

Kinetic Study on Dodecylbenzene Sulfonation in a Mixed Batch Reactor

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Abstract A mixed batch autoclave reactor was used to investigate the sulfonation reaction kinetics of pure samples of DodecylBenzene (DB). The effect of temperature in the range between 20 and 50 °C, and the effect of the concentrations of Sulfur Trioxide and DodecylBenzene upon the sulfonation reaction rate were studied. Two sets of experiments were performed. The first is applying high SO₃/DB molar ratio $C_{SO_3}/C_{DB} \gg 1$, the second is with high DB/SO₃ molar ratio ($C_{DB}/C_{SO_3} \gg 1$). It was shown that the sulfonation reaction is a 0.74 order with respect to DB and a 1.59 order with respect to SO₃. The reaction rate constant *k* was determined for both sets. The values determined for the frequency factor and activation energy were as per the following equation: $k = 2.2172 \times 10^3 \exp\{-5207/R_g T\}$ (1). The kinetic model for the sulfonation reaction is $R_{D,B} = k * C_{SO_3}^{1.59} * C_{D,B}^{0.74}$ (2). The progress of the reaction was determined from SO₃ concentration vs. time data conducted at different time intervals. Evaluations of SO₃, DB concentrations and reaction rates were based on titrations of the inorganic phase with caustic soda standard solutions.

Keywords Sulfonation, Dodecylbenzene, Kinetics, Sulfonic Acid, Homogeneity, Detergents

1. Introduction

The recent developments in detergents industry reflect the worldwide trend in detergent products and quality.

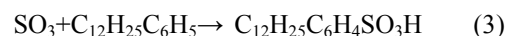
The challenge of the recent decades for detergents industry is to produce cleaning products which are of essential role in our daily lives, which can safely and effectively remove soils, germs and other contaminants, help us to stay healthy, care for our homes and possessions, and make our surroundings more pleasant [1,2].

Dodecylbenzene sulfonate's biodegradability and its high cleaning capability were the reasons for the producers went toward the production of large amounts of this detergent and to focus their attention on the chemical process techniques of the sulfonation of the DB [3].

Recent studies had led to the conclusion that the monomer SO₃ is the true active ingredient in Oleum while H₂O is acting as solvent. The SO₃ Hydrates present at low temperatures are the monohydrates (SO₃.H₂O or 100% H₂SO₄) and the dihydrates (SO₃.2H₂O or 84.5% H₂SO₄) and the pyrosulfuric acid (2SO₃.H₂O or 44.5% Oleum [4,5,6].

In USA, 51 out of 101 working sulfonation plants apply Oleum, 44 of them apply SO₃ while 5 units apply chlorosulfonic acid and one plant applies sulfoxidation [2].

Basic Chemistry supports that Sulfur trioxide (SO₃) reacts with the Dodecylbenzene to form a sulfur-carbon bond. One of the characteristics of this process is that the resultant Dodecylbenzene sulfonic acid is a stable molecule [3,4,5,6,7] as per the following equation



Studies on the sulfonation of organic compounds were carried by Dresel and Hinshelwood (1944) [8], Stubbs, Williams and Hinshelwood (1948) [9] and more recently by Torres et al.(2008) [10]. Torres accepted a second order model for the reaction rate, first order with respect to both methyl esters and sulfur trioxide, while Dresel and Hinshelwood (1944), Stubbs, Williams and Hinshelwood (1948), performed kinetic studies on different Alkylbenzenes with SO₃ and concluded that the reaction rate constant of this sulfonation reaction depends on the Arylbenzene being sulfonated with values ranging between 48.8 to 7.85×10^{-6} [liters/gmole.sec] and the activation energy is in the range of [4320 – 11400] cal/gmole.

Ratcliff (1954) [11], studied the sulfonation of benzene with SO₃ and concluded that the reaction is 0.57 order with respect to Benzene and 1.24 with respect to SO₃.

The primary aim of this study is to investigate the sulfonation of Dodecylbenzene with Oleum 22 wt%.

