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Modelization and kinetic simulation of naphthalene sulfonation by 20% oleum

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Summary — This study represents a modelization procedure for the kinetic analysis of naphthalene sulfonation using 20% oleum at temperature 393 K. The sulfonation involves many consecutive, parallel and reversible reactions. Representative samples of the reaction mixture are analyzed by high-performance liquid chromatography for quantitative determination of the produced sulfonic acid isomers as well as of the remaining naphthalene. The kinetics obtained this way allow to suggest a model describing the concentration evolution of four components in the reaction mixture. Therefore, six main reactions are taken into account, the kinetic parameters of which are estimated by the fitting of experimental data, using a weighed least-squares method based on minimizing the deviation between calculated and experimental data.

modelization / naphthalene sulfonation / 20% oleum / kinetics / naphthalenesulfonic acid

Résumé — Modélisation et simulation cinétique de la réaction de sulfonation du naphtalène avec de l'oléum 20 %. Ce travail représente une procédure de modélisation de la réaction de sulfonation du naphtalène avec de l'oléum 20 % à 393 K. L'avancement de la réaction a été suivi par chromatographie liquide haute pression sur des échantillons représentatifs du milieu réactionnel. Les produits faisant l'objet de cette étude sont les acides sulfoniques obtenus ainsi que le naphtalène restant. Pour le modèle proposé, considérant la concentration de quatre composés dans le mélange, six réactions importantes ont été retenues. L'estimation des paramètres cinétiques se fait par la méthode des moindres carrés.

modélisation / sulfonation du naphtalène / oléum 20 % / cinétique / acide naphtalènesulfonique

Introduction

Naphthalene sulfonation [1–5], generally considered as one of the most fundamental industrial chemical reactions, is widely used for industrial chemical applications.

When carried out with sulfuric acid, naphthalene sulfonation leads to a mixture of α- and β-monosulfonic acids, naphthalene disulfonic acids and some other more complex sulfonation products. By carefully chosen working conditions (temperature, sulfonation agent concentration), good yields can be obtained for the desired product (β-naphthalenesulfonic acid).

This work is based on bibliographic data in order to propose an adapted mechanism to describe the actual reaction behaviour with 20% oleum. We used 20% oleum since this way it is possible to get a better elimination of the gradually formed water, thus moving the equilibrum towards sulfonation, increasing the reaction rates. Furthermore, it enables to save energy by spontaneous heating up of the reaction mixture.

First of all, we had to determine which reactions among all those occurring in this medium would have to be taken into account in order to allow reliable validation of the chosen model.

Bibliographic studies

The modelization of naphthalene sulfonation has been studied by several authors [6–8] such as Passet et al, whose work [9] led to a better knowledge of the sulfonation process of naphthalene. They suggested the sulphonating agent to be either SO_3, HSO_3^+ or S_2O_6, and they showed that the sulfonation reaction is due to both SO_3 and HSO_3^+, involving two different mechanisms.

Kniezek et al [10] have not taken into account the formation of diacids and the transformation of α into β. They proposed the following mechanism to describe naphthalene sulfonation by 98% sulfuric acid:

$$N + S \xrightarrow{k_1} \alpha + W$$

$$\alpha \xrightarrow{k_2} N + SO_3$$

$$N + S \xrightarrow{k_3} \beta + W$$

* Correspondence and reprints

$$\beta \xrightarrow{k_4} N + SO_3$$

$$H_2SO_4 + H_2O \xrightarrow{k_5} H_2SO_4{\cdot}H_2O \quad \text{(dilution)}$$

$$SO_3 + H_2O \xrightarrow{k_6} H_2SO_4$$

where
S: sulfuric acid H_2SO_4,
N: naphthalene $C_{10}H_{10}$,
W: water H_2O,
α: 1-naphthalenesulfonic acid $C_{10}H_9SO_3H$,
β: 2-naphthalenesulfonic acid $C_{10}H_9SO_3H$.
These authors found a good agreement between their theoretical model and experimental data at different temperatures (368, 403 and 433 K).

