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ORIGINAL CONTRIBUTION

Detail Kinetic Study of Linear Alkyl Benzene Sulfonation

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ABSTRACT

Sulphonation is one of the mostly used unit processes that are practiced in process industries to synthesize value added products. The common sulfonating agents used for such reactions are sulfur tri-oxide gas, oleum or sulfuric acid in varying degree of concentrations. Generally, the sulphonation reaction is associated with generation of heat or exothermicity. Operational success of such reaction systems are identified by high reaction yield, desirable product quality, and zero or minimum amount of by product formation. In many cases, successful operation is determined by properly removing the evolved heat from reaction mass.

In the present study, it was investigated the Sulphonation of Linear Alkyl Benzene(LAB) to obtain the sulphonated product having enough commercial importance. Scope of the study encompasses investigation of the effects of sulphonation time, stirring speed, concentration of sulphonation agent and sulphonation temperature on the degree of sulphonation. The study also establishes a reliable operational recipe for practice of the synthesis of Linear Alkyl Benzene Sulfonic Acid (LABSA) from Linear Alkyl Benzene (LAB). The reaction is carried out in a semi-batch reactor in which LAB is the limiting reactant and sulfuric acid is added in excess of its stoichiometric requirement. The reactor is operated at a temperature of about 600C to obtain the required product quality. It is found that the reaction progresses according to a first order kinetics.

Keywords- LAB, Sulfonation, exothermicity, semi batch reactor

1. INTRODUCTION

Sulfonation process has extensively been used in chemical synthesis and fuel refining [Akovali et. al. 1986]. Various aromatic structures have been sulfonated with sulfuric acid to give the corresponding arylsulfonic acids [Bailly et. al. 1987]. The sulfonic acid group is strongly acidic and thus useful for modifying the properties of aromatic compounds. Indeed, some of poly-(aryl sulfonic acid)s have been commercialized; for example, poly(styrenesulfonic acid) is used as a flocculent and a rheology modifier of water and alkyl benzene sulfonic acid is used as a raw material of detergent. [Yasuhito 2001, Stubbs 1948]Cross-linked poly (styrene sulfonic acid) is used as an ion exchange resin [Goethals 1970]. Studies of Aromatic sulfonation kinetics are useful for commercial production and have been studied by Martinsen in 1908 [Katritzky 2009]

followed by Cerfontain [1968] and Taylor [1972]. The sulfonation kinetics of Linear alkyl benzene (LAB) with different initial concentrations of LAB, Sulfuric acid at different temperature was studied. First, the kinetic study showed an optimum time requirement for sulfonation and the molar ratio is very much important for conversion and degree of sulfonation. First-order irreversible, first-order reversible, second order irreversible and negative effect of the sulfonated aromatic ring on sulfonation; all the reaction kinetics were investigated. A predictive model has been developed, which is able to predict the degree of sulfonation at different initial concentrations of the acid. The simulated results were found to correspond properly with the experimental results with good correlation coefficients.

The following equation has commonly been used to express the aromatic sulfonation rate in aqueous sulfuric acid: [Cerfontain 1968 and Taylor 1972]

$$-\frac{d[C_{Ar}]}{dt} = k \frac{[C_{Ar}][C_{H_2SO_4}]^2}{[C_w]} \quad (1)$$

Where. $[C_{Ar}]$ = concentration of aromatic ring to be sulfonated,

$[C_{H_2SO_4}]$ = activity of sulfuric acid, which is proportional to the concentration of H_2SO_4 in the system,

C_w = activity of water, which is proportional to the concentration of water in the system,

k = reaction rate constant and

t = reaction time.

In this expression, the rate is first order with respect to the aromatic ring compound. The second order of the concentration of the acid has been used because of reaction of two H_2SO_4 molecules producing the sulfonation species.

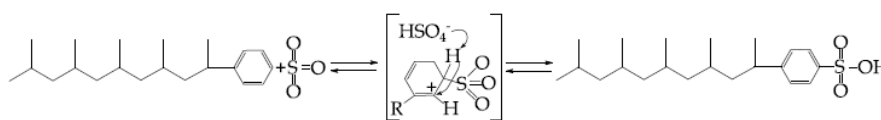


Figure I: - Sulfonation of alkyl benzene (Foster, 1997).

The effect of water on the reaction species has been considered to result in the reaction retardation and appear as the inverse term. These terms are more or less constant for a narrow concentration range of sulfuric acid. In the lower mole ratio of key reactant (LAB) water produced is a byproduct that slows the aromatic sulfonation [Cerfontain 1968 and Taylor 1972] since it dilutes the sulfuric acid to affect reactivity of the sulfonating species.

2. MATERIALS AND METHODS

The experimental conditions are carefully chosen to beat a very low concentration of the substrate (aromatic ring to be sulfonated) and/or at low conversion to reduce the effect of water produced in the reaction as in the semi-batch mode of reaction or higher concentration of sulfuric acid. Experimental results and the reported sulfonation of other aromatic ring compounds show that, the rate is clearly first order with respect to the substrate [Kilpatrick et al 1961].

However, in spite of carefully chosen conditions, some data did not follow the simple first-order rate expression with respect to the substrate [Cowdrey 1949]. The rate is seen to gradually

slow down from that of the expected first-order rate. It is not possible to attribute this retardation to water only. Aromatic sulfonation by sulfuric acid has been known to be complicated being due to its reversibility as well as by the water produced by reaction. Some arylsulfonic acids have been reported to affect the transition state of aromatic sulfonation in sulfuric acids [Cerfontain 1968].