The sulfonation is carried out in a well-mixed autoclave reactor ensuring homogeneity.

The kinetic study reported in this investigation was carried out in a stainless steel 316 alloy cylindrical autoclave (Figure. 1) equipped with a stirrer for agitation (80 R.P.M) with a total volume of 4868 cm³, having an internal diameter *D_i* of 135 mm and a height *H* of 340 mm. The height of the

hemispherical head (d_x) is 33.75 mm ($d_x=0.25 D_i$), the diameter of the agitating blade dt is 40.5 mm, the distance between agitator and bottom of the reactor ht is 67.5 mm, the width of the blades w is 10 mm and the width of the baffles w_b is equal to 13 mm.

2. Raw Materials

Dodecylbenzene is an Organic compound, colorless waxy solid consists of a Dodecyl group ($C_{12}H_{25}$) attached to a Phenyl group (C_6H_5). Dodecylbenzene is a precursor for Sodium dodecylbenzenesulfonate[12].

Sulfur trioxide is a clear oily colorless liquid. It may contain a haze and be off-white to light brown in appearance. Oleum is normally turbid and off-white in appearance [13].

The strength of Oleum used is 22 wt%(1.3458 $SO_3 \cdot 1H_2O$). SO_3 molar mass is equal to 80 and density at 30°C (ρ) = 1.890 gr/cm^3 .

Some of the properties of Dodecylbenze are given below:

- Chemical formula $C_{18}H_{30}$.
- Molar Mass 246.43 g/mole.
- Appearance colorless liquid.
- Density 0.857 g/cm^3 .
- Melting point - 7 °C.
- Boiling point 290 to 410 °C
- Solubility in water insoluble

The properties of Oleum with different strengths are shown in **Table 1**.

Table 1. Properties of Oleum with different strengths

Properties	SO_3	65% Oleum	30% Oleu.	20% Oleu.
Melting point(°C)	17	2	19	-10
Boiling point (°C)	45	58	121	142
Density at(g/cm^3)30°C	1.88	1.975	1.92	1.88

3. Experimental

The first set of experiments was performed applying high (CSO_3/ CDB) molar ratio. 1666 cm^3 of Oleum 22% and 1000 cm^3 of Dodecylbenzene were loaded to the reactor, see Figure 1. These amounts contain 33.7439 gmoles of SO_3 (N_{SO_3}) and 3.484 gmoles of DB. All experiments of the first set were initiated with $C(SO_3) = 33.7439/2666 = 1.2657 \times 10^{-2}$ gmole / cm^3 while $C(DB) = 3.484/2666 = 1.3068 \times 10^{-3}$ gmole/ cm^3 , thus $C(SO_3)/C(DB) = 9.6854 \gg 1$.

Dodecylbenzene concentration changes were determined at different times. Samples of the reacting mixture of approximately 4 cm^3 were picked at different time intervals, washed with 10 cm^3 of distilled water and then left for approximately 6 hours for the separation of the organic phase in a burette.

The H_2SO_4 solution is then titrated with 1 M NaOH solutions. The amount of soda solution needed to neutralize sulfuric acid is used to evaluate the amount of H_2SO_4 and hence the SO_3 present in the solution and thus the moles of D.B not reacted.

The proposed kinetic model for the sulfonation reaction rate is:

$$-R_{DB} = k(C_{DB})^{\alpha_1} \cdot (C_{SO_3})^{\alpha_2} \quad (4)$$

Where C_{DB} and C_{SO_3} are the concentrations of DB and SO_3 . α_1 and α_2 are the reaction orders with respect to SO_3 and DB respectively.