Servinski et al [11] studied naphthalene sulfonation by 85% sulfuric acid at different temperatures (398 and 428 K). The model they proposed is the following:

$$N + S \xrightarrow{k_1} \alpha + W$$

$$N + S \xrightarrow{k_2} \beta + W$$

$$\alpha + W \xrightarrow{k_3} N + S$$

$$\beta + W \xrightarrow{k_4} N + S$$

$$\alpha + S \xrightarrow{k_5} D + W$$

$$\beta + S \xrightarrow{k_6} D + W$$

where D:
naphthalenedisulfonic acid isomers $C_{10}H_8(SO_3H)_2$.
Servinski suggested a general equation to describe the rates of the different reactions taking place in the mixture as follows:

$$r_i = k_i C_{Ar} C_{H_2SO_4}^{m_i} C_{H_2O}^{n_i}$$

where $i = 1, 2, ..., 6$ (number of the reaction);
for $i = 1$ and 2, Ar is $C_{10}H_{18}$,
$i = 4$ and 6, Ar is β-$C_{10}H_7SO_3H$,
m, n: partial orders of each reagent.

Nowicki et al [12] presented the expression of the sulfonation speed as follows:

$$r_i = k_{0i} \exp\left(\frac{-E_i}{RT}\right) C_{Ar} \exp\,(b_i C_S)$$

where
i = number of the reaction (1 to 6),
b = constant of each reaction,
C_s = sulfuric acid concentration,
E = activation energy,
C_{Ar} = aromatic concentration.

Hawash et al [13, 14] studied naphthalene sulfonation with 98% sulfuric acid involving different naphthalene-to-sulfuric acid molar ratios (from 0.7 to 1.5) at temperatures between 388 and 443 K. They showed that diacid formation from β-naphthalenesulfonic acid is not probable. Their final model is the following one:

$$N + S \xrightarrow{k_1} \alpha + W$$

$$N + S \xrightarrow{k_2} \beta + W$$

$$\alpha \xrightarrow{k_3} \beta$$

$$\alpha + S \xrightarrow{k_4} D + W$$

$$D + W \xrightarrow{k_5} \beta + S$$

This bibliographic study shows that, although many works deal with naphthalene sulfonation simulation, only a few of them use oleum as a sulfonating agent.

First, the aim of this work was to determine a model allowing to estimate with a sufficient accuracy the composition of the reacting mixture; second, to determine how the use of oleum 20% can lead to the formation of several products, including naphthalenesulfonic diacids.

Experimental section

In our work, the sulfonation reaction of naphthalene by 20% oleum has been carried out in a Mettler RC1 calorimetric reactor. The reactor volume was 2000 cm^3. The $SO_3/C_{10}H_8$ molar ratio ($R = 1.31$) was the same for all our tests.

The RC1 Mettler calorimeter is a computer-assisted lab reactor. It is fitted with a safety system designed for isothermal and adiabatic reaction runs, aiming at the determination of thermal data and constants.

The reactor is double-walled, so that the jacket as well as the reaction mixture temperatures can be very precisely determined. By these means, a good determination of the heat flow through the vessel walls can be reached.

The reactor contains 5 mol solid naphthalene. Its temperature is raised up to 393 K. Then, 616 g 20% oleum is slowly added at a constant rate (5.94×10^{-8} m^3/s) over a period of 90 min in order to keep the temperature constant (± 0.1 K).

In order to determine the kinetic constants, samples have been taken at several times ($t = 0$ at the beginning of the introduction of oleum).

In order to stop the reaction, the samples are immediately cooled to 273 K and diluted with cold methanol. The proportions of the isomeric sulfonic acids (α, β and diacids) and of naphthalene are determined by HPLC.

The HPLC device is constituted of a volumetric pump (Spectra Physics 8700), a Lichrosorb RP8 – 5 μm 250 × 4.6 column, and a UV detector (280 nm).