Sulfonation Kinetics

Different chemical kinetics e.g., 1st order, 2nd order and the negative effect of the sulfonated aromatic ring on sulfonation and their contribution to the rate expression have been studied. The study is intended to establish a reliable operational recipe of practice for the synthesis of an industrially important species from its raw materials where the most important step that determines the total process performance is the reaction between two reactants. The reactants are Linear-alkyl-benzene (LAB) and Sulfuric Acid (SA), and the target product is Linear-alkyl-benzene-sulfonic acid (LABSA) [Moreno 2003]. Principal use of this product is as the active ingredient in industrial and domestic detergent formulation [Davidsohn et al 1978].

Kinetic Expression 1 –Negative Effect of Sulfonated Aromatic Ring on the Rate Expression.

If the quantities of sulfuric acid consumed and the produced water are both very small compared with their initial amounts, the factor of $\frac{[C_{H_2SO_4}]^2}{[C_w]}$, in eq (1) changes insignificantly. If the product, sulfonated aromatic ring has a negative effect on the sulfonation of the reactant aromatic ring, the contribution may appear as an inverse term in the rate expression as:

$$-\frac{dC_A}{dt} = \frac{k_1 C_A}{k_d (C_{A0} - C_A)} \quad (2)$$

where C_A = substrate (LAB) concentration at a time t ,

C_{A0} = Initial substrate concentration at $t = 0$,

k_1 = rate constant of sulfonation, k_d = constant for the negative effect of the product, sulfonated aromatic ring, and

$(C_{A0} - C_A)$ = the product (sulfonated aromatic ring) concentration at a time t .

This equation can be integrated from C_{A0} to C_A to give eqs (3) and (4).

$$-\int_{C_{A0}}^{C_A} \left(\frac{C_{A0} - C_A}{C_A} \right) dC_A = \frac{k_1}{k_d} \int_0^t dt \quad (3)$$

$$-\frac{C_{A0} - C_A}{C_{A0}} - \ln \frac{C_A}{C_{A0}} = \frac{k_1}{k_d} \frac{t}{C_{A0}} \quad (4)$$

Here, the concentration of the un-reacted substrate is described as:

$$C_A = C_{A0}(1 - X_A) \quad (5)$$

where X_A stands for sulfonation conversion. X_A is zero at the beginning of the reaction and goes to 1 at the end of the reaction. In the case of sulfonation, X_A may be regarded as the degree of sulfonation per repeat unit. As a consequence, C_A in eq (4) is substituted by $C_A = C_{A0}(1 - X_A)$ to give eq (6).

$$C_{A0} \left\{ -X_A - \ln(1 - X_A) \right\} = \frac{k_1}{k_d} t \quad (6)$$

The data calculated via eq (6) have been plotted as a function of time in Figure I. The straight line in figure I is the least-squares fit of the plots and correlation coefficient is given in table I.

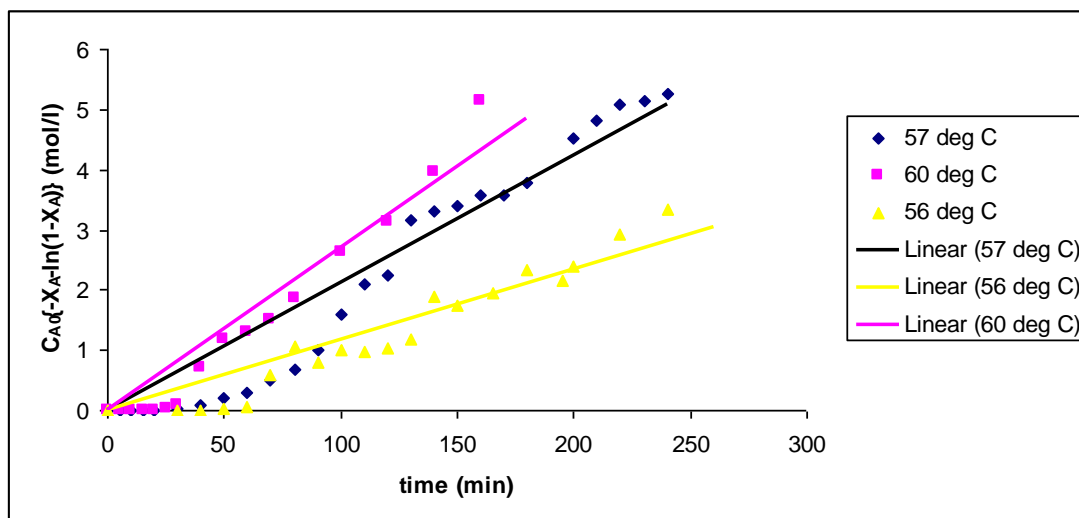


Figure.I: - Aromatic Sulfonation with Negative Effect.

Kinetic Expression 2, First-Order Irreversible Rate Expression.

Equation (1) may be simplified as eq (7) at nearly constant concentration of sulfuric acid and water. The situation may arise in the case of using excess sulfuric acid with respect to stoichiometric ratio where the dilution of acid is minimum.