Since SO_3 is in excess, its concentration is assumed constant (not altered throughout the experiment) and is considered to be equal to:

$$(C_{SO_3})_{ave.} = \{C(SO_3)_0 + C(SO_3)_f\} / 2. \quad (5)$$

The number of SO_3 moles not reacted are calculated as per the following equation:

$$N(SO_3)_i = [V_{iNaOH} * 1.0 * \{2666 - \sum_{i=1}^n (v_{si})\}] / (v_{si} * 1000), \quad (6)$$

where $V_{i(NaOH)}$ is the volume of 1.0 M caustic soda solution needed to neutralize $v_{si} cm^3$, 1.0 is the molarity of the caustic soda solution, v_{si} is the volume in cm^3 of the sample picked in the i^{th} sampling, n is the total number of samples. The number of unreacted DB moles is calculated as follows:

$$(N_{D.B})_i = (N_{D.B})_0 - \Delta(N_{SO_3})_i. \quad (7)$$

where $\Delta(N_{SO_3})_i = N(SO_3)_0 - N(SO_3)_i$

The D.B concentrations are estimated by dividing the number of un reacted moles by the remaining volume which is equal to $(2666 - \sum v_{si}) cm^3$.

Four classes of experiments were conducted, the first was at 20, the second at 30 °C, the third at 40°C while the fourth was at 50 °C, for each class we estimated the observed reaction rate constant k'_{Ti} which is equal to the intrinsic reaction rate constant k multiplied by the average concentration of sulfur trioxide ($C_{SO_3}_{ave}$ raised to the power α_2 which is equal to $[(C_{SO_3})_{ave}]^{\alpha_2}$.

In the second set of experiments, we performed classes with excess in DB moles against SO_3 .

We used 3000 cm^3 of DB with 95 cm^3 of Oleum 22% in the first three classes and 3000 cm^3 of DB with 65 cm^3 oleum 22% in the fourth class of experiments. In this second set, we initiated our experiments with 10.4512 gmoles of DB against 1.926 moles of SO_3 in the first three classes and 1.295 gmole SO_3 in the fourth class of the second set against 10.4512 gmoles of DB.

Experimental runs were performed at 20, 30, 40, and 50°C. Experimental data was treated and values of the observed rate constant k'_{Ti} were deduced, Where k'_{Ti} is equal to k multiplied by $(C_{DB})_{ave}$ raised to the power α_1 which is equal to $[(C_{DB})_{ave}]^{\alpha_1}$.

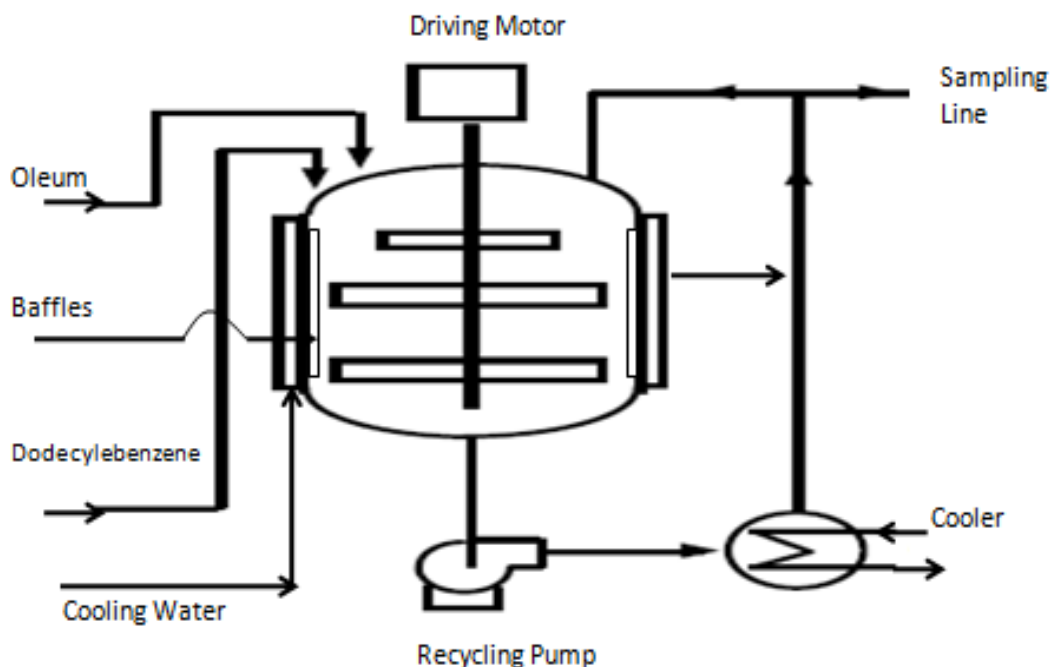


Figure 1. Sulfonation Reactor

Table 1. Typical Experimental Data Sheet Showing the Measured and Calculated Variables in Each Experiment