The mobile phase consists of three eluents:
- A: methanol/water (36:64, v/v) mixture added for 0.4 g/L of TBAB (tetrabutyl ammonium bromide);
- B: methanol added for TBAB (4 g/L);
- C: methanol/water (70:30, v/v) mixture.

The determinations are carried out at a 1 mL/min rate at 333 K, with an eluent gradient ramping from 100% A, 0% B to 100% B and 0% A.

The choice of the kinetic model

To make the simulations, we used Batchcad software [15], allowing the calculation of kinetic parameters using several algorithms and several integration methods (Euler, Runge–Kutta).

With regard to the experimental results, we made the following assumptions:

– only monosulfonic (α and β) and disulfonic acids are formed (the latter term including all possible isomers);

– the sampling is carried out without any change in reaction volume (the sample volume is neglected);

– the reacting medium is perfectly homogeneous and the reaction is isothermal. A strong stirring of the mixture solves the problem of mass transfer between naphthalene and 20% oleum.

Considering the already mentioned models, we suggest to add modifications taking into account some supplementary reactions, so that the global contributions can be described by the following reactions:

$$N + H_2SO_4 \xrightarrow{k_1} \alpha + W \quad (1)$$

$$N + H_2SO_4 \xrightarrow{k_2} \beta + W \quad (2)$$

$$\alpha + W \xrightarrow{k_3} N + H_2SO_4 \quad (3)$$

$$\beta + W \xrightarrow{k_4} N + H_2SO_4 \quad (4)$$

$$\alpha + H_2SO_4 \xrightarrow{k_5} D + W \quad (5)$$

$$\beta + H_2SO_4 \xrightarrow{k_6} D + W \quad (6)$$

$$D + W \xrightarrow{k_7} \alpha + H_2SO_4 \quad (7)$$

$$D + W \xrightarrow{k_8} \beta + H_2SO_4 \quad (8)$$

$$\alpha \xrightarrow{k_9} \beta \quad (9)$$

The rates for the occurring reactions are as follows:

$$r_i = k_i C_1^{a_i} C_2^{b_i}$$

where

$i = 1, 2, 3, \ldots$: reaction identification number,
1,2: reagents corresponding to each reaction,
a_i, b_i, ...: partial orders of the reagents,
C: concentration.

The rate constants k_i are temperature-dependent. Their variations follow Arrhenius' law:

$$k_i = A_i \exp\left(\frac{-E_i}{RT}\right) \text{ where } i = 1, 2, \ldots, 9.$$

The model related to these equations is the following:

$$\frac{d[\alpha]}{dt} = k_1[N]^{a1}[S]^{b1} - k_3[\alpha]^{a3}[W]^{b3} - k_9[\alpha]^{a9} + k_7[D]^{a7}[W]^{b7} - k_5[\alpha]^{a5}[S]^{b5}$$

$$\frac{d[\beta]}{dt} = k_2[N]^{a2}[S]^{b2} - k_4[\beta]^{a4}[W]^{b4} + k_9[\alpha]^{a9} - k_6[\beta]^{a6}[S]^{b6} + k_8[D]^{a8}[W]^{b8}$$

$$\frac{d[D]}{dt} = k_5[\alpha]^{a5}[S]^{b5} + k_6[\beta]^{a6}[S]^{b6} - k_7[D]^{a7}[W]^{b7} - k_8[D]^{a8}[W]^{b8}$$

$$[N] = [N_0] - ([\alpha] + [\beta] + [D])$$

$$[S] = [S_t] - ([\alpha] + [\beta] + 2[D])$$

where $[S_t] = \dfrac{[S_0] \cdot Q \cdot t}{V_0 + Q \cdot t}$ for $0 < t < 5400$ s

$$[S] = [S_T] - ([\alpha] + [\beta] + 2[D])$$

where $[S_T] = [S_{t=5400}]$ for $t > 5400$ s

$$[W] = [\alpha] + [\beta] + 2[D]$$

where

[N]: naphthalene concentration,
[α]: 1-naphthalenesulfonic acid concentration,
[β]: 2-naphthalenesulfonic acid concentration,
[D]: sulfonic diacid total concentration,
[S]: sulfuric acid concentration,
[S_t]: sulfuric acid concentration at time t,
[W]: water concentration,
[S_0]: the initial sulfuric acid concentration (20% oleum),
Q: rate of addition of oleum (m^3/s),
V_0: the initial volume of the naphthalene.

