

Study on acidic degradation of SLES and its impact on phase behavior.



A thesis submitted towards partial fulfillment of BS-MS Dual Degree Programme

By

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CERTIFICATE

This is to certify that this thesis entitled "study of acidic degradation of SLES and its impact on phase behavior" submitted towards the partial fulfillment of the BS-MS dual degree programme at the Indian institute of Science Education and Research (IISER), Pune represents original research carried out by Pooja Prasanthan T at Unilever R&D, Bangalore, under the supervision of Mr.Jiji Kottukapally during the academic year 2014-2015


Jiji Kottukapally

Date: 25/03/2015

DECLARATION

I hereby declare that the matter embodied in the report entitled "study of acidic degradation of SLES and its impact on phase behavior" are the results of the investigations carried out by me at the House hold care unit of, Hindustan Unilever research center, Bangalore, under the supervision of Mr. Jiji Kottukapally and the same has not been submitted elsewhere for any other degree.



Pooja Prasanthan T

Date: 25/03/2015

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ABSTRACT

Sodium Lauryl ether sulfates (SLES) are widely used anionic surfactants in liquid detergents. The understanding of hydrolysis of SLES under acidic conditions during manufacture and storage is critical in formulating antimicrobial liquid products at lower p^H . In this work degradation kinetics of SLES has been studied under various conditions. The effect of ethoxylation and other typical formulation ingredients in a detergent liquid like electrolytes, hydrotope and organic acids on the kinetics of hydrolysis was examined. In addition changes in interfacial properties and phase behavior of SLES due to degradation also been investigated. Rate constant of hydrolysis under various study conditions have been determined. Rate of hydrolysis of SLES found to be increase with increase in number of ethoxyl groups. Presence of buffers, low molecular weight organic acids like citric acid and electrolytes were found to reduce the kinetics of hydrolysis. No significant influence of the hydrotope was observed on the degradation kinetics .As a result of hydrolysis SLES showed a phase change from isotropic solution to lamellar phase. Surface occupation of degradation products of SLES such as dodecanol or dodeyl ethers leads to lowering of surface tension of SLES solutions.

1. Introduction

Surfactants (Surface active agents) form a unique class of chemical compounds which are widely used and find a large number of applications in industrial, cosmetics and pharmaceutical products. The demands on surfactants systems have increased over the last decades. Millions of metric tons of surfactants are produced annually throughout the world. There are a large variety of surfactants used in the industry depending on the area of application. They can be used as detergents, wetting agent, emulsifiers, foaming agents, and dispersants. *Surfactants are substances that, when present at low concentration in a system, have the property of adsorbing onto the surfaces or interfaces of the system and of altering to a marked degree the surface or interfacial free energies of those surface* The term interface indicates a boundary between any two immiscible phases; the term surface denotes an interface where one phase is a gas, usually air. ^[1]. This adsorption behavior is attributed to the chemical structure of surfactants which incorporate both hydrophobic and hydrophilic parts. The hydrophobic group is a long chain hydrocarbon residue and the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are classified as anionic, cationic, Zwitter ionic (amphoteric) and non ionic. Anionic surfactants are negatively charged, and cationic are those that are positively charged, Zwitter ionic has both positive and negative charges while nonionic are those that are uncharged in solution

Among the three classes of surfactants, anionic surfactants are most commonly used because of their excellent cleansing action. These are the key components of laundry detergents, household, and personal care products and constitute more than 50 % percentage of total surfactant production ^[2]. Widely used anionic surfactants are alkyl sulphates, alkyl ethoxylate sulphates, linear alkyl benzenesulfonate (LAS), and fatty acid salts (soaps). Most commonly used anionic surfactant are sodium salts of linear alkyl benzene sulfonic acid (NaLAS), sodium salts of lauryl sulphates, $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$ (SDS) and sodium salts of lauryl ether sulphates (SLES) $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Na}$ where n denotes no ethoxyl groups in the chemical structure. Lauryl sulphate has good foaming ability and biodegradability so they have been used in detergents and emulsifiers. SLS is superior in detergents and

widely used for industrial applications. Lauryl ether sulphates are more soluble in water and milder than Lauryl sulphates. Sodium lauryl ether sulphates, SLES are a workhorse surfactant for liquid detergents. SLES is an inexpensive and very effective foaming agent is often used in laundry and hand and dish washing detergents. It is considered mild and useful as typically used to formulate cosmetic products (normally facial or body cleansers and shampoos).

SLES are typically used in detergent formulations at near to neutral pH or alkaline pH. Typically these surfactants are not used in the acidic pH as they are prone to hydrolysis under acidic environment. However in the recent past, there has been an active interest in the industry to develop products at acidic pH for dish washing and surface cleaning due to the self preserving and antimicrobial benefits obtained at lower pH^[3,4]. In many of these compositions, low molecular weight organic acids like lactic acid are further used to obtain antimicrobial benefits. The understanding of hydrolysis of SLES under acidic conditions during manufacture and storage is critical in formulating antimicrobial products at lower pH. Hydrolysis of anionic surfactants like alkyl sulphates are well reported in the literature, however the kinetics of hydrolysis of alkyl ether sulphates is not well understood especially at lower temperatures, relevant to the long term storage of these samples. The aim of the present work is to study the degradation kinetics of SLES under acidic conditions and arrive at rate constants for hydrolysis under various conditions. The present work also aims to understand the influence of ethoxylation on the hydrolysis of SLES. The influence of other typical formulation ingredients in a detergent liquid like electrolytes, hydrotone and organic acids on the kinetics of hydrolysis is also studied. The work further aims to understand the changes brought about by this degradation in SLES on its interfacial properties and phase behavior.