i	Time [sec.]	V_s cm^3	V_{NaOH} cm^3	N_{SO_3} $gmol$	$N_{D.B}$ $gmol$	$C(D.B)$ $gmole/lit.$	$-\{\Delta C_{D.B}/\Delta t\}$ $\times 10^3$	$(C_{D.B})_{ave}$ $gmole/lit.$	$V_{r,m}$ cm^3
1	0	3.5	44.3	33.7439	3.484	1.30683	0.715944	1.14222	2666
2	460	3.5	43.2	32.8629	2.6029	0.97762	0.558389	0.812984	2662.5
3	1050	3.5	42.1	31.9840	1.7240	0.6484	0.462020	0.597997	2659
4	1267	3.5	41.8	31.7143	1.4543	0.5476	0.341990	0.397264	2655.5
5	2300	3.5	40.8	30.9174	0.655	0.2469	0.152762	0.16792	2652
6	3171	3.5	40.3	30.4956	0.2356	0.0889	0.082910	0.052819	2648.5
7	4042	3.5	40.1	30.3041	0.0441	0.01669			2645

4. Batch Sulfonator

A schematic presentation of the sulfonation process is shown in Figure 1. The desired amounts of Oleum and DB are loaded to the sulfonation reactor which is equipped with an agitating system and jacketed for evolved heat removal. The reacting mixture is withdrawn from the reactor through an opening in the bottom with the aid of a pump and returned to the top of the reactor after being cooled properly in the cooler. Sampling is done from the recycling line optionally at different time intervals.

5. Results and Discussion

Illustration of the Experimental data obtained, is shown in Table 1. The operating conditions are as follows: $T_f = 20$ ($^{\circ}C$),

the pressure is $P = 1.1$ atma, the rotational speed of the agitator $RPM = 80$, and the initial total volume is $V_{t0} = 2666$ cm^3

Similar treatments are carried for all other experiments for the temperatures applied, 30, 40 and 50 $^{\circ}C$.

The number of samples picked for each class(i) ranged between 7 and 9, Where $\{\Delta C_{D.B}/\Delta t\} \times 10^3$ is the rate of consumption of DB in $[gmol\ DB / lit. sec.] \times 10^3$

The slope (α_i) and the intercept ($\ln k' T_i$) of the line:

$$\ln(-RDB) = \ln k' T_i + \alpha_i \ln(C_{DB}) \quad (8)$$

were obtained.

The slope is equal to the order of reaction (α_i) with respect to DB. The intercept is equal to $\ln k' T_i$, where $k' T_i$ is the observed reaction rate constant = $k T_i * [(C_{SO_3})_{ave}]^2$, $k T_i$ is the intrinsic reaction rate constant.

The results of the first set of experiments are given in

Table 2.

Thus the order of the reaction with respect to DB (α_1) is taken as the average value of all the obtained values of α_1 for the four temperatures applied, i.e. $(\alpha_1)_{ave} = (0.72+0.71+0.68+0.83)/4 = 0.74$

This study showed that an increase in the temperature from 20 to 30 °C led to an increase in the reaction rate constant by 1.74 times and the increase in temperature from 30 to 40 °C increased the rate constant by 1.82 times while the increase in temperature from 40 to 50°C increased the rate constant by 1.31.