At the initial time, when $t = 0$:

$$[N] = [N_0]$$

$$[S] = [\alpha] = [\beta] = [D] = [W] = 0$$

The parameters are estimated by minimizing the following objective function:

$$F = \sum_{i=1}^{m} \sum_{j=1}^{n} (C_{ij}^{\text{meas}} - C_{ij}^{\text{theo}})^2$$

where i = number of samples, j = number of elements, C_{ij}^{meas} = measured concentration, C_{ij}^{theo} = calculated concentration.

Results and discussion

A first series of simulations of the sulfonation reaction by 20% oleum at 393 K based on the nine-reaction model was carried out in two steps:

(1) By fixing the partial reaction orders of all reactions at unity. Although the decreasing of naphthalene concentration could be well described (fig 1), the best value we could simulate in this manner for the time of the maximum concentration of α-naphthalenesulfonic acid is nearly 50% less than the observed time. On the other hand, such a model poorly describes the diacid formation. The model shows a very late formation of such species, with a slow increase versus time. On the other hand, the observed experimental values show a rapid initial formation, leading after a short time to a constant value of their concentration (fig 1).

(2) Therefore, we were led to assume variable partial orders for some reactions. Although the results were slightly better than using this method, the nine equations remained too complicated in order to lead clearly to reliable values of the reaction orders.

On the other hand, it seems that the hydrolysis (3 and 4) of the naphthalenesulfonic acids is difficult. The water produced by reactions (1) and (2) is transformed

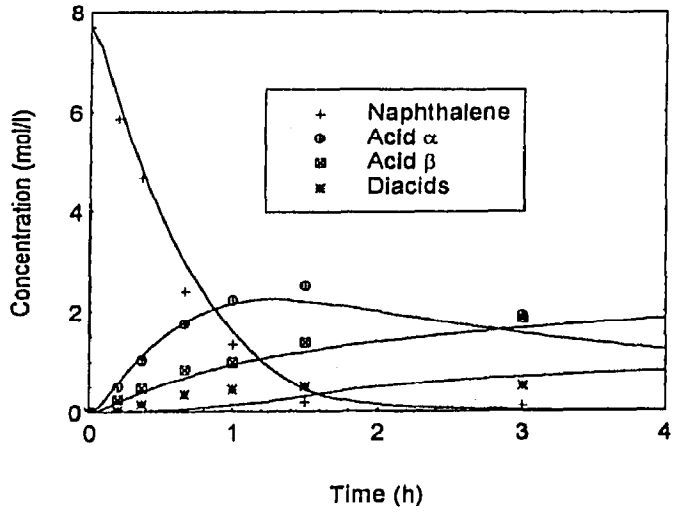

Fig 1. A nine-equation model: evolution of concentrations versus time (sulfonation of naphthalene with 20% oleum at 393 K, $R = 1.31$).

into sulfuric acid by the excess of SO_3. The water which is formed when all SO_3 has been transformed does hydrolyse the diacids which are also produced by the reaction. Table I shows that the rate constant of reaction (7) is about 6×10^2 times higher than that of reaction (3) (formation of α); similarly the rate constant of reaction (8) is about 2×10^2 times higher than that of reaction (4) (formation of β). Therefore, we decided to neglect the hydrolysis of monoacids but not the hydrolysis of diacids.

Table I. Values of rate constants and partial order at 393 K, nine-reaction model.