Numbers of literatures had been published on alkaline and acidic hydrolysis of various anionic surfactants with specific focus on hydrolysis of alkyl sulphates. Hydrolysis of alkyl sulphates and alkyl ether sulphates can take place via three distinct pathways hydrogen-ion catalysed, hydroxide-ion catalysed and neutral (uncatalysed) hydrolysis. The mechanism of the three processes for alkyl sulphates explained in detail some time ago by a number of workers. Fast acid-catalysed reaction involves sulphur-oxygen cleavage and proceeds through a protonation equilibrium of the

sulphate group followed by attack of water on the sulphur. Since SLS (Sodium Lauryl Sulphates) is a major component in many detergent products many studies were carried out on the hydrolysis of this compound. Kinetics of hydrolysis of SLES is similar to SLS. SLS upon hydrolysis produce dodecanol and hydrogen sulphate anions. Donald et al^[5].2001 explained kinetic form and mode of catalysis of acidic hydrolysis of SLS. They have been proposed that SDS hydrolysis shows an auto catalytic pathway in initially neutral solutions, which arises from the production of hydrogen sulphate ions produced as a result of hydrolysis. And hydrogen ion catalysed pathway, involves unimolecular cleavage of SO_3 from dodecyl hydrogen sulfate, with concerted intramolecular proton transfer. Kurz,^[6] found that the acid catalysed process undergoes a sharp increase in reaction rate upon micellisation, which leads to a shift in the protonation equilibrium due to the high electrostatic potential of the micellar surface. Motsavage and Kostenbauder^[7] also measured the rate of the acid catalysed hydrolysis of SLS but took only two concentrations of the ester, one above and one below the CMC. They also found an enhanced reaction rate above the CMC, by a factor of 35, attributing this to the binding of solvated protons to the sulphate head groups of the micelles. Effect of 1-dodecanol on rate of hydrolysis of SLS has been investigated by S.Yokoyama et al^[8]. They found that. The effectiveness of increase in rate constant by different alcohols varies below and above CMC. Number of literatures published on rate of hydrolysis of SLES is very few. Kinetics of acid catalysed hydrolysis of SLES in concentrated micellar solutions had been thoroughly studied by Garnet et al^[9,10] The reaction was carried out in SLES 2EO samples in isotropic micellar phase (up to 0.6M surfactant) at 70⁰C. The effects of counter ion, electrolytes, acid concentration and surfactant concentration on the rate of hydrolysis were studied and analyzed in terms of a pseudo-phase/ion-exchange model. They have shown that the reaction is in fact rather slow, particularly at high pH and electrolytes have an inhibitory effect on hydrolysis^[9]. Rate of acidic hydrolysis of SLES samples at lower temperature conditions as well as variation of properties of surfactant systems upon hydrolysis has not been widely studied.

In Present work we investigate difference in kinetics of hydrolysis of sodium lauryl ether sulfates with different degree of ethoxylation (SLES 1EO and SLES 2EO) under various temperatures (particularly 40⁰ and 50⁰C) and initial p^H conditions. Kinetic

runs were performed at lower and higher temperatures conditions with 20% SLES solutions. Effects of salts such as NaCl and MgSO₄, hydrotope, dodecanol and initial concentration of surfactants on hydrolysis kinetics of SLES 2EO also studied at 50⁰C. In addition difference between kinetics of organic and inorganic acid catalysed hydrolysis also been analyzed The works further intend to identify the changes as a result of this degradation in SLES on its interfacial properties and phase behavior.

2. Materials and Methods

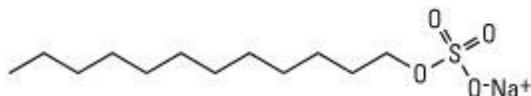
2.1 Materials

Kinetic studies were carried out using mainly three surfactants

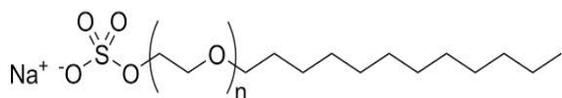
Surfactant	Company	Purity
SLS	Sigma Aldrich	98%
SLES 1EO	Galaxy Surfactants	70%
SLES 2EO	Galaxy Surfactants	70%

Other used chemicals used: Sodium Chloride (NaCl), Magnesium sulfate hepta hydrate, (MgSO₄.7H₂O), Propane-1,2-diol(C₃H₈O₂), Hydrochloric acid(HCl), Citric acid(C₆H₈O₇) and dodecanol. All chemicals were analytical grade and purchased from Sigma Aldrich

Chemical Structures of surfactants used



Sodium Lauryl sulfate (SLS)
Molecular weight 288



n – No of ethoxyl groups

Sodium Lauryl Ether sulfate (SLES)

2.2 Experiment Details

Hydrolysis reactions were carried out on surfactant solutions of concentration well above CMC. About 20% surfactant solutions were prepared by dissolving appropriate amount of surfactant in distilled water. The exact concentration of the prepared solution was measured using two phase colorimetric titration. Initial p^H of the sample solutions were adjusted using Hydrochloric acid. The effect of dodecanol, propane -1, 2 diol and electrolyte on hydrolysis was studied by mixing known amount of these components to acidic surfactant solutions. Kinetics of hydrolysis has been studied under both stirred and stagnant conditions.