In the second set, experiments conducted at $T_j = 20, 30$ and 40°C with $(\text{CDB}/\text{CSO}_3) \gg 1.0$, were initiated with 3000 cm^3 of DB and 179.55 gr . Oleum 22% (95 cm^3) fed to the reactor, thus ensuring that the initial number of DB moles (N_{DB})^o are 10.451 gmole and those for SO_3 are $(N_{\text{SO}_3}) = 1.923 \text{ gmole}$. At 50°C the run was initiated with 122.85 gr Oleum 22% (65 cm^3 Oleum) and 3000 cm^3 of DB. For titrating the

picked samples we applied a 0.1 M NaOH solution. The results of the second set of experiments are given in Table 3. α_2 is the reaction order with respect to SO_3 and the observed reaction rate constant

$$k_{Tj}'' = k_{Tj}^* [(C_{\text{DB}})_{ave}]^{\alpha_1}$$

Thus the average value of $\alpha_2 = (\alpha_2)_{ave} = (1.91+1.72+1.41+1.33)/4 = 1.59$, which means that the sulfonation reaction is 1.59 order with respect to SO_3 .

From the above mentioned values of α_1 , α_2 , k_{Ti}' and k_{Tj}'' , k_{Ti} and k_{Tj} are calculated by the following relations:

$k_{Ti} = k_{Ti}' / [(C_{\text{SO}_3})_{ave}]^{\alpha_2}$ “(9)”, for $T_i = 20, 30, 40$ and 50°C .

And $k_{Tj} = k_{Tj}'' / [(C_{\text{DB}})_{ave}]^{\alpha_1}$. “(10)”, for $T_j = 20, 30, 40, 50^\circ\text{C}$.

Determined values of k_{Ti} and k_{Tj} are shown in Table 2 and Table 3.

Table 2. Results of the First Set of experiments.

Temperature T_i , ($^\circ\text{C}$)	20	30	40	50
Average SO_3 concentration, gmole/L	12.0571	12.2875	12.0429	12.0857
α_1	0.72	0.71	0.68	0.83
$\ln k'$	-7.3395	-6.75296	-6.18595	-5.90286
k_{Ti}'	6.49375×10^{-4}	1.16742×10^{-3}	2.0581×10^{-3}	2.7316×10^{-3}
k_{Ti}	1.23971×10^{-5}	2.16262×10^{-5}	3.9364×10^{-5}	5.19523×10^{-5}

Table 3. Results of the Second Set of Experiments

Temperature T_j $^\circ\text{C}$	20	30	40	50
Average D.B Concentration, mole/l	3.2569	3.2145	3.0851	3.2107
α_2	1.91	1.72	1.41	1.33
$\ln k''$	-6.83	-6.4521	-5.8641	-5.0541
k_{Tj}''	1.0809×10^{-3}	1.5772×10^{-3}	2.8396×10^{-3}	6.3831×10^{-3}
k_{Tj}	1.6535×10^{-4}	2.4636×10^{-4}	4.7350×10^{-4}	9.9894×10^{-4}

The overall intrinsic reaction rate constant k at 20, 30, 40 and 50 ($^\circ\text{C}$) is determined from the following relation :

$$k = \{k_{Ti}^* k_{Tj}\}^{1/2} \quad (11)$$

Values of k evaluated for each temperature are shown in Table 4.

Table 4. Values Obtained for the Intrinsic Reaction Rate Constant k .

T_i	20 $^\circ\text{C}$	30 $^\circ\text{C}$	40 $^\circ\text{C}$	50 $^\circ\text{C}$
k_T	4.5275×10^{-5}	7.2992×10^{-5}	1.3652×10^{-4}	2.2781×10^{-4}

The frequency factor and the activation energy of the specific reaction rate $k_T = k_0 \exp(-E/R_g T)$, were determined by plotting $\ln k$ versus $(1/T)$.

The graphical presentation of $\ln k$ versus $(1/T)$ is shown in Figure 2.

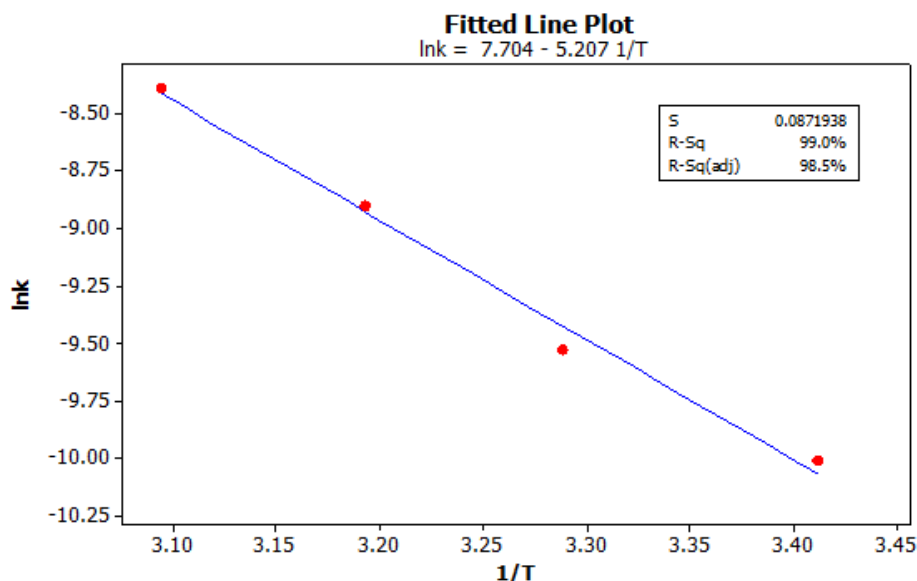


Figure 2. Graphical presentation of $\ln k$ versus $1/T$, $T[K]$

Hence $\ln k_0 = 7.704$, $k_0 = 2.2172 \times 10^3$

The slope of the line is equal to -5207 and the activation energy $E = 8.314 \times 5207 = 43290.99$ J/mole, ($R = 8.314$ J./mol.K).

6. Conclusions

The mixed batch reactor proved to be a successful research tool for the investigation of the technical kinetics of sulfonation systems, demonstrating a superior performance compared to other types of operating chemical reactors.

It ensures reasonable determinations of Dodecylbenzene sulfonation intrinsic kinetic parameters. Thus for sound intrinsic kinetic parameters evaluation, preference should be given to the mixed reactor. The results obtained in this study showed that reaction orders deduced with respect to both components support that sulfur trioxide is more active than D.B and that the temperature influence on the intrinsic rate constant depends on the range of temperature applied in this sulfonation reaction.

Oleum as a sulfonating agent and reaction technical kinetic parameters (temperature, SO_3 and Dodecylbenzene concentrations) is well determined applying this type of reacting system, ensuring homogeneity in all reaction parameters all over the reaction space with the aid of the agitating operating system.

7. Nomenclature

1. α_1, α_2 : reaction orders with respect to DB and SO_3 respectively.
2. C_{DB} : concentration of DB, gmole/liter
3. C_{SO_3} : concentration of SO_3 , gmole/liter
4. $C_{(i)\text{ave}}$: average concentration of reagent (i), gmole/liter.

5. k : intrinsic reaction order
6. k' : $k * [(C_{\text{SO}_3})_{\text{ave}}]^{a_2}$
7. k'' : $k * [(C_{\text{DB}})_{\text{ave}}]^{a_1}$
8. M_{NaOH} : molarity of NaOH
9. N_{SO_3} : number of SO_3 gmole
10. $N_{\text{D.B}}$: number of DB gmole
11. P : the pressure in the reactor, atma
12. R : universal gas constant, J/mol.K
13. $-R_{(\text{D.B})}$: the rate of the sulfonation reaction, gmole/l.t.s
14. RPM: revolutions per minute
15. Sec: seconds
16. T : temperature, K
17. V_t : total volume, cm^3
18. V_{si} : volume of each sample, cm^3 .
19. $\Sigma[V_{\text{S}(i-1)}]$, $i = 1, 2, 3, \dots, n-1$: the summation of the volumes of all samples including the $(i-1)^{\text{th}}$ sample. cm^3
20. V_{NaOH} : the volume of NaOH solution needed for titration, cm^3 .
21. $V_{\text{r.m}}$: the remaining volume of the reacting mixture after the i^{th} , cm^3

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