Reactions	K_i	a_i	b_i
r_1	4.13×10^{-4}	1	1
r_2	1.30×10^{-4}	1	1
r_3	1.06×10^{-16}	1	1
r_4	4.72×10^{-17}	1	1
r_5	4.75×10^{-5}	1	1
r_6	3.02×10^{-10}	1	1
r_7	6.57×10^{-14}	1	1
r_8	8.18×10^{-12}	1	1
r_9	4.27×10^{-5}	1	1

In order to verify this assumption (hydrolysis of α and β), α- and β-naphthalenesulfonic acid has been heated at 393 K with an excess of water in a sealed glass reactor for different times up to 30 h. Even for such long hydrolysis durations, the amount of free naphthalene formed by the reactions (3) and (4) was less than two percent (molar ratio). Since the reaction we deal with is carried out within less than 10 h, and in the presence of oleum instead of free water, the contribution of the reactions (3) and (4) to the evolution of the composition of our system is nearly zero.

Thus we tried to develop the model by neglecting the reactions (3), (4) and (6). The nine-equation system can be reduced to a six-equation system as follows:

$$N + H_2SO_4 \longrightarrow \alpha + H_2O \quad (1)$$

$$N + H_2SO_4 \longrightarrow \beta + H_2O \quad (2)$$

$$\alpha + H_2SO_4 \longrightarrow D + H_2O \quad (5)$$

$$D + H_2O \longrightarrow \alpha + H_2SO_4 \quad (7)$$

$$D + H_2O \longrightarrow \beta + H_2SO_4 \quad (8)$$

$$\alpha \longrightarrow \beta \quad (9)$$

A second series of simulations has been carried out under the same conditions but using the simplified six-equation model. The results, shown in figure 2 and table II are much more satisfactory.

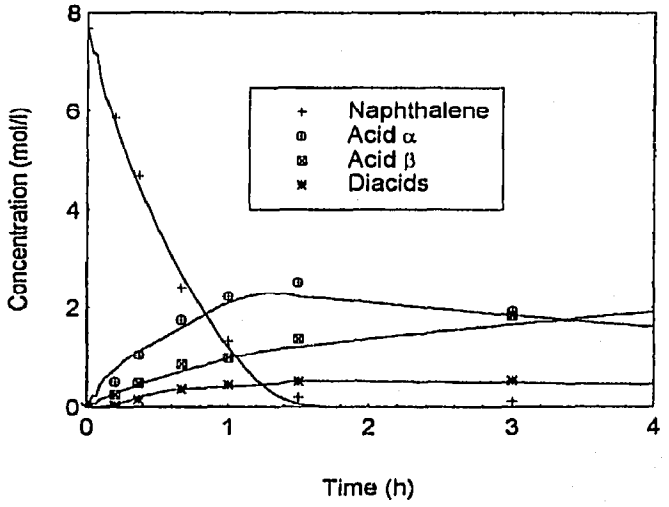

Fig 2. A six-equation model: evolution of concentrations versus time (sulfonation of naphthalene with 20% oleum at 393 K, $R = 1.31$).

Table II. Values of rate constants obtained at 393 K by the reduced six-reaction model.

Reactions	K_i	a_i	b_i
r_1	2.79×10^{-3}	1	1
r_2	8.62×10^{-4}	1	1
r_5	9.76×10^{-4}	1	0.5
r_7	3.52×10^{-4}	2	2
r_8	1.33×10^{-7}	2	2
r_9	4.02×10^{-5}	1	–

The simplified model of six equations, using partial order equal to one for all main reactions (1), (2) and (9) leads to rather good agreement between calculated and experimental values. The observed differences are within determination uncertainties.

Conclusion

The proposed model allows a good description of the naphthalene sulfonation by 20% oleum at 393 K. The improvement of the calculated values needs some second-order reactions to be taken into account. This observation seems to indicate complex mechanisms involving the presence of water-stabilised species before hydrolysis of diacids occurs. The use of oleum enables both an equilibrium displacement toward sulfonation as well as a gain in heating energy. Moreover, a higher percentage (15%) of diacids, the yields of which are satisfactorily described by the developed model, can be obtained this way.

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