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Kinetic Study of Sulfonated Chitosan by Sulfuric Acid

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Abstract: The proton exchange membrane (PEM) for fuel cell applications is synthesized from hydrophilic chitosan (CS) via sulfonation using sulfuric acid under different conditions. Sulfonation is confirmed by Nuclear Magnetic Resonance (^{1}HNMR). Two reaction kinetics models, namely the first-order reversible and first-order irreversible models, are evaluated. The kinetics follow the first-order irreversible model, with the activation energy (Ea) calculated to be 35.6 kJ/mol for the CS repeat unit, indicating a non-spontaneous reaction.
Keywords: Chitosan; degree of sulfonation; kinetic study, rate of reaction, activation energy.

Nomenclature:

CS	Chitosan
SCS	Sulfonated chitosan
PEM	Proton exchange membrane
PEMFC	Proton exchange membrane fuel cell
DS	Degree of sulfonation
IEC	Ion exchange capacity
C	Concentration of reactive sites (functional groups)
C_o	Initial concentration of reactive sites
x	Conversion (fraction of sulfonated sites)
k_1, k_2, k_3	Rate constants for forward and backward sulfonation reactions
k	Reaction rate constant
K	Equilibrium constant (k_2/k_3)
Ea	Activation energy
A	Frequency factor (Arrhenius constant)
R	Universal gas constant
T	Temperature
t	Time
MWs	Molecular weight of sulfur
$MW_{-}SO_3H$	Molecular weight of sulfonic acid group ($–SO_3H$)
MCS	Molecular weight of chitosan monomer

1 Introduction

Environmental pollution and dwindling natural resources have emphasized the need for clean sustainable energy. Proton exchange membrane fuel cells (PEMFCs) have recently garnered significant attention. At the core of PEMFCs is the proton exchange membrane (PEM), which acts as an ionic conductor between electrodes, binds the electro-catalyst, and prevents electron and gas cross-leakage [1].

Perfluorosulfonate-based membranes like Nafion are widely used in PEMFCs [2], offering high proton conductivity and chemical stability [3]. However, Nafion's high cost [4], limited operational temperatures [5], and

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fluorination-related pollution have hindered its widespread commercialization [6]. As a result, non-fluorinated PEMs were created, which decreased the price of PEMFC systems. Non-fluorinated PEMs have studied, including polymers such as polyether ether ketone (PEEK) [7], polyethersulfone (PES) [8], polybenzimidazole (PBI) [9], and chitosan (CS).

CS stands out among these because of its tunable proton conductivity, mechanical, thermal, and chemical properties depending on the degree of sulfonation (DS) [10]. CS, derived from N-deacetylated chitin, is a biodegradable, non-toxic polymer with excellent biocompatibility. Its free amino and hydroxyl groups on the saccharide backbone allow easy modification [11-13]. Because of its ideal properties, CS has been studied as a potential membrane material for proton exchange [14-17]. To improve swelling and mechanical performance, CS membranes are often modified using bifunctional cross-linking agents. Sulfonation, an electrophilic substitution reaction [18, 19], is a common method to tailor membrane properties. Sulfonation modifies polymers to serve as ion exchange membranes by controlling the DS with sulfonating agents. The process is restricted to a single sulfonate group per repeat unit, located at one of the four chemically equivalent positions on the phenyl ring, which is surrounded by ether groups [20].

Sulfonation reactions typically exhibit a high reaction rate but low selectivity and yield in conventional reactors due to insufficient micro-mixing. Various polymer structures have been sulfonated using sulfuric acid to form aryl sulfonic acids [21]. The sulfonic group is strongly acidic, making it useful for modifying polymer properties. Understanding the kinetics of polymer sulfonation is crucial for optimizing reaction rates and scaling up for commercial production. The kinetics of aromatic polymers have been studied since 1908 [22], with earlier work examining the sulfonation of atactic polystyrene using concentrated sulfuric acid, where the phenyl ring served as the reactive site [23].

Kinetic analysis revealed that protonation is the rate-limiting phase in the membrane's adsorption of sulfuric acid. While sulfuric acid cross-linked CS membranes have been studied using methods such as X-ray diffraction, Fourier Transform Infrared spectroscopy, and Nuclear Magnetic Resonance spectroscopy (^{1}HNMR), detailed insights into the interaction between sulfuric acid and CS are still limited [18, 23-25].

In the search for alternative PEM materials for fuel cell (FC) applications, sulfonation of CS with sulfuric acid has been explored. The resulting PEM demonstrated efficiency and suitability for fuel cells [26]. This paper presents kinetics and the reaction mechanism of CS sulfonation with sulfuric acid, a critical aspect of chemical process design [27].

2 Experimental

2.1. Chemicals

CS with a molecular weight of 100,000–300,000 was purchased from Acros Organics. Sulfuric acid (98%) was supplied by Piochem, while acetic acid (99.8%) and sodium hydroxide (NaOH, 98%) were sourced from Sigma-Aldrich.

2.2 Equipment

The experimental setup for studying the sulfonation kinetics of CS with sulfuric acid is shown in Fig.1, which involves a hot plate with a magnetic stirrer and a three-neck round-bottom flask. One neck is connected to a condenser to reflux evaporated vapor, the second neck is used for mixing reactants via an ultrasound or mechanical stirrer, and the third neck allows for sampling during the reaction process. This setup ensures proper mixing, temperature control, and sampling for kinetic studies.

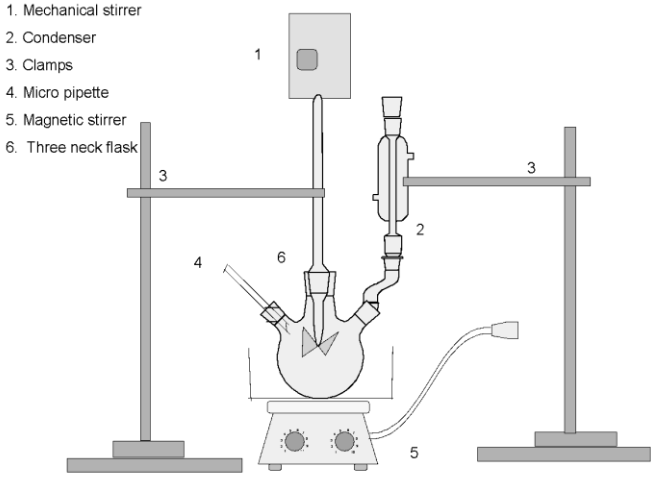

Fig. 1: Experimental set up of CS sulfonation.

2.3 Determination of Ion Exchange Capacity (IEC) and degree of sulfonation (DS)

IEC and DS of the sulfonated CS were determined by measuring the percentage of sulfur attached to the dry sample through elemental analysis. The IEC was then calculated using the following Eq. 1

$$IEC = \frac{1000 * S_C}{MW_S} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1)}$$

where Sc is the sulfur content in percentage weight rate, MWs is the molecular weight of sulfur, and 1000 is the multiplication factor (to obtain IEC value in mmol/g).

The IEC obtained from Eq 1 was used to obtain the DS of CS using the relationship in Eq.2

$$Degree\ of\ sulonation\ (DS) = \frac{IEC * M_{CS}}{1-(IEC * MW_{-SO3H})} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

where; M_{CS} is the molecular weight of the CS (g/mol) and MW_{-SO3H} is the molecular weight of $-SO_3H$ (g/mol).

2.4. Sulfonation of chitosan with sulfuric acid

A known quantity of CS (10 g) was dissolved in 1000 mL of 1 wt. % acetic acid as a solvent, stirred mechanically at 400 rpm. Gradually, 4M sulfuric acid was added, and the mixture was vigorously stirred in a four-neck round-bottom flask reactor. The sulfonation reaction proceeded for varying time intervals, and ice was used to terminate the reaction. The precipitated sulfonated CS was recovered, washed with deionized water until a neutral pH (6-7) was reached, and then analyzed. Fig. 2 illustrates the chemical structure of CS and its modifiable functional groups.

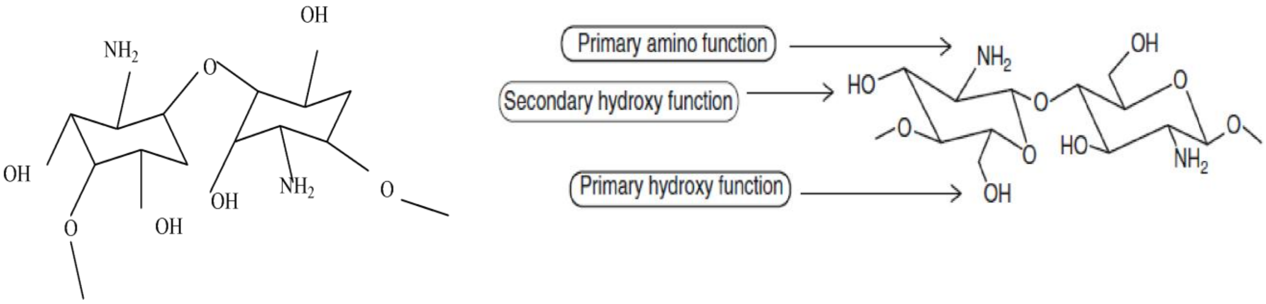

Fig. 2 a) The chemical structure of chitosan, b) Functional groups in chitosan that can be modified.

3 Results and Discussion

3.1 Determination of degree of sulfonation (DS)

The conductivity of sulfonic acid-based membranes depends heavily on the DS and IEC, as these parameters influence the number of acid groups and their dissociation in water. The hydrophilic domain formed by the -SO_3H group enhances water absorption and proton transport [28], essential for PEM [29]. The DS and IEC of SCS at various sulfonation times at constant weight (1 g) and at constant predetermined conditions: 4M H_2SO_4, temperature 50 ^oC, and stirring rate 400 rpm are reported [30]. Sulfonation results showed that DS and IEC increased up to 12 hours, with a peak DS of 57.82% and IEC of 0.3679 mmol/g. Beyond 12 hours, both parameters decreased due to polymer degradation and excessive sulfonation. Optimal sulfonation time is determined to be 12 hours for achieving the best PEM properties, while longer sulfonation times could negatively affect membrane integrity and water solubility [28]. Thus, reaction kinetics were examined within 12 hours.

3.2 Sulfonation of Chitosan Mechanism

CS is a natural biopolymer characterized by free hydroxyl and amino groups, allowing for various chemical modifications, including sulfonation to enhance ionic conductivity and create ion exchange sites. The mechanism of CS sulfonation (Fig.3) involves the uptake of sulfuric acid, which depends on diffusion within the membrane and the chemical reaction of binding -SO_3H to active sites. According to kinetic analysis, sulfuric acid adsorption limiting factor is chemical binding, not diffusion, aligning with the observed trends in protonation and sulfuric acid content over time.

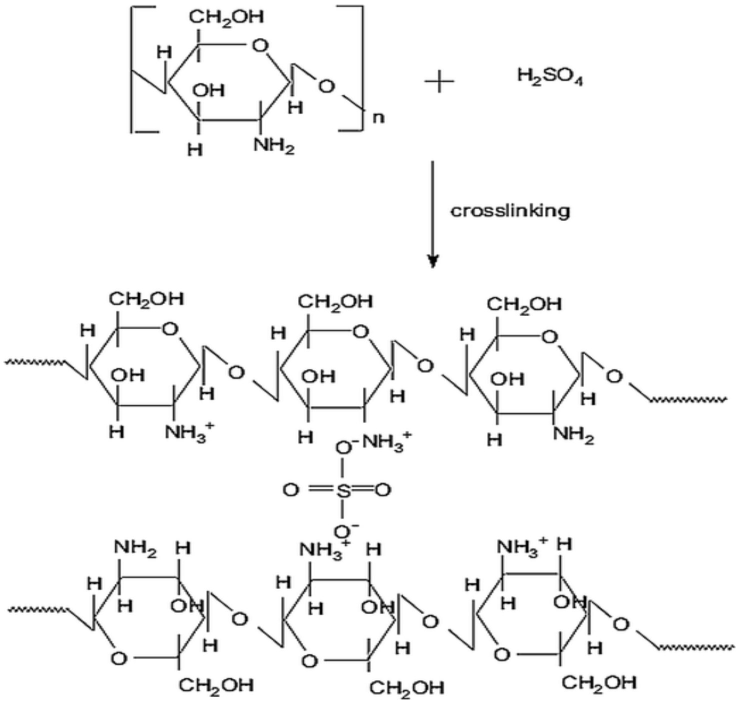

Fig.3: The mechanism of CS sulfonation.

3.3 The kinetic study of sulfonation of CS with H_2SO_4

1. The kinetic study of CS sulfonation with sulfuric acid aims to determine the reaction rate, activation energy, and mechanism involved. The relationship between conversion and time at different sulfonating temperatures (30–60°C) using 4 M sulfuric acid and a stirring speed of 400 rpm for 1-12 hours is shown in Fig. 4.

The curves in Fig. 4 indicate that the sulfonation rate increases with time due to CS degradation [28]. Additionally, varying the temperature affects the degree of sulfonation, confirming the significant role in the reaction.

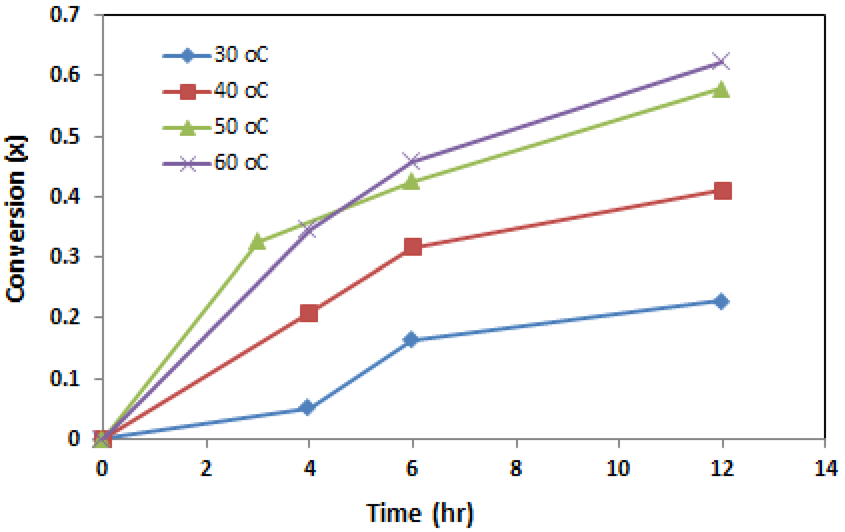

Fig. 4: Kinetics of CS sulfonation using sulfuric acid at different temperatures.

The conversion results presented in Table 1 indicate that both time and temperature play significant roles in the sulfonation process. However, high conversion rates can cause membrane swelling, leading to decreased mechanical properties. As with other organic reactions, improper sulfonation can result in unwanted side reactions like chain cleavage, affecting the membrane's integrity [29, 31]. To prevent such issues, extreme caution must be exercised during the sulfonation process to ensure optimal reaction conditions and avoid negative effects.

Table 1: Converted amount of chitosan to sulfonated chitosan results.

		At 30 ºC		
Time (h)	0	4	6	12
Conversion (x)	0	0.0523	0.1634	0.2284
		At 40 ºC		
Time (h)	0	4	6	12
Conversion (x)	0	0.2084	0.3167	0.4099
		At 50 ºC		
Time (h)	0	3	6	12
Conversion (x)	0	0.3264	0.4246	0.5782
		At 60 ºC		
Time (h)	0	4	6	12
Conversion (x)	0	0.3459	0.4588	0.6231

Sulfonation, being an electrophilic substitution reaction, occurs at active sites determined by electron density. In CS, sulfonation typically takes place at hydroxyl or amino positions on the ring's repeat unit. Only one $-SO_3H$ group can attach per repeat unit. The following assumptions are made in the kinetic reaction:

1. Each repeat unit sulfonates one at a time.
2. Volume changes are ignored.
3. Water may or may not impact the reaction.

Two proposed mechanisms are:

A. No de-sulfonation occurs (H_2O has no effect).
B. De-sulfonation occurs (H_2O affects the process).

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Additionally, it has been reported that the rate of sulfonation reactions follows first-order kinetics concerning concentration [23].

3.3.1 Rate of reaction in case (A) mechanism

The sulfonation rate of CS follows a first-order reaction as reported in previous studies [23]. In this study, the concentration of reactive sites available for sulfonation is denoted by C and is expressed in moles per liter (mol/L). These reactive sites are located at specific positions on the CS monomer: the primary amine group at carbon C2, and the hydroxyl groups at carbons C3 (secondary hydroxyl) and C6 (primary hydroxyl) of the glucosamine ring. For simplicity in kinetic modeling, the CS monomer is treated as a small molecule, and the reaction is assumed to occur at these defined functional sites. The extent of the sulfonation reaction is represented by the conversion variable x, which indicates the fraction of reactive groups that have been successfully sulfonated over time.

Eq.3 presents the irreversible reaction between CS and H_2SO_4.

$$CS + H_2SO_4 \longrightarrow CSHSO_3 + H_2O \qquad (3)$$

The mass balance for the sulfonation of CS, assuming a first-order reaction with concerning the concentration (C) of CS repeat units in a batch reactor system and considering no effect of water (H_2O) on the reaction, is shown in Eq. 4.

$$\frac{-dC}{dt} = k_1 C \qquad (4)$$

Where t represents the reaction time and k_1 is the rate constant. This equation is integrated from the start of the reaction ($C = C_o$ at t = 0) to a concentration (C at t = t) to derive Eqs. 5 and 6.

$$-\int_{C_o}^{C}\frac{dC}{C} = k_1\int_0^t dt \qquad (5)$$

$$-ln\frac{C}{C_o} = k_1 t \qquad (6)$$

Eq. 7 describes the reaction conversion:

$$\frac{C_o - C}{C_o} = x \qquad (7)$$

Where x represents the reaction conversion. For a first-order irreversible reaction, a plot of $-\ln(1 - x)$ against t should yield a straight line, as shown in Fig. 5.

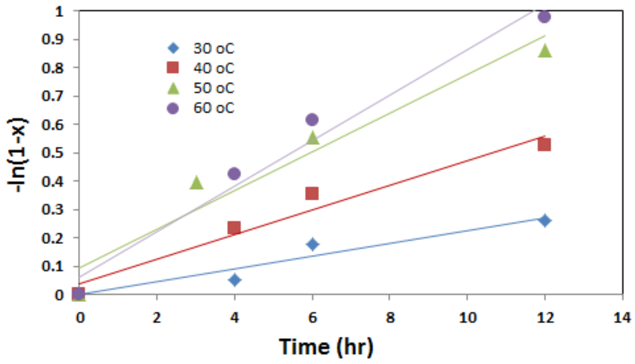

Fig. 5: -ln(1-x) versus time.

The different values of the rate constant (k) at various temperatures are shown in Table 2. The results indicate that the k value increases with temperature.

Table 2: The different values of k at different temperatures.

Temperature, K	303	313	323	333
k values	0.0226	0.0436	0.0667	0.0802
1/T, K^{-1}	0.0033	0.0032	0.0031	0.0030

3.3.2 Rate of reaction in case (B) mechanism

The potential effects of water on de-sulfonation in the reaction system are presented in Eq. 8.

$$CS + H_2SO_4 \underset{\substack{K_3 \\ K_2}}{\rightleftharpoons} CS\,SO_3 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where k_2 and k_3 are the rate constants for the forward and backward reactions, respectively. The mass balance, assuming a first-order reaction concerning the CS repeat unit concentration (C) in a batch reactor system and considering the effect of water on the reaction, is presented in Eq. 9.

$$\frac{-dc}{dt} = \frac{k_2\,C}{k_3(C_o - C)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Integrating Eq. 9 from C_o to C results in Eq. 10.

$$-\int_{Co}^{C} \frac{C_o - C}{c}\,dC = \frac{k_2}{k_3}\int_0^t \mathrm{dt}$$

$$-\int_{C_o}^{C} \frac{C_o\,dC}{C} + \int_{C_o}^{C} \frac{C}{C}\,\mathrm{dC} = \left[\frac{k_2}{k_3}\,t\right]_0^t$$

$$-C_o\,[lnC]_{C_o}^{C} + [C]_{C_o}^{C} = \left[\frac{k_2}{k_3}\,t\right]_0^t$$

$$-C_o\,(lnC - \ln C_o) + (C - C_o) = \frac{k_2}{k_3}\,t$$

$$-C_o\,(ln\frac{C}{C_o}) + (C - C_o) = \frac{k_2}{k_3}\,t$$

$$-C_o\,ln\frac{C}{C_o} + C - C_o = \frac{k2}{k_3}\,t$$

$$-C_o\,ln\frac{Co(1-x)}{Co} + C_o - C_o x - C_o = \frac{k_2}{k_3}\,t$$

$$-C_o \ln(1-x) - C_o x = \frac{k_2}{k_3}\,t$$

$$-C_o\,(\ln(1-x) + x) = \frac{k_2}{k_3}\,t$$

But $\frac{k_2}{k_3} = Kc = K\ (equilibrium\ constant)$

Then

$$C_o\,(1 - ln(1-x)\ - x) = Kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Eq. 10 can as well be expressed as:

$$C_o\ \ (-x - ln(1-x)\,) = Kt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (11)$$

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The sulfonation kinetics of CS in 4M H_2SO_4 were measured at four constant temperatures ranging from 303 K to 333 K over different time intervals. The origin of the time scale was set at an approximate time of complete dissolution of CS. A plot of $Co\ (-x - ln(1-x))$ against time t yields a straight line, as shown in Fig. 6.

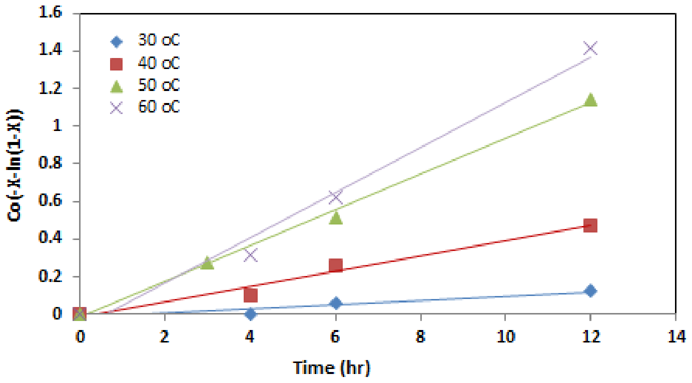

Fig. 6: First-order effect of H_2O on CS sulfonation using sulfuric acid

The plot in Fig. 6 shows a straight line for all experiments, with each least squares fit not intersecting at (0, 0). This suggests that the H_2O produced during the reaction has no significant effect on the sulfonation of CS, indicating that the H_2O produced has no effect on the sulfonation of CS, causing no desulfonation and thus inducing the irreversibility of the process. This may be due to the minimal negative impact of the sulfonated repeat units during the early stages of the reaction [21]. Fig. 6 indicates that increasing temperature accelerates the sulfonation rate. The different rate constants (k) at various temperatures are presented in Table 3, which shows that k increases with temperature.

Table 3: Rate Constant values at different sulfonation temperature using mechanism (B).

Temperature	303K	313 K	323 K	333 K
K values	0.011	0.0404	0.091	0.1201

3.4 Activation energy calculation for CS Sulfonation

The activation energy (Ea) of the process is thus obtained from Arrhenius Eq. 12.

$k= Ae^{-Ea/RT}$ ……………..……………..………………………………….........…… (12)

Where k is the rate constant, A is the frequency factor, R is the gas constant (0.00814 kJ/mol·K), and Ea is the activation energy in kJ/mol. To determine the activation energy, the natural logarithm (ln) is applied to both sides of Eq. 12, resulting in Eq. 13.

$\ln k = \ln(Ae^{-Ea/RT})$

Solving Eq.12 further:

$\ln k = \ln(A) + \ln(e^{-Ea/RT})$

$\ln k = \ln(A) + (-Ea/RT) = \ln(A) – (Ea/R)(1/T)$

$\ln k = – (Ea/R)(1/T) + \ln(A)$ …………..………….…………………………...…..…(13)

The activation energy (Ea) can be determined from Fig. 7 by plotting ln(k) versus 1 /T. The slope of the line represents Ea/R. The calculated activation energy (Ea) is 35.6 kJ/mol, indicating the minimum energy required to initiate the chemical reaction.

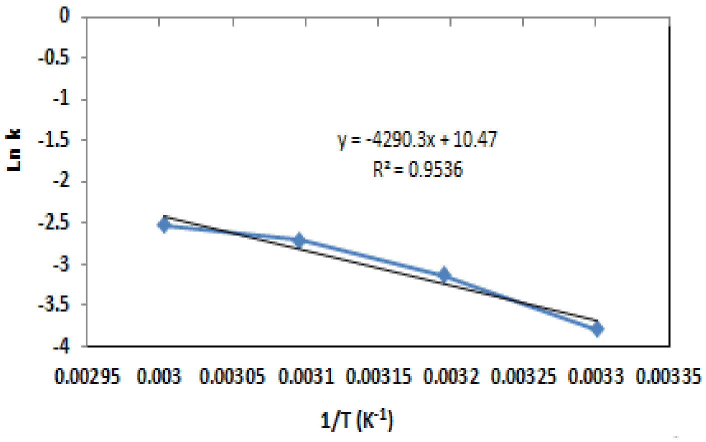

Fig. 7: Logarithm of rate of reaction versus the reciprocal temperature.

4 Conclusions

The sulfonation kinetics of CS for the synthesis of a proton exchange membrane for Fuel cell applications has been studied using sulfuric acid. Results showed that the sulfonation process follows a first-order irreversible reaction due to the absence of significant effects from the water produced during sulfonation. Additionally, the process exhibited high activation energy, indicating that the reaction requires substantial energy input to proceed efficiently. This highlights the strong chemical bond formation during sulfonation and its importance in membrane performance for fuel cells.

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgment

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