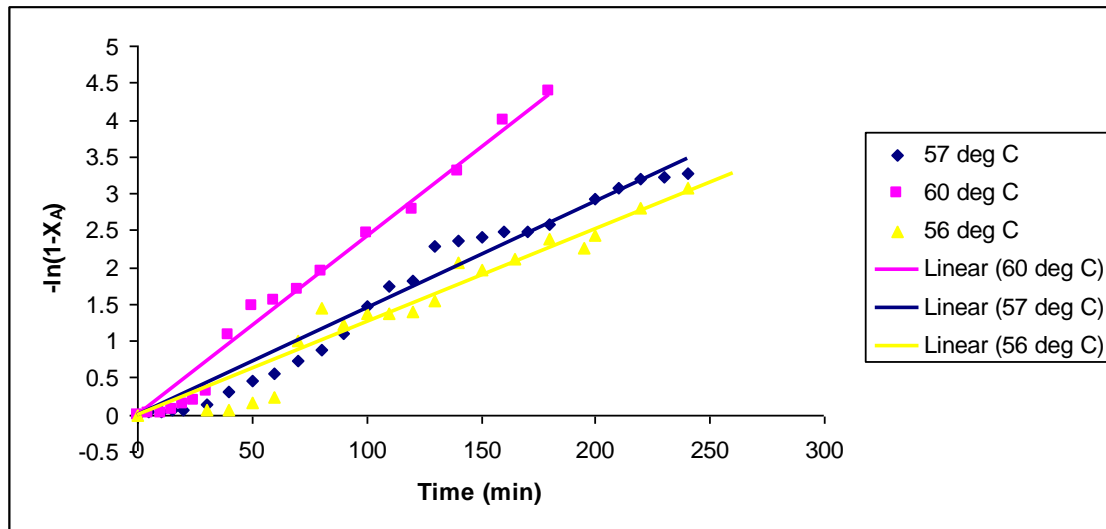
$$-\frac{dC_A}{dt} = k_1 C_A \quad (7)$$

Where k_1 represents the first-order rate constant. This equation can be integrated from the beginning of the reaction ($C_A = C_{A0}$ at $t = 0$) to a concentration ($C_A = C_A$ at $t = t$)

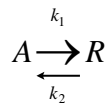
$$-\ln \frac{C_A}{C_{A0}} = k_1 t \text{ or } -\ln(1 - X_A) = k_1 t \quad (8)$$

If the rate is first order with respect to the substrate, a plot of $-\ln(1 - X_A)$ vs. time will fit to a straight line.

The data calculated through eq (8) have been plotted as a function of time, which is given in Figure II and correlation coefficient is given in table I.

Figure.II: - 1st Order Kinetics.

Kinetic Expression 3, First Order reversible type Reaction



$$-r_A = -\frac{dC_A}{dt} = \frac{dC_R}{dt} = C_{A0} \frac{dX_A}{dt} = k_1 C_A - k_2 C_R \quad (9)$$

$$= k_1 (C_{A0} - C_{A0} X_A) - k_2 (M C_{A0} + C_{A0} X_A) \quad (10)$$

Where $M = C_{R0}/C_{A0}$

At equilibrium $-dC_A/dt = 0$. By simplifying

$$\frac{(M + X_{Ae})}{(1 - X_{Ae})} = \frac{k_1}{k_2} = K_c \quad (11)$$

K_c is termed as equilibrium constant.

Combining the above equations can be written in terms of equilibrium conversion

$$\frac{dX_A}{dt} = \frac{k_1(M+1)}{(M+X_{Ae})} (X_{Ae} - X_A) \quad (12)$$

Integrating eq(12)

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = \frac{(M+1)}{(M+X_{Ae})} k_1 t \quad (13)$$

If $-\ln\left(1 - \frac{X_A}{X_{Ae}}\right)$ vs time plot fitted by a straight line then the reaction is reversible first order

reaction. Corresponding X_{Ae} values are given in table I. The data calculated through eq (13) have been plotted as a function of time, which is given in Figure III and correlation coefficient is given in table I.

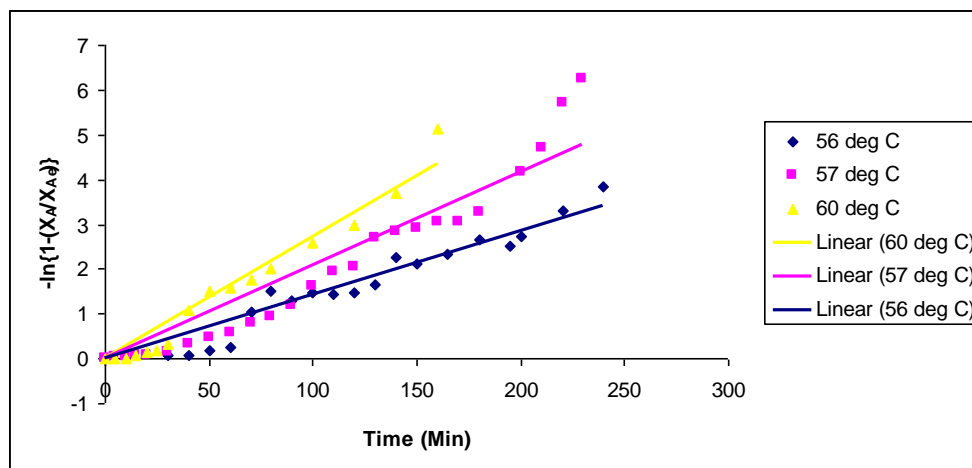


Figure.III: - Reversible 1st order kinetics.

Kinetic Expression 4, Irreversible type second Order Reaction

As per stoichiometry the reaction occurs like $A+B \rightarrow C + D$

And the kinetic expression may be represented as

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k_1 C_A C_B \quad (14)$$

where $C_{A0} \cdot X_A = C_{B0} \cdot X_B$ and substituting this, eq (14) can be written as

$$-r_A = C_{A0} \frac{dX_A}{dt} = k_1(C_{A0} - C_{A0}X_A)(C_{B0} - C_{A0}X_A) \quad (15)$$

Now, if $M = C_{B0}/C_{A0}$, the eq (15) can be rewritten as

$$-r_A = C_{A0} \frac{dX_A}{dt} = k_1 C_{A0}^2 (1 - X_A)(M - X_A) \quad (16)$$

Integrating eq(16) when 't= 0 at $X_A = 0$ ' and 't = t at $X = X$ '

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0} k_1 \int_0^t dt \quad (17)$$

after integration the form is

$$\ln \frac{M - X_A}{M(1 - X_A)} = C_{A0}(M - 1)k_1 t \quad (18)$$

If C_{B0} is much larger than C_{A0} , C_B remains approximately constant at all the time and it approaches $-\ln(1 - X_A) = k_1 t$, that is 1st order reaction.

The data calculated through eq (18) have been plotted as a function of time, which is given in Figure IV and correlation coefficient is given in table I.

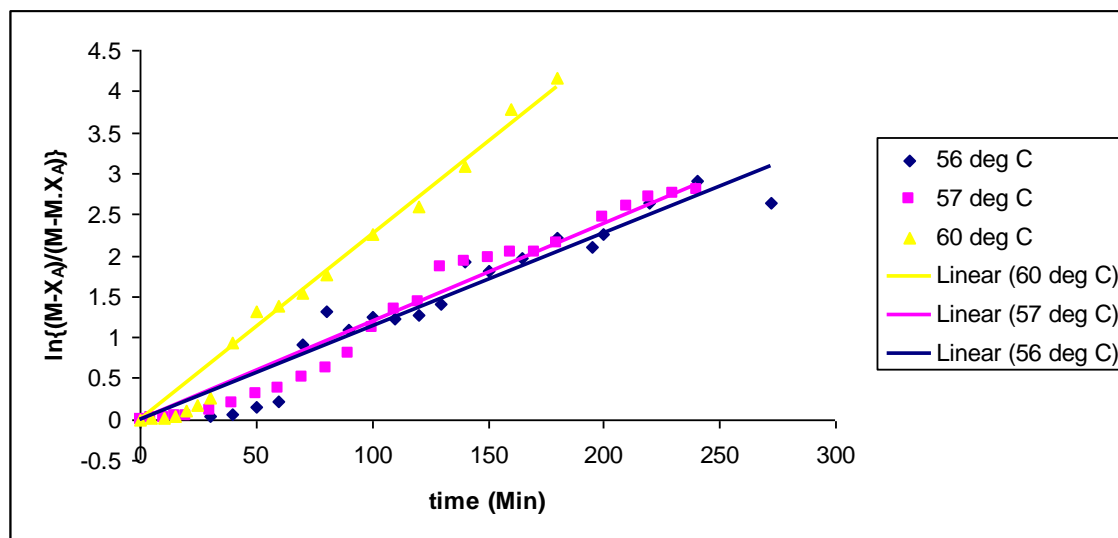


Figure IV: - 2nd Order kinetics.

Table I: - The Correlation coefficients of the Least Squares fit of the Plots as the result of the kinetic treatments according to the first order, Negative contribution of the Phenyl Group, reversible first order and second order sulfonation

Average Temp. ($^{\circ}\text{C}$)	X_{Ae}	C_{A0+} Moles/Lt	C_{B0} Moles/Lt	Aromatic Sulfonation with Negative Effect		1 st Order		Reversible 1 st Order		2 nd Order	
				Slope	R^2	Slope	R^2	Slope	R^2	Slope	R^2
56	0.9619	1.5762	9.6823	0.0124	0.920	0.0128	0.941	0.012	0.5	0.012	0.949
57	0.9748	2.2785	5.7992	0.0245	0.957	0.0167	0.973	0.021	0.972	0.0138	0.957
60	0.9874	1.70702	8.9613	0.0283	0.941	0.0241	0.98	0.0201	0.49	0.0225	0.977

As per the correlation coefficient calculated from linear least square technique its found that Linear alkyl Benzene sulfonation follows 1st order kinetics and negative effect of the phenyl group contributes to some extent. So we restrict our analysis within 1st order and 1st order with negative effect.

Optimum Mole Ratio

In LAB Sulfonation with concentrated sulfuric acid LAB is the key component with respect to price. Excess sulfuric acid is used to reduce the dilution effect due to the production of water during the course of the reaction.

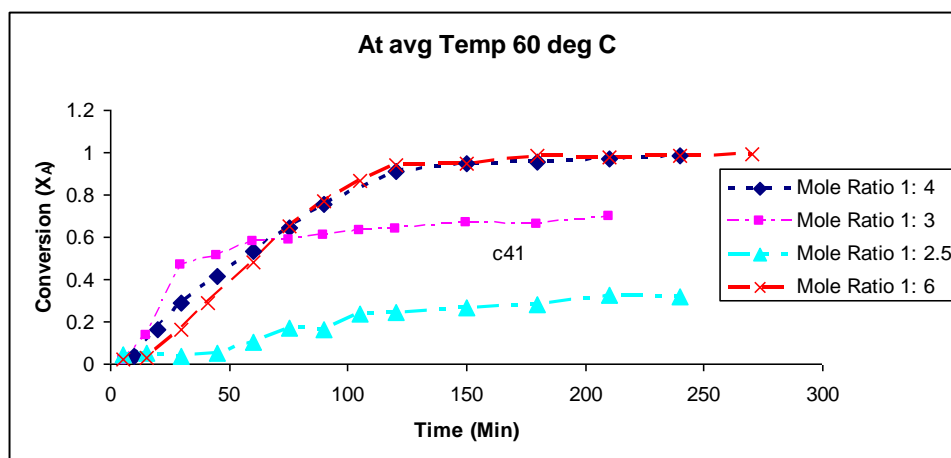


Figure V: - Conversion vs. different mole ratio

It is clear from the Figure. V that below the mole ratio 1:4 (LAB: H₂SO₄) the conversion is below 70 percent and it again proves the dilution effect of sulfonation. At mole ratio 1:6 the conversion is 99 percent and at 1:4 the conversion in the stipulated time period is 98%. To get faster conversion it is therefore better to maintain the mole ration at about 1:5.