Kinetic study under stagnant state:

- Prepared solutions were transferred to 50 ml plastic containers and kept in an oven maintained at constant temperature. Containers were tightly capped to avoid water loss during the study.
- Kinetic runs were carried out at $50^{\circ}C$ and $40^{\circ}C$.
- About 5ml of solution was removed at 48 hrs time intervals. Analysis has been continued till 400 hours

Kinetic study under stirred state

- About 500 ml of prepared surfactant solution transferred to 2000 ml three necked round bottom flask
- Continuous stirring of reaction mixture has been achieved by an over head stirrer.
- Temperature of the system maintained constant using water bath. Reflux condenser is fixed at one neck to avoid water loss during reaction.
- Aliquot of 5ml was withdrawn from reaction mixture at 2 hr time intervals till 16 hrs.

Aliquoted sample was used to determine p^H and surfactant concentration . p^H values were measured using a p^H meter. Two phase colorimetric titration method was used for determination of surfactant concentration. Samples were also analyzed through

polarized optical microscopes to identify the phase changes of surfactant solutions as a result of hydrolysis. Experimental set up is shown in fig 1.

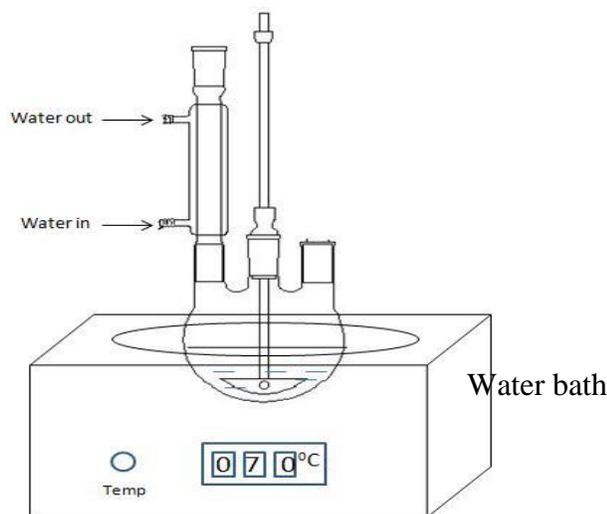


Fig 1: Schematic diagram of experimental set up

2.3 Determination of Concentration of anionic surfactant by a two phase titration

This method for determining the concentration of anionic surfactants in aqueous solution is based on the formation of salts between the anionic surfactant and cationic organic species, which are more soluble in an organic phase than in an aqueous phase. The surfactant is titrated against a cationic titrant in the presence of a dye, which is a mixture of anionic and cationic in nature. Initially the surfactant forms a salt with the cationic dye to produce a colored organic layer, while the anionic dye gives a color to the aqueous layer. Adding the cationic titrant displaces the dye from the surfactant-dye salt to form a salt between the titrant and the surfactant, and then when all the surfactant is taken up by this salt, the excess titrant then forms a colored salt with the anionic dye which is soluble in the organic layer, while the cationic dye passes into the aqueous layer. Thus, as the two dyes produce different colors, the end point occurs when the color of the organic layer changes. The mixed indicator method was found to be widely applicable to anionic surfactants, including alkyl sulphates, solvents and ethoxy sulphates, and dialkyl sulphosuccinates. It is not affected by the presence of other compounds, for example alcohols, electrolytes, non-ionic detergents, etc., and is reproducible up to + 2%.

Method

Titrant: - 0.004M Hyamine 1622 solution.

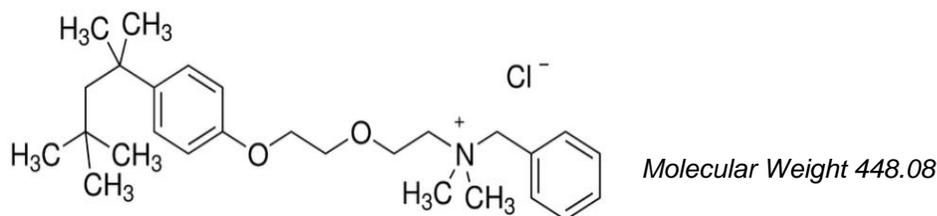


Fig 2.2 Hyamine ($C_{27}H_{42}ClNO_2$)

Indicator: - 0.5gm Dimidium Bromide and 0.25gm Disulphine Blue in 250ml of solution. 20 ml of this the solution was added to 20ml of 2.5M H_2SO_4 and diluted to 500ml to make the working solution.

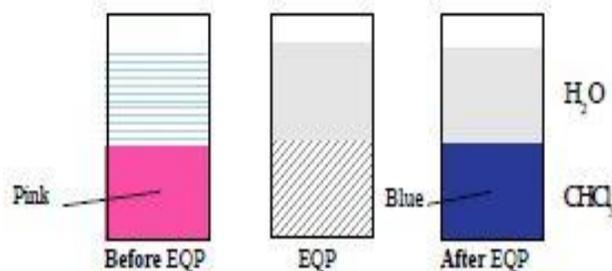


Fig 2: Schematic representation of Hyamine titration^[11]

The surfactant sample was diluted to 100 ml and 2ml of this was placed in a stoppered measuring cylinder along with 2ml chloroform, 2 ml of the indicator solution. This mixture was then titrated with the Hyamine solution with vigorous shaking. As the end point approached, the emulsion formed by adding the titrant began to break easily. The end point was found when the color of the chloroform layer changed from pink to a pale blue color

2.4 Determination of Critical Micellar Concentration (CMC)

The CMC of surfactant solution was determined with a tensiometer by measuring the surface tension of concentration series. At lower concentration surfactants occupies only on the surface. As concentration increases surface tension reduces rapidly until surface became fully saturated. Further increase in concentration results in formation of

micelle. The concentration at which micelles are formed is called CMC^[1]. Above CMC surface tension is not affected by increase in concentration. Because monomeric form of surfactants can only cause reduction in surface tension surface tension is plotted against logarithm of concentration. The CMC was obtained from the sharp break in the plot. Surface tension was measured by wilhelmy plate method at 25⁰C.

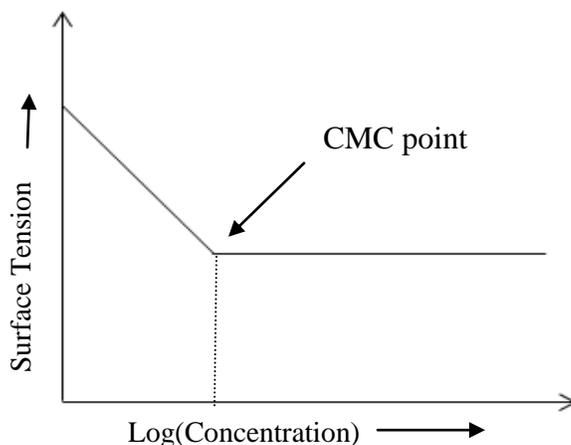


Fig 3 Schematic diagram of surface tension vs. Logarithm of concentration plot

Wilhelmy plate technique

A vertical thin plate made of platinum is used in this technique. The metal plate was cleaned properly to remove the presence of any organic solvent and then heated to red with a busen burner before the experiment. Cleaning and roughening of the plate surface helped to maintain good wetting of the plate by the sample solutions. Plate is brought into contact with the interface. If it is completely wetted by solution, this liquid will adhere to the probe and climb as the result of capillary force, increasing the interfacial area and leading to a force tending to pull the probe toward the plane of the interface. This restoring force can be determined by a microbalance. The force (F) acting along the three-phase contact line is exactly equal to the weight of the liquid meniscus standing above the plane of the fluid-fluid interface^[12]. This force, measured by the microbalance, is used to calculate the interfacial tension:

$$\text{Surface Tension } \gamma = \frac{F}{p \cos \theta} \quad [12]$$

Where p is the perimeter of the three-phase contact line and θ is the contact angle measured for the liquid meniscus in contact with the object surface

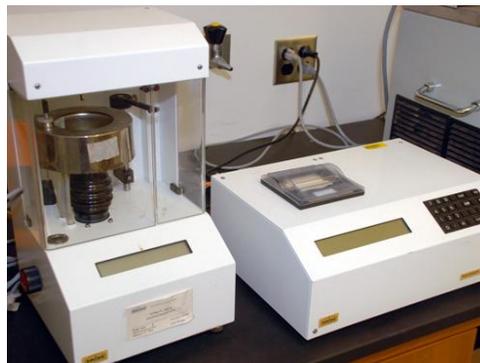
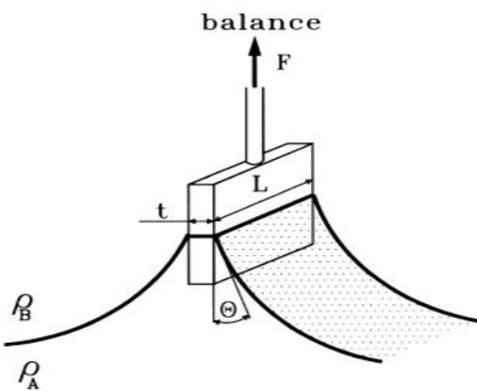


Fig4: (a) A schematic of Wilhelmy plate technique^[11]. (b) Tensiometer

2.5 Determination of rate constant from concentration time data

For any given kinetic run we have the following:

- (a) Initial acid concentration $[H^+]_0$
- (b) Initial surfactant concentration, $[surf]_0$
- (c) The concentration of acid and surfactant at times t, $[H^+]_t$ and $[surf]_t$

The rate of reaction is dependent on both the acid and the surfactant concentrations, and as HSO_4 is a product of the reaction, the reaction is autocatalytic. For an autocatalytic reaction the integrated rate equation used to obtain the rate constant k_2 , observed should be^[7]

$$k_{2, \text{observed}} = \frac{\text{Slope of } [\ln([H^+]_t/[surf]_t)] \text{ vs. time}}{[H^+]_0 + [surf]_0} \quad [9]$$

2.6 Study of phase behavior of hydrolyzed surfactants

Surfactants form different phases in aqueous solutions depending on concentration; temperature and presence of additives. Basic stable aggregate of surfactants is known as micelles. The concentration at which micelles are formed is known as critical micellar concentration (CMC). The driving force for aggregation behavior is the interactions of the surfactant molecule with water and with each other. At very high concentrations

surfactants form larger entities termed mesomorphic phases (*mesophases*) A mesophases is an intermediate, phase that exhibits certain aspects of both solid and liquid states while also possessing properties that are not found in either solid^[13]. Lyotropic structures range from cubic to hexagonal cylindrical array to the lamellae. Two major types identified mesophases are the middle phase and neat phase. Middle phase is characterized by a hexagonal array of indefinitely long, mutually parallel, rods and the neat phase, has a lamellar structure. In aqueous solutions the cylindrical structures of the middle phase usually have a hydrocarbon core surrounded by an interfacial layer of hydrated polar groups^[14]. Some surfactants system exhibited a viscous isotropic phase in between middle phase and neat phase mesophases. Phase behavior at a particular concentration depends on temperature, ionic strength of aqueous phase and presence and absence of solutes especially surface active substances^[15]. Hydrolysis of ethoxy sulphates and ether sulphates produces corresponding alcohols. Presence of alcohols affects the mesophases formed by surfactants

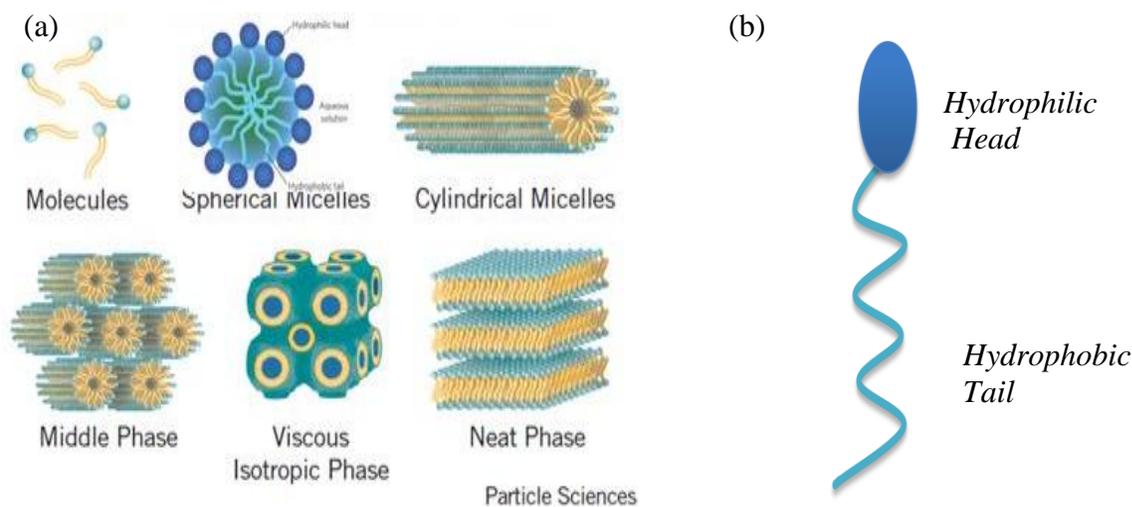


Fig 5. (a) Different phases formed by surfactants^[13] (b) Chemical structure of a surfactant

Variation of phase behaviour of surfactants solutions upon hydrolysis has been studied by microscopic observations. Microscopic imaging was done using *Olympus Bx51 fluorescence microscope*. Polarized light microscopes are used to observe, photograph specimens that are visible primarily due to their optically anisotropic character. It has two polarizing filters - the polarizer and analyzer. Hydrolysed surfactant samples were

collected and analysed through the microscope to identify phase changes of surfactants as a result of hydrolysis. Different phases can be easily distinguished by microscopic analysis. Polarized light microscopy helps us to identify into the internal structure of crystals

2.7 Determination of pH of the solutions

pH values were determined using a pH meter (Thermo scientific Orion Verstar bench top pH meter). Before measurement instrument was calibrated with standard pH 4 and pH 7 buffer. After each single measurement, the probe is cleaned with deionized water to remove traces of the solution being measured, and a tissue paper is used to remove any remaining water and then quickly immersed in another solution for measurements.

3. Results and Discussion

3.1 Effect of number of ethoxyl group on kinetics of hydrolysis of 20% Sodium Lauryl Ether Sulfates (SLES) solutions

Kinetics of hydrolysis of SLES 1EO and SLES 2EO has been investigated to identify the effect of increasing ethoxyl groups in dodecyl ether sulfates and to derive rate constant of acidic hydrolysis of these surfactants at lower temperatures (40°C and 50°C). The kinetics of hydrolysis at 40 and 50 deg has been done at stagnant conditions to emulate storage conditions. The kinetics of hydrolysis is slow and since tracking of the experiment has to done over a long time, it was also practical for these experiments to be done under stagnant conditions. Fig6a, 6b shows concentration vs. time plot for SLS, SLES 1EO and SLES 2EO. It can be seen in fig that all three surfactants exhibited a similar trend of degradation at a particular temperature. Rate of hydrolysis showed a regular increase with increase in no of ethoxyl groups. Order of rate of degradation obtained is SLS<SLES 1EO<SLES 2EO.

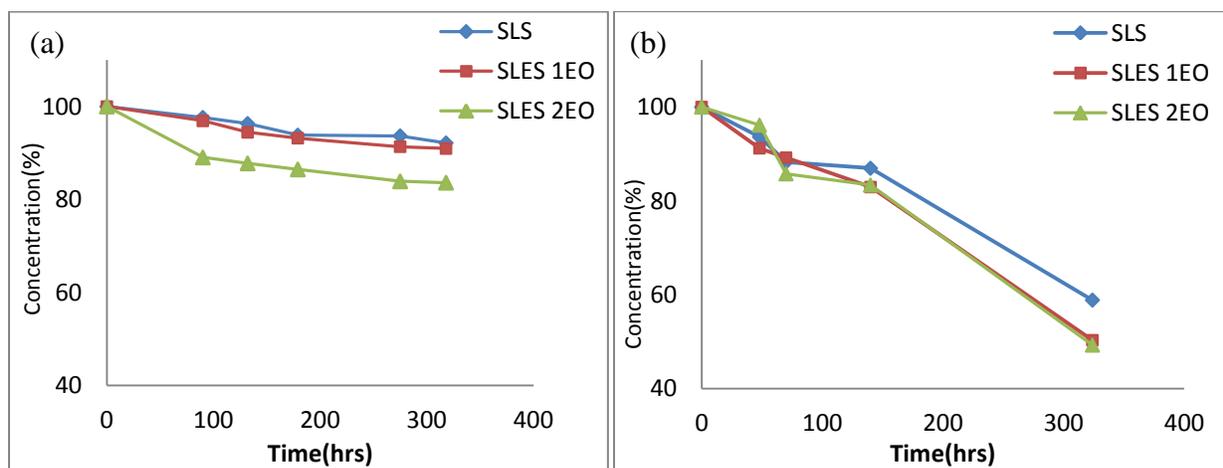


Fig6 Variation of concentration SLS, SLES 1EO, SLES 2EO (20% by weight) at p^H2 (adjusted using HCl) with time (a) 40°C (Stagnant) (b) 50°C (Stagnant).

Experimentally determined value of rate constant of hydrolysis of 20% SLES solutions at 40°C and 50°C is given in table 1. Higher reaction rate in SLES 2EO compared to SLES 1EO and SLS samples can be attributed to the presence of ethoxyl groups. Mechanism of acidic hydrolysis of dodecyl ether sulfates assumed to be same as dodecyl sulfates. Hydrolysis proceeds through protonation of sulfate group of

micelles followed by unimolecular cleavage of SO_3 from dodecyl hydrogen sulphate, with the concerted intramolecular proton transfer [5]. The enhancement in rate of hydrolysis might be due to enhancement in hydrogen ion binding to sulfate group of SLES 2EO micelle in presence of hydrophilic ethoxyl groups. Hydrogen bonding interactions between oxygen atom of ethoxyl group and acidic hydrogen can facilitates protonation of sulfate group of SLES molecules. With increase in number of ethoxyl group rate of hydrogen binding to the sulfate group of SLES also increases. This results in higher rate of acidic hydrolysis.

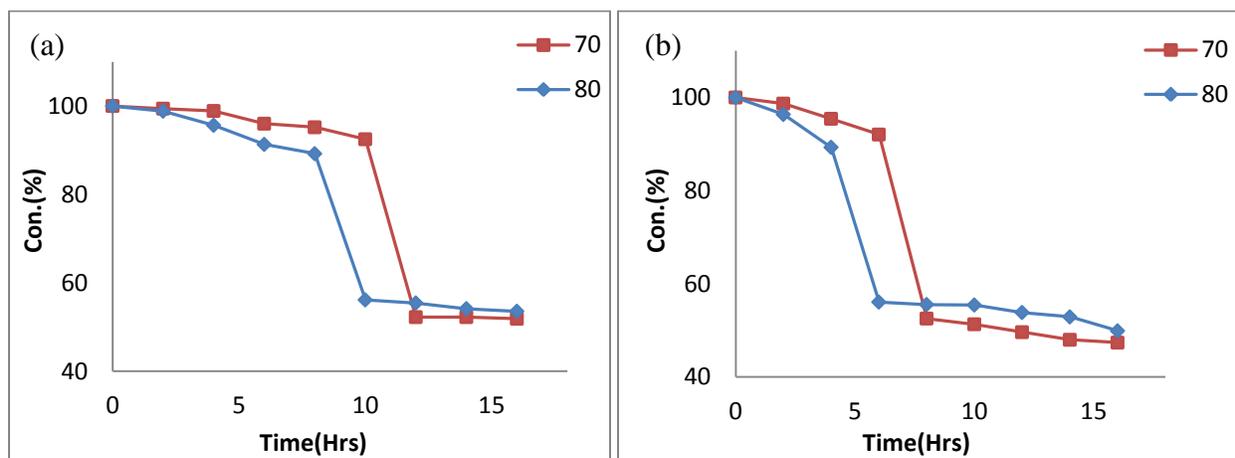


Fig7: Change in con. with time at 70^oC and 80^oC, initial pH2 (a) SLES 1EO (b) SLES 2EO

Kinetic analysis at 70^oC and 80^oC: Detailed analysis of kinetics of acidic degradation of SLES 1EO and SLES 2EO was studied under stirred reaction conditions at higher temperature range (70^oC and 80^oC). Change of surfactant concentration with time for SLES 2EO and SLES1EO (p^H 2) at 70^oC and 80^oC is plotted in Fig 7a and 7b. The variation of concentration with time showed a similar trend at both temperatures. As can be seen from plot hydrolysis characterized by an initial slow phase followed by a rapid acceleration and final slowing down. Deviation from straight line behavior of plots can be attributed to increasing concentration of dodecanol with reaction time. Dodecanol and dodecanol ethers are the major product of SLES degradation. At 80^oC both SLES 2EO and SLES 1EO the fast change in concentration plot appeared when dodecanol/SLES mole ratio is around 0.24. At 70^oC break point appears for dodecanol/SLES ratio of 0.12 for both surfactants. These values of dodecanol/SLES mole ratio obtained are consistent with solubilization limit of dodecanol in SLES at

respective temperatures. So we can say that rate of reaction is enhanced above solubilization limit of dodecanol; rate of hydrolysis increases with increase in dodecanol. Slow reaction rate below the break point is assumed to be caused by solubilization of dodecanol by SLES micelles. Solubilization of hydrophobic dodecanol inside the micelles leads to reduction in negative charge density on micellar surface causes a reduction in hydrogen ion binding. Same vale of limit of solubilization obtained for SLES 1EO and SLES 2EO indicates solubility of Dodecanol is independent of no of ethoxyl group. Final slow phase in reaction profile at both temperatures is possibly the result of change in state of aggregation of SLES solutions upon hydrolysis

3.2 Effect of initial p^H on rate of Hydrolysis of 20% SLES 1EO and SLES2EO solutions

The rate of hydrolysis of SLES solutions found to be increase with decrease in initial p^H . Concentration of SLES 1EO and SLES 2EO with different initial p^H 's (p^H 2, p^H 3, p^H 4, p^H 5) as a function of time at $50^{\circ}C$ is plotted in Fig 8. Both SLES 1EO and SLES 2EO exhibited a similar trend in degradation at p^H 2 and p^H 3. By 324 hours, hydrolysis of SLES 1EO proceeds to 42% and 24% at p^H 2 and p^H 3 respectively. Whereas for SLES 2EO percentage hydrolyzed was increased to 52% at p^H 2 and 48 % at p^H 3. But degradation kinetics is much slower at p^H 4 and above .Under the same reaction conditions SLES 2EO and 1EO undergone only less than 10% hydrolysis above p^H 4. This could be due to increase in number of H^+ ions bound to the micelles increases with the total acid concentration.

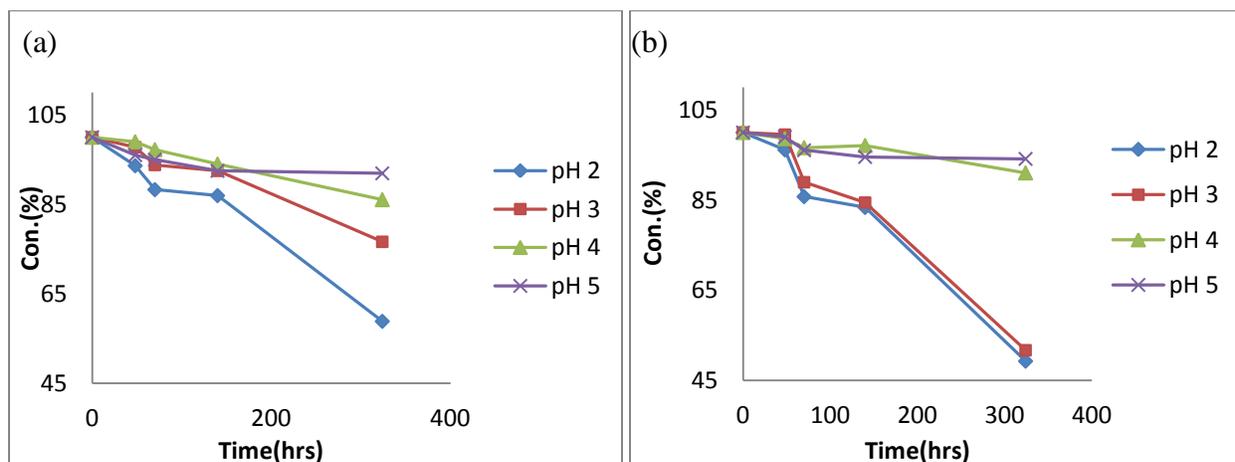


Fig 8. Variation of Surfactant concentration with time under various initial p^H at $T=50^{\circ}C$ (a) SLES 1EO (b) SLES 2EO

Rate constants obtained from $\ln([H^+]/[surf])$ vs. time plots are given in table 1. Variation of rate constant with p^H is plotted in Fig 9. It can be seen from fig 9 that the at 50°C reduction of rate constant with p^H is more pronounced in SLES 2EO than SLES 1EO which could be due to greater preferential binding of H^+ ions to micelles of SLES 2EO compared to SLES 1EO. That results from enhancement in the cooperative effect of ethoxyl groups in Hydrogen bonding with increase in number of ethoxyl groups. But at 40°C , for SLES 2EO rate coefficient is invariant with change in p^H at higher p^H values ($p^H 4$ and $p^H 5$).

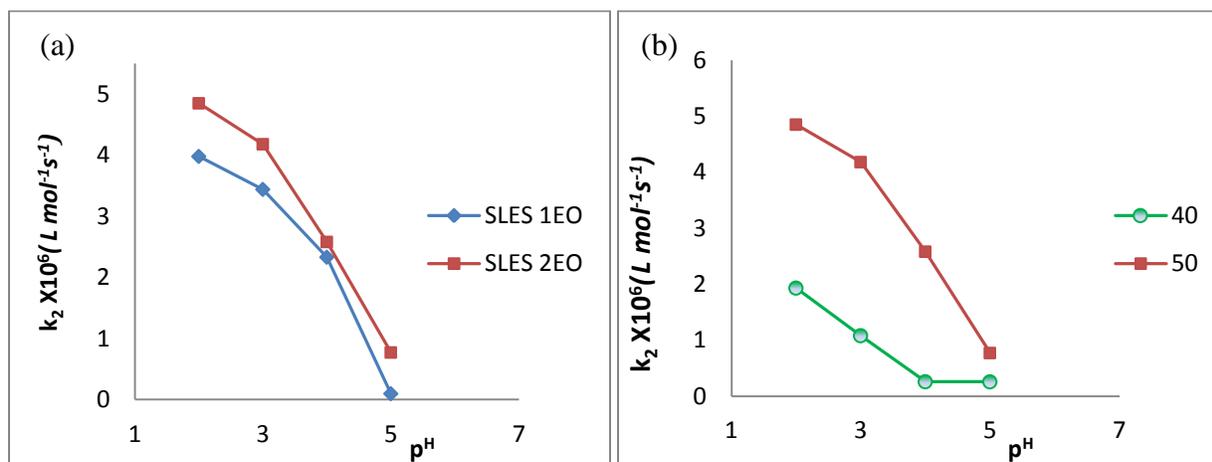


Fig9 Change in rate constant of hydrolysis with initial pH (a)for SLES 1EO SLES2EO at 50°C (b)For SLES 2EO at 40°C and 50°C

Table: 1 Rate constant for SLES 1EO and SLES 2EO at 50°C and 40°C at various p^H 's

Temp	Rate constant, $k_{2,obs}$ (L mol ⁻¹ s ⁻¹)			
	50°C		40°C	
pH	<u>SLES 1EO</u>	<u>SLES 2EO</u>	<u>SLES 1EO</u>	<u>SLES 2EO</u>
2	3.98145×10^{-06}	4.85242×10^{-06}	2.82156×10^{-06}	2.93392×10^{-06}
3	3.44×10^{-06}	4.18×10^{-06}	2.50611×10^{-06}	2.64919×10^{-06}
4	2.3331×10^{-06}	2.58027×10^{-06}	1.22789×10^{-07}	2.5653×10^{-07}
5	9.51196×10^{-08}	7.7735×10^{-07}	9.08779×10^{-08}	2.56064×10^{-07}

Kinetic analysis at 80°C : Hydrolysis carried out under stirred conditions for SLES 1EO showed a much higher difference in amount hydrolyzed at $p^H 2$ and $p^H 3$ at 80°C . About 47% hydrolysis had occurred by 18 hrs at $p^H 2$ and percentage hydrolyzed reduced to

20% under p^H 3 conditions. At $80^\circ C$ rate constant of hydrolysis at p^H 2 is 2.42 times larger than rate constant at p^H 3. Relationship between percentages hydrolyzed and time at p^H 2 and p^H 3 for SLES 1EO at $80^\circ C$ is plotted below. p^H values of sample solutions collected at various time intervals showed an increase in acid concentration with time. Hydrolysis of SLES slows down after a certain degree of hydrolysis as the viscosity of the reaction mass increases due to phase changes in the surfactant system

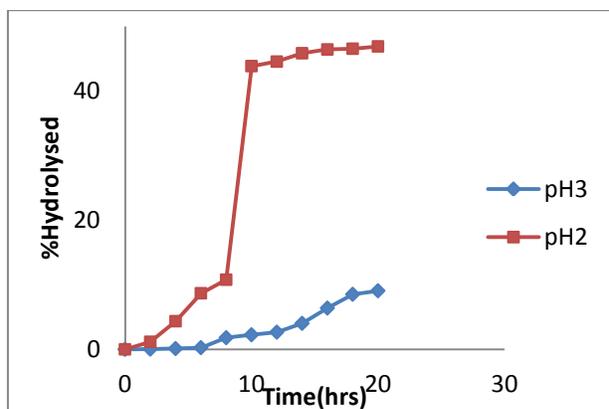


Table 2 :Rate constant k , degradation of SLES 1EO at $80^\circ C$

p^H	$k_{2,observed} (Lmol^{-1}s^{-1})$
2	8.5310^{-05}
3	3.0510^{-05}

Fig 10 Percentage of 20% SLES 1EO hydrolyzed with time at initial p^H of 2 and 3, (pH adjusted using HCl) at $T=80^\circ C$

3.3 Hydrolysis kinetics of SLES 2EO in a p^H 2 buffer system

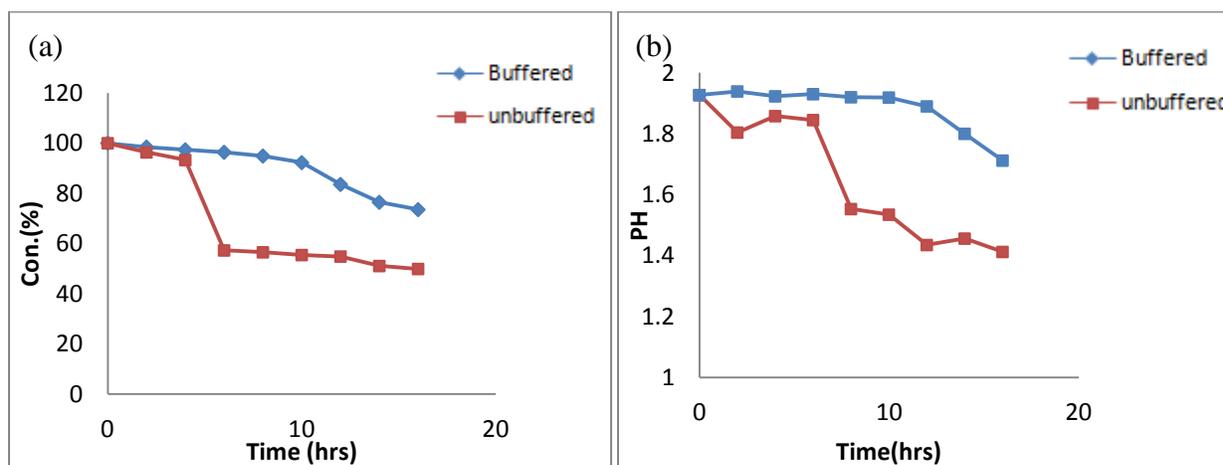


Fig11: (a) Variation of concentration with time for buffered and unbuffered SLES 2EO (20%, p^H 2) at $80^\circ C$ stirred **(b)** p^H values of SLES 2EO solutions as a function of time

Hydrolysis of SLES 2EO in aqueous buffer solutions (p^H 2 Hydrochloric acid-Potassium Chloride buffer) followed a slow kinetic pathway compared to unbuffered SLES 2EO solutions with an initial p^H of 2 adjusted using hydrochloric acid. Amount of

surfactant decreased to 74% of initial concentration by 16 hrs in buffer solutions at 80°C whereas only 49% of surfactant remained in unbuffered solution. Buffer system effectively suppresses the rate of hydrolysis in initial hours of reaction by resisting small changes in acid concentration. In unbuffered system pH measurements showed a regular decrease with time. Whereas in buffered system pH remained almost unchanged until 10% of SLES got hydrolyzed. After that changes in pH could not be resisted by buffer and SLES degraded at a much higher rate.

3.4 Effect of added salts on hydrolysis of 20% SLES 2EO solutions

Rate of acidic degradation of SLES is reduced in presence of added salt concentration. Kