bands of average intensity situated at 1120 and 630 cm^{-1} are characteristic of free sulfate ions [28]. The bands detected at 1096, 996 and, 815 cm^{-1} are specific respectively to SXS, SBS and, STS or SXS.

The yields of benzenesulfonic, toluenesulfonic and xylenesulfonic acids can be determined directly from the aqueous phase by ionic HPLC after neutralisation and indirectly

Table III. Experimental design and responses.

Run	D (X_1)	C (X_2)	T (X_3)	E [a] (X_4)	t (X_5)	R (X_6)	y_B (%)	y_T (%)	y_X (%)	S
1	5^H	97 % H_2SO_4	95°	(-)	10 min	0.8	3.20	28.08	64.27	11.76
2	9^H	97 % H_2SO_4	95°	(-)	30 min	0.8	3.12	29.26	66.47	12.55
3	5^H	Oleum	95°	(-)	30 min	1.2	7.78	54.08	81.44	7.89
4	9^H	Oleum	95°	(-)	10 min	1.2	8.28	62.08	83.93	8.20
5	5^H	97 % H_2SO_4	110°	(-)	10 min	1.2	4.49	48.33	75.08	12.35
6	9^H	97 % H_2SO_4	110°	(-)	30 min	1.2	4.39	54.91	79.18	13.98
7	5^H	Oleum	110°	(-)	30 min	0.8	5.83	31.86	70.94	7.25
8	9^H	Oleum	110°	(-)	10 min	0.8	4.80	39.37	73.69	10.10
9	5^H	97 % H_2SO_4	95°	(+)	30 min	1.2	4.67	54.00	80.55	13.06
10	9^H	97 % H_2SO_4	95°	(+)	10 min	1.2	5.13	63.25	83.63	13.40
11	5^H	Oleum	95°	(+)	10 min	0.8	3.84	36.48	74.13	12.10
12	9^H	Oleum	95°	(+)	30 min	0.8	5.77	42.47	75.80	8.91
13	5^H	97 % H_2SO_4	110°	(+)	30 min	0.8	3.41	35.93	74.96	13.65
14	9^H	97 % H_2SO_4	110°	(+)	10 min	0.8	3.61	49.21	82.49	16.10
15	5^H	Oleum	110°	(+)	10 min	1.2	6.57	67.91	86.64	11.09
16	9^H	Oleum	110°	(+)	30 min	1.2	8.03	75.57	89.19	9.86

[a] E(–) and E(+): Without and with azeotropic elimination of water respectively.

from the organic phase by gas chromatography. The results obtained are very close and confirmed by the volumetric analysis of free sulfates.

The fractional factorial design 2_{IV}^{6-2}

Experimental design and estimate of effects

The experimental design and the measured responses are summarised in table III.

From the obtained results, estimates of the main effects and aliases of confounded two-variable interaction effects can be computed [25]. These values are shown on table IV, where b_0 is the average. The interaction effects between three and four variables are small as compared to main effects or two-variable interaction effects. This may indicate that no important variable has been omitted in this study.

Significance of the effects

The significance of the estimated parameters of each response is assessed from a Normal probability plot. Figure 4 shows the normal probability plot of the estimated effects of the four responses studied. For benzene, two linear coefficient b_2 and b_6 deviate from the normal probability line. It can therefore be concluded that these main effects are the only effects distinguishable from noise and that the range of variation of X_1, X_3, X_4 and X_5 in the experiments does not have any influence on the sulfonation yield of benzene.

For toluene, four linear coefficients b_1, b_2, b_3, b_4, b_6 and one alias "$b_{34} + b_{26}$" deviate from the normal probability line.

Table IV. Estimated effects.

Effects	y_B	y_T	y_X	S
$l_0 = b_0$	5.18	48.30	77.65	11.39
$l_1 = b_1 + b_{245} + b_{356}$	0.21	3.72	1.65	0.25
$l_2 = b_2 + b_{145} + b_{346}$	1.18	2.93	1.82	–1.97
$l_3 = b_3 + b_{246} + b_{156}$	–0.04	2.09	1.37	0.41
$l_4 = b_4 + b_{125} + b_{236}$	–0.05	4.80	3.28	0.88
$l_5 = b_5 + b_{124} + b_{136}$	0.19	–1.04	–0.33	–0.50
$l_6 = b_6 + b_{234} + b_{135}$	0.98	11.72	4.81	–0.16
$l_{12} = b_{12} + b_{45}$	0.15	–0.07	–0.47	–0.41
$l_{13} = b_{13} + b_{56}$	–0.14	0.66	0.47	0.47
$l_{14} = b_{14} + b_{25}$	0.30	0.81	0.21	–0.45
$l_{23} = b_{23} + b_{46}$	–0.01	0.36	–0.73	–0.26
$l_{24} = b_{24} + b_{15} + b_{36}$	–0.26	–0.42	–1.31	0.19
$l_{34} = b_{34} + b_{26}$	0.32	1.96	1.02	0.00
$l_{16} = b_{16} + b_{35}$	0.08	0.22	–0.12	–0.12
$l_{123} = b_{123} + b_{345} + b_{146} + b_{256}$	–0.11	–0.52	–0.32	0.10
$l_{134} = b_{134} + b_{235} + b_{126} + b_{456}$	0.05	0.05	0.20	0.04

Similar results are obtained for xylenes but two aliases "$b_{34} + b_{26}$" and "$b_{24} + b_{15} + b_{36}$" are found to be significant; this is, however, difficult to confirm with the normal probability plot. A clearer plot (half-normal probability plot [20,21]) can be obtained if the absolute values of the estimated effects are plotted as shown in figure 5.

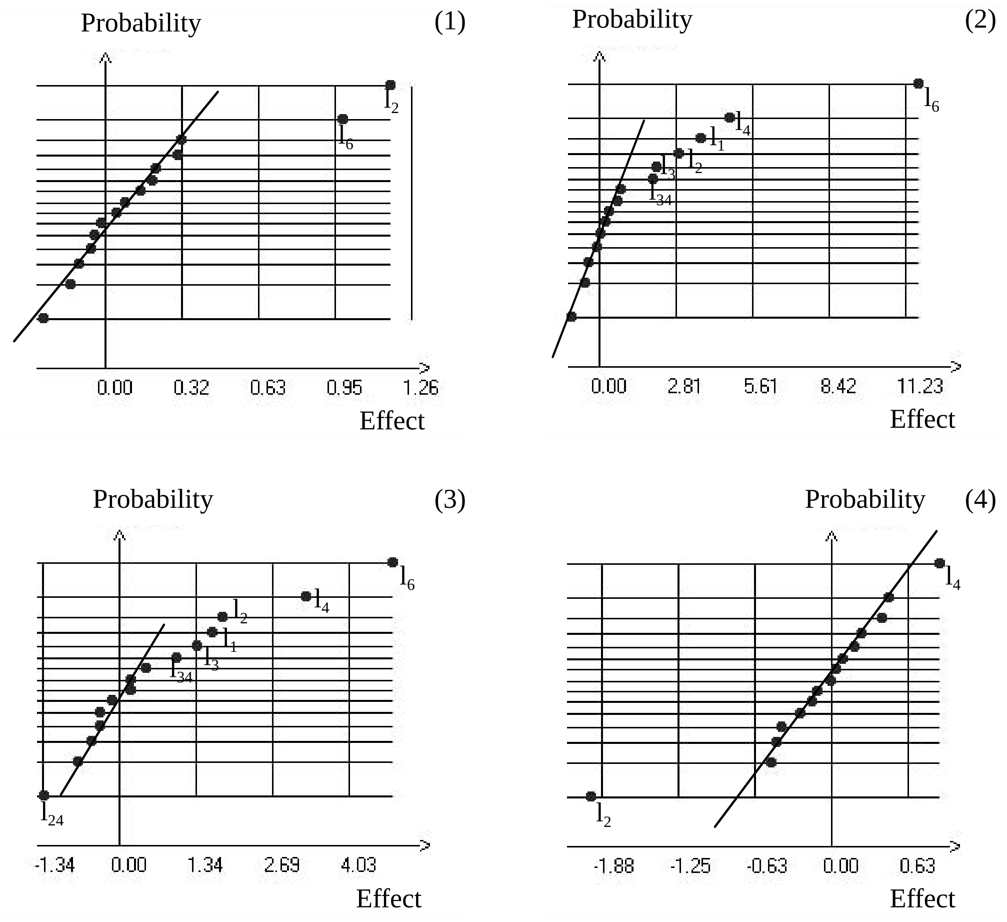


Figure 4. Normal probability plot of the estimated effects of:
(1) y_B: percentage of benzene sulfonation;
(2) y_T: percentage of toluene sulfonation;
(3) y_X: percentage of xylenes sulfonation;
(4) $S = y_{(T+X)/B}$: the ratio of the percentage of toluene and xylenes sulfonation to the percentage of benzene sulfonation.

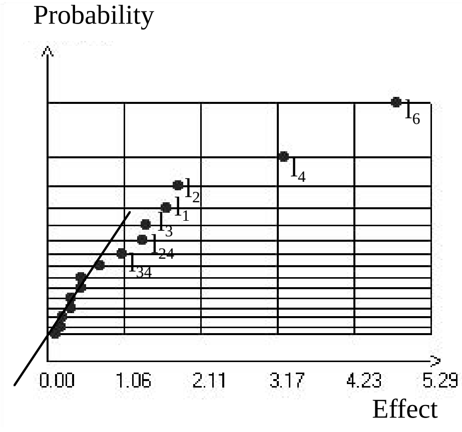


Figure 5. Half-normal probability plot of the estimated effects of y_X.

For selectivity, only the effects of the variables X_2 and X_4 are significant.

This statistical study agrees with an analysis of variance based on a determination of the experimental error by duplication of two experiments carried out as indicated in table V. These conditions allow us to estimate the sum of squares of pure error for each response with two degrees of freedom. Table VI summarises the results of the analysis of variance based on the Fisher test, (comparison of F ratios to critical $F_{0.05}(1,2)$) [21,22].

Discussion

Experimental design

In this study, the results are very simple and the information can be obtained directly from the values of the effects. It is

Table V. Replicated runs.

Run	*D* (X_1 = 0)	*C* (X_2 = 0)	*T* (X_3 = 0)	*E* [a] (X_4 = ±1)	*t* (X_5 = 0)	*R* (X_6 = 0)	y_B (%)	y_T (%)	y_X (%)	*S*
17	7^H	Oleum (3.5 % SO_3)	102.5°	(-)	20 min	1.0	6.17	43.18	75.82	8.80
17’	7^H	Oleum (3.5 % SO_3)	102.5°	(-)	20 min	1.0	6.71	45.01	74.19	8.03
18	7^H	Oleum (3.5 % SO_3)	102.5°	(+)	20 min	1.0	5.97	53.69	82.04	10.47
18’	7^H	Oleum (3.5 % SO_3)	102.5°	(+)	20 min	1.0	5.21	54.71	79.91	11.87

[a] *E*(-) and *E*(+): Without and with azeotropic elimination of water respectively

Table VI. Significance of effects by ANOVA.

	y_B		y_T		y_X		*S*	
Effects	*F cal.* [a]	*Test* [b]	*F cal.* [a]	*Test* [b]	*F cal.* [a]	*Test* [b]	*F cal.* [a]	*Test* [b]
$l_1 = b_1 + b_{245} + b_{356}$	3.21		201.30	**	24.17	*	1.53	
$l_2 = b_2 + b_{145} + b_{346}$	102.52	**	125.02	**	29.49	*	96.86	*
$l_3 = b_3 + b_{246} + b_{156}$	0.13		63.50	*	16.74		4.15	
$l_4 = b_4 + b_{125} + b_{236}$	0.21		336.38	**	95.39	*	19.44	*
$l_5 = b_5 + b_{124} + b_{136}$	2.73		15.75		0.99		6.19	
$l_6 = b_6 + b_{234} + b_{135}$	71.44	*	2001.7	***	205.46	**	0.66	
$l_{12} = b_{12} + b_{45}$	1.63		0.07		1.93		4.10	
$l_{13} = b_{13} + b_{56}$	1.50		6.41		1.95		5.44	
$l_{14} = b_{14} + b_{25}$	6.52		9.49		0.38		5.09	
$l_{23} = b_{23} + b_{46}$	0.01		1.92		4.70		1.65	
$l_{24} = b_{24} + b_{15} + b_{36}$	4.84		2.61		15.14		0.85	
$l_{34} = b_{34} + b_{26}$	7.42		56.34	*	9.34		0.00	
$l_{16} = b_{16} + b_{35}$	0.49		0.71		0.13		0.34	
$l_{123} = b_{123} + b_{345} + b_{146} + b_{256}$	0.85		3.88		0.94		0.24	
$l_{134} = b_{134} + b_{235} + b_{126} + b_{456}$	0.19		0.04		0.35		0.05	

a: *F* cal. = $(SS_j / ddl_j) / (SS_E / ddl_E)$

b: (*) $F^{\text{crit.}}_{0.05}$ (1,2) = 18.51, (**) $F^{\text{crit.}}_{0.01}$ (1,2) = 98.49 and (***) $F^{\text{crit.}}_{0.001}$ (1,2) = 998.50

not necessary to write second order interaction models and to plot three-dimensional projection of the models to give a satisfactory description of the influence of the variables.

By a visual inspection of the responses in table III, it is immediately seen (without any calculations) that the sulfonation yields of benzene (y_B) are low and their variations are not large (3 to 8 %). Therefore, no large effects of the variables on this response can be expected. It is also clear that the sulfonation yield of toluene and xylenes are high and vary in the same direction. Furthermore, it appears (Tab. IV) that one variable (the molar ratio) shows a very highly significant action on the sulfonation yields of toluene (y_T) and xylenes (y_X) and that four variables (*D*, *C*, *T* and *E*) show a relatively high influence on these two responses.

The estimates of the average b_0 vary between the three-sulfonation yields. They decrease in the order b_0 (xylenes) > b_0 (toluene) > b_0 (benzene). This agrees with the natural ranking of reactivity of these three aromatic hydrocarbons.

In the case of toluene sulfonation, among the confounded interaction effects, “$b_{34} + b_{26}$” is significant. It is not possible to determine which of these confounded effects contributes to the slightly high value of the estimate. To be able to separate the confounded interaction effects, we should run a second 2^{6-2}_{IV} fractional factorial design corresponding to the independent generators (5):

$$I = 1245 = -\,2346. \qquad (5)$$

In the absence of this complementary fraction design we can assume that b_{26} (interaction between the concentration of the sulfonating agent and the molar ratio of sulfuric acid to toluene plus xylenes) is the dominating term since X_6 has the greatest effect on this response. But an interaction (b_{34}) between temperature and azeotropic elimination of water is also plausible and expected. These data clearly indicate that these interaction effects tend to highly increase the sulfonation yield of toluene when reactions are carried out at high temperature with azeotropic elimination of water and/or with high concentration of the sulfonating agent and a high molar ratio.

Similar results are obtained for the xylenes sulfonation. In this case, however, b_3, "$b_{34} + b_{26}$" and "$b_{24} + b_{15} + b_{36}$" are only significant at the 90 % confidence level when using an analysis of variance based on replicated experiments data (Tab. VI).

For the selectivity, the interpretation is also evident by mere regarding the estimated effects. They are rather small but two main effects b_2 (–1.97) and b_4 (0.88) are larger than the others. The signs of b_2 (negative) and b_4 (positive) indicate that selectivity would drop considerably when increasing the SO_3 concentration of the sulfonating agent and/or when carrying out reactions without azeotropic elimination of water.

From the above analyses, the following conclusions can be drawn as to which experimental conditions should be used in the pilot plant experiment. These conditions would ensure maximum conversion of toluene and xylenes with minimum conversion of benzene:

- X_1 and X_3: the reaction time and the temperature should be at their high level (9 hours and 110 °C) since these factors don't affect the selectivity or benzene conversion but increase the sulfonation of toluene and xylenes.
- X_2: the SO_3 concentration of the sulfonating agent should be at a low level. However, it is not possible to use less than 97 % H_2SO_4 concentration since the global yield of the sulfonation could dramatically decrease. Crook and White [27] showed that with an initial concentration of sulfuric acid lower than 75 %, the sulfonation of toluene alone might not proceed.
- X_4: sulfonation reactions should be carried out with azeotropic elimination of water to increase selectivity and global sulfonation of toluene and xylenes;
- X_5: the time of addition of sulfonating agent is not critical. A short time is convenient (15 min);
- X_6: the molar ratio of sulfuric acid to toluene plus xylenes should be at its low level to minimise the conversion of benzene.

These conditions are similar to those of experiment number 14 in the design. The product of this experiment designated by BTXS 14 is then selected to check its hydrotropic properties.

Testing hydrotropic properties of BTXS 14

The performance of BTXS 14 has been evaluated by comparing the effect of this blend on the clear point of a typical premium formulation of a concentrated liquid detergent (25 % dodecylbenzenesulfonate, 15 % laurylethersulfate and 6 % lauryldiethanolamide) [1] with that of STS or SXS, the most important hydrotrope in light duty liquids.

Tests show that in all cases, the use of BTXS 14 leads to a reduction in the viscosity and an improvement in the stability of the concentrated detergent. Performances of the blend are between those of SXS and STS.

The clear points of the concentrated liquid detergent containing about 3 % of the different hydrotropes are respectively: 29, 18 and, 10 °C for STS, BTXS 14 and SXS. The clear point of the detergent without hydrotrope is 45 °C. The addition of about 3 % of pure SBS increases the clear point to 57 °C.

Finally, it can be concluded that BTXS 14 can be used in concentrated liquid detergents to reduce their clear point but also to bring them into a desirable viscosity range.

Conclusion

The use of designed experiments and several analytical techniques allows us to choose suitable experimental conditions to carry out sulfonation of the BTX fraction of the Tunisian natural gas MISKAR in order to prepare hydrotropes for detergents. The product obtained using the proposed conditions show good hydrotropic properties when applied to concentrated liquid detergent. However, further studies carried out in a pilot plant are needed if the procedure is to be used in large production scale. An industrial plan seems to be very attractive since the by-product of the sulfonation reaction, the organic phase, has a similar composition than that of the BTX fraction of the natural gas and can thus be marketed as solvent.

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