3. SEMI BATCH OPERATION

In this case sulfuric acid is added in discrete time interval, semi batch wise maintaining the mole ratio about 1:5.2 and it was found that 1st order kinetics is well fitted as given in figure VI.

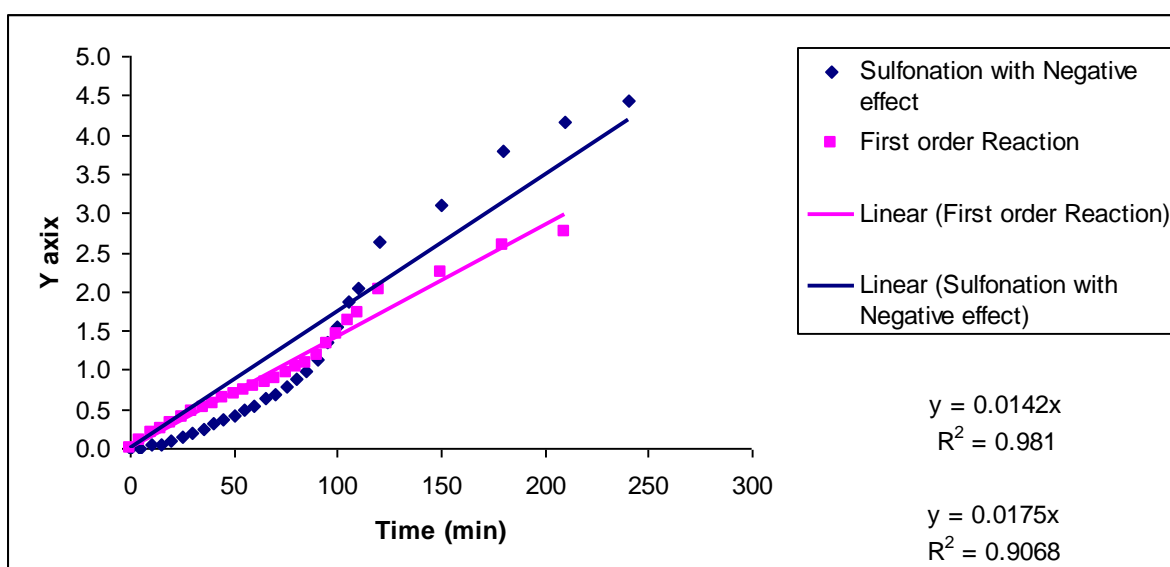


Figure VI: - Test for Semi Batch Reactor Operation Conversion vs. different mole ratio

Y axis: For Sulfonation with Negative Effect $C_{A0} \{-X_A - \ln(1 - X_A)\}$

Y axis: For 1st order reaction $-\ln(1 - X_A) = k_1 t$

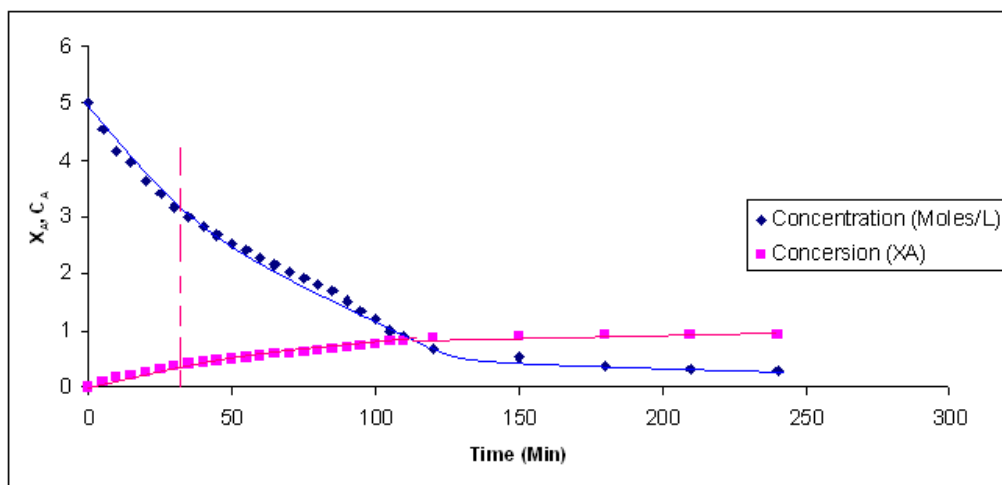


Figure VII: – Time vs. Concentration and conversion for a semi batch process

The method of manufacture involves carrying out the reaction in a semi-batch reactor in which LAB is the limiting reactant and SA is put in excess of its stoichiometric requirement. The reaction has considerable exothermic heat generation aspect, but if not conducted at a controlled temperature, the obtained product quality becomes poor. In this particular experimentation mole ratio is maintain at 1:5.2 and sulfuric acid is added in every 5 minutes interval and an amount of 9 gm. It is evident that at low concentration the rate of conversion is

higher in Figure VII. At initial state where the LAB concentration is higher the conversion is poor and is valid upto the stoichometric ratio but in this region heat generation is maximum and chilled water is required for circulation in the jacket. Here the negative effect is prominent as shown in fig VIII as dotted line at the initial state. But when the excess sulfuric acid is added to the reactor the rate of conversion is increased and the negative effect is reduced as the concentration if sulfuric acid is at higher level.

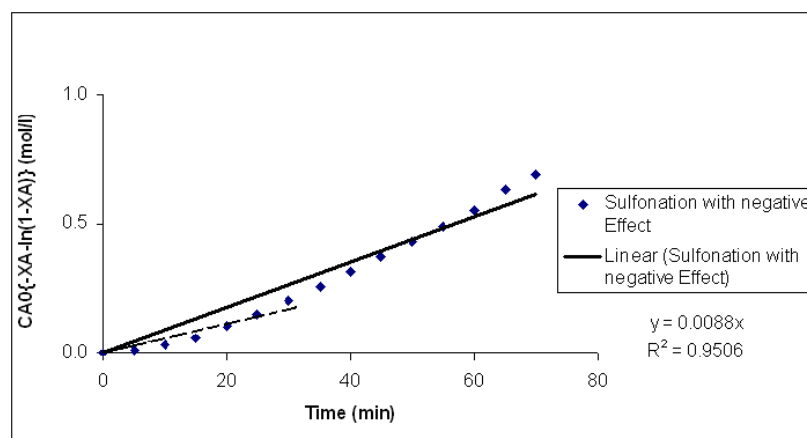


Figure VIII: - Negative effect of sulfonation in Semi Batch Operation

In so many experimentation, it is found that the negative effect is applicable above the concentration of 2 moles / lt of LAB.

4: ACTIVATION ENERGY

It is clear from the analysis given above that in all cases the reaction follows first order type. Several sets of experiment were carried out at different temperature and corresponding rate constants are calculated as given in table II.

Table II – Temperature vs Rate Constant (1st Order)

	T	1/T	K	Ln(k)
52	325	0.003076923	0.01209	-4.42002
53.6	326.6	0.003061849	0.0128	-4.35831
57	330	0.003030303	0.0167	-4.09235
59.5	332.5	0.003007519	0.0241	-3.72554
65	338	0.00295858	0.03471	-3.36073

The Arrhenius equation for the heterogeneous LAB sulfonation reaction is estimated as:

$$k = k_0 \cdot e^{(-E/R.T)} \quad (19)$$

Where k = Rate constant at Temperature, (T)

k_0 = Rate Constant, E = Activation Energy at Temp., (T), R = Gas Constant

Now, applying Log on both sides it can be written as,

$$\ln(k) = \ln(k_0) + (-E/R). (1/T) \quad (20)$$

A plot of $\ln(k)$ vs $1/T$ gives the intercept at $\ln k_0$ and slope is $(-E/R)$ as shown in figure IX

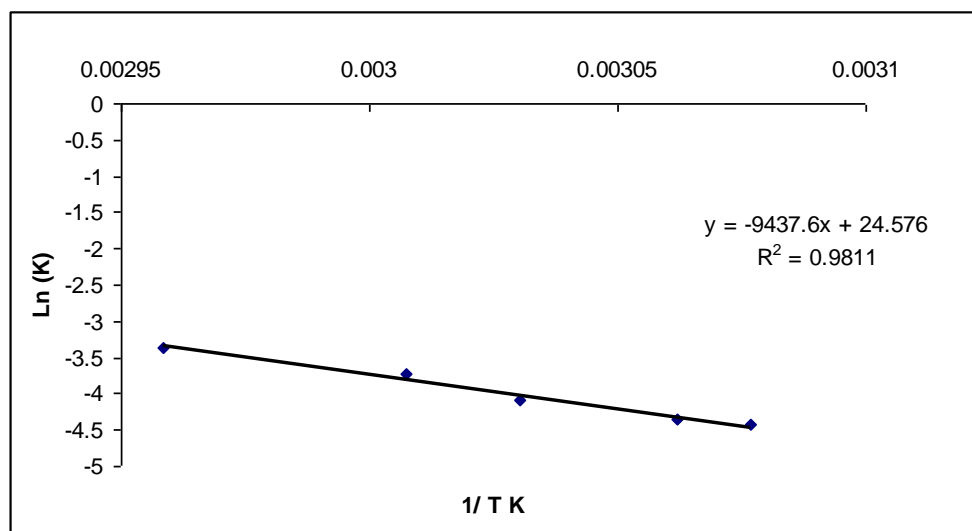


Figure.IX: - Ln(k) vs 1/T.

$$k_0 = 4.712 \times 10^{10}$$

$$E = -18752.5 \text{ Cal/mol}$$

So the Arrhenius equation for the heterogeneous LAB sulfonation is

$$k = 4.712 \times 10^{10} \exp\left(\frac{-18752.5}{RT}\right) \quad (21)$$

Variable volume Reactor operation

In literature, [16-17] it is found that the increase in yield using variable volume reactor with an isothermal first order exothermic reaction is feasible. Codell and Engel showed that when the reaction rate passes through a maximum, semi-batch operation can give better yield than CSTR or PFR based on residence time basis.

In the semibatch reactor, it is charged with pure LAB (A) and H_2SO_4 (B) is fed slowly to A in the vat. Of the two types of semibatch reactors, the main attention is given primarily on the one with constant molar feed. The reaction is in liquid-phase in which reactant B is slowly added to a well-mixed vat containing reactant A.

Mole balance on species A yields

$$[\text{Rate in}] - [\text{Rate out}] + [\text{Rate of Generation}] = [\text{Rate of Accumulation}]$$

$$0 - 0 + (r_A)V(t) = dN_A/dt \quad (23)$$

Three variables can be used to formulate and solve semibatch reactor problems: the concentrations, C_j , the number of moles, N_j , and the conversion, X .

Writing the Semibatch Reactor Equations in Terms of Number of Moles

Recalling that the number of moles of A, N_A , is just the product of concentration of A, C_A , and the volume, V , we can rewrite Equation (23) as

$$r_A V = \frac{d(C_A V)}{dt} = V \frac{d(C_A)}{dt} + C_A \frac{d(V)}{dt} \quad (24)$$

It is noted that since the reactor is being filled, the volume, V , varies with time. The reactor volume at any time t can be found from an **overall mass balance** of all species:

$$[\text{Rate in}] - [\text{Rate out}] + [\text{Rate of Generation}] = [\text{Rate of Accumulation}]$$

$$\rho_0 v_0 - 0 + 0 = \frac{d(\rho V)}{dt} \quad (25)$$

For a constant-density system, $\rho = \rho_0$, and

$$\frac{d(V)}{dt} = v_0 \quad (26)$$

with the initial condition $V = V_0$ at $t=0$, integrating for the case of constant volumetric flow rate v_0 yields

$$V = V_0 + v_0 t \quad (27)$$

Substituting Equation (26) into the right-hand side of Equation (24) and rearranging gives that

$$-v_0 C_A + V \cdot r_A = V \frac{d(C_A)}{dt}$$

The balance on A [i.e., Equation (24)] can be rewritten as

$$\frac{dC_A}{dt} = r_A - \frac{v_0}{V} C_A \quad (28)$$

A mole balance on B that is fed to the reactor at a rate F_{B0} is

[Rate in] – [Rate out] + [Rate Generation] = [Rate Accumulation]

$$F_{B0} - 0 + (r_B)V(t) = dN_B/dt$$

Rearranging

$$\frac{dN_B}{dt} = r_B V + F_{B0} \quad (29)$$

$$\frac{d(V.C_B)}{dt} = V \frac{d(C_B)}{dt} + C_B \frac{d(V)}{dt} = r_B V + F_{B0} = r_B V + v_0 C_{B0} \quad (30)$$

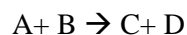
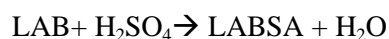
Substituting Equation (27) in terms of V and differentiating, the mole balance on B becomes

$$\frac{dC_B}{dt} = r_B + \frac{v_0(C_{B0} - C_B)}{V} \quad (31)$$

At time $t = 0$, the initial concentration of B in the vat is zero, $C_{B_i} = 0$. The concentration of B in the feed is C_{B0} . If the reaction order is other than zero- or first-order, or if the reaction is non-isothermal, we must use numerical techniques to determine the conversion as a function of time. Equations (28) and (31) are easily solved with an ODE solver.

Semi-Batch LAB Sulfonation Simulation

The production of Linear Alkyl Benzene Sulfonic Acid occurs isothermally in a semi batch reactor.



Feed rate of B is 1.818 gm/ Sec or 0.988 cc/sec and concentration is 0.018 mol/cc.

LAB is taken in the reactor and volume is 111.905 cc and concentration is 5.019 mol/cc

The specific rate constant is 0.0241/sec

Now symbolically we can write

$$-r_A = k.C_A$$

$$\frac{dC_A}{dt} = -kC_A - \frac{v_0}{V} C_A$$

$$\frac{dC_B}{dt} = -kC_A + \frac{v_0(C_{B0} - C_B)}{V}$$

$$V = V_0 + v_0 t$$

Similarly for C and D we have

$$\frac{dN_C}{dt} = r_C V = -r_A V$$

$$\frac{dN_C}{dt} = \frac{d(C_C V)}{dt} = V \frac{dC_C}{dt} + C_C \frac{dV}{dt} = V \frac{dC_C}{dt} + v_0 C_C$$

$$\frac{dC_C}{dt} = kC_A - \frac{v_0 C_C}{V} \quad \text{and} \quad \frac{dC_D}{dt} = kC_A - \frac{v_0 C_D}{V}$$

The conversion of A can be calculated as

$$X = \frac{N_{A0} - N_A}{N_{A0}} = \frac{C_{A0} V_0 - C_A V}{C_{A0} V_0}$$

the initial condition at $t=0$, $C_{A0} = 5.019$ moles/lit, $C_{B0} = 18$ moles/Lt, $C_{C0} = 0$, $C_{D0} = 0$, $V_0 = 0.111905$ Lt, $v_0 = 0.000988$ Lt/Sec

For the above given system it is easily solved by a polymath program and the details report is give in table III.

Table III : - POLYMATH Report
a) Calculated values of DEQ variables

	Variable	Initial value	Minimal value	Maximal value	Final value
1	Ca	5.019	0.0049505	5.019	0.0049505
2	Cb	18.	15.47215	18.	16.39575
3	Cc	0	0	2.527847	1.60425
4	Cd	0	0	2.527847	1.60425
5	k	0.0241	0.0241	0.0241	0.0241
6	rate	2.177242	0.0019561	2.177242	0.0019561
7	t	0	0	240.	240.

b) General

Total number of equations	10
Number of differential equations	4
Number of explicit equations	6
Elapsed time	1.157 sec
Solution method	RKF_45
Step size guess. h	0.000001
Truncation error tolerance. eps	0.000001

c) Explicit equations

1	$k = 0.0241$
2	$v_0 = 0.000988$
3	$V_0 = 0.111905$
4	$V = V_0 + v_0 * t$
5	$X = (0.005019 * V_0 - Ca * V) / (0.005019 * V_0)$
6	$rate = k * Ca$

d) Differential equations

1	$d(Ca)/d(t) = -k*Ca-v0*Ca/V$
2	$d(Cb)/d(t) = -k*Ca+v0*(18-Cb)/V$
3	$d(Cc)/d(t) = k*Ca-v0*Cc/V$
4	$d(Cd)/d(t) = k*Ca-v0*Cd/V$

The Concentration Profile of the Components are given in Figure X.

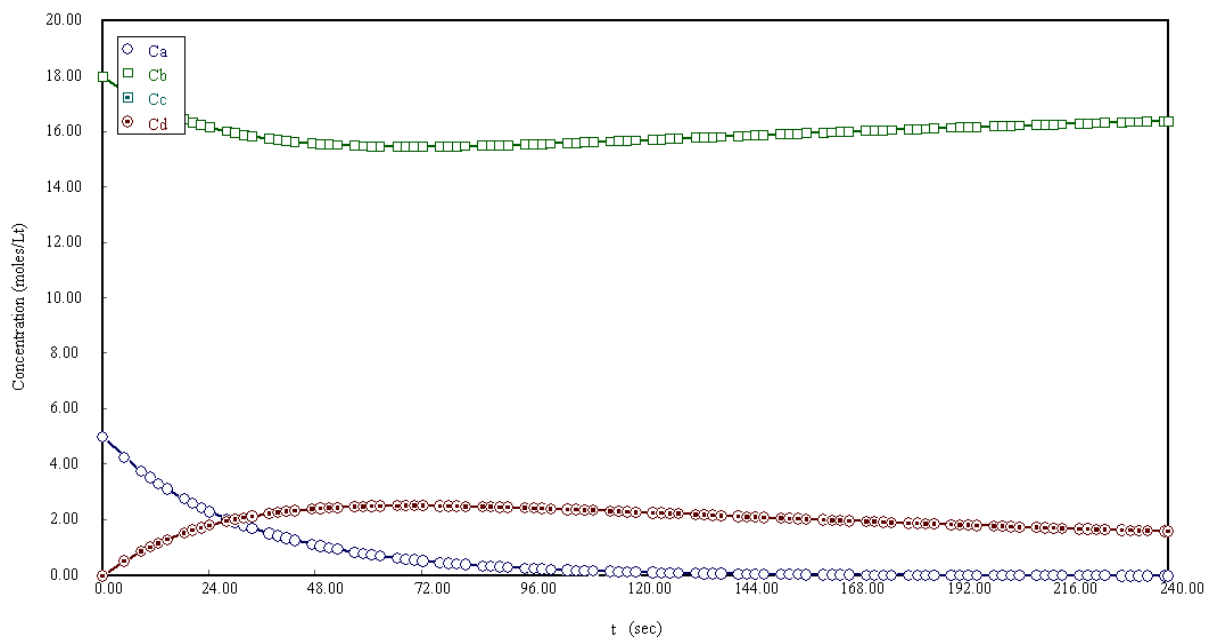


Figure X:- Concentration Profile of the reactants and Product at the given conditions.

The conversion data is plotted against time in Figure XI.

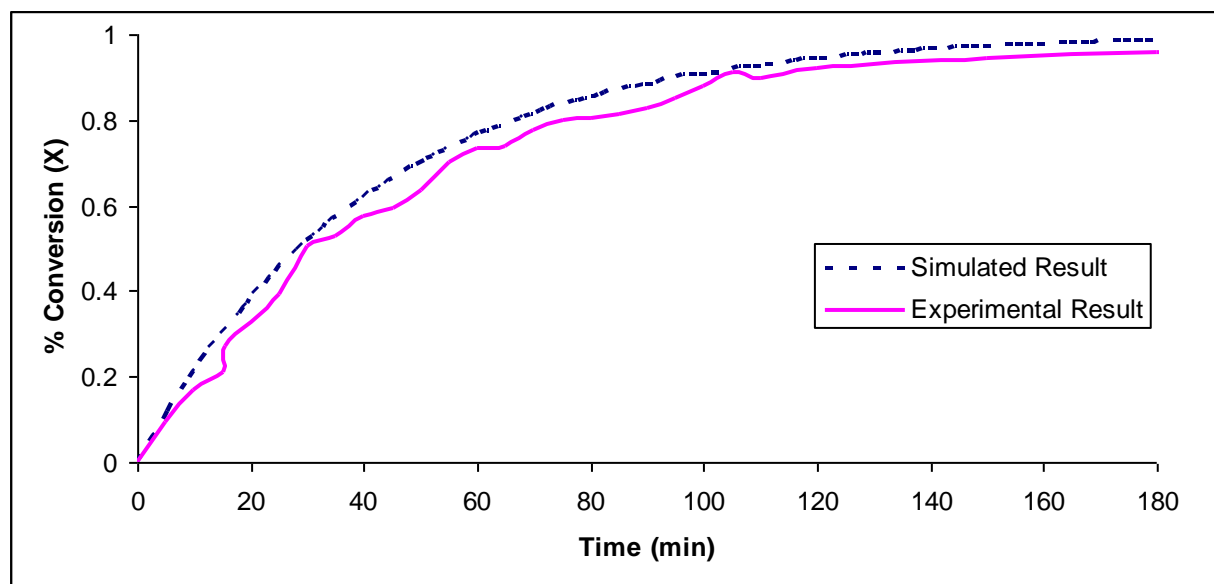


Figure XI: - Simulated and experimental conversion result.

5. CONCLUSION

The overall stoichiometry of the sulfonation reaction using concentrated sulfuric acid is although simple; the reaction pathways are invariably more complex and not fully understood. The concentration changes of water and H_2SO_4 are found not to contribute primarily slowing down the reaction rate if excess sulfuric acid is added. The reaction rate is first order and it is found that the excess sulfuric acid is required more than 1: 4 mole ratio for maximum

conversion as LAB is key component. It is more reasonable to enlighten the slowing down of the first order reaction rate by a negative effect of the sulfonated aromatic ring as well as the water produced during the course of reaction. Though the correlation coefficient of negative effect sulfonation is not up to the mark compared to first order kinetics but this can be associated with desulfonation or a type of retardation on a reaction intermediate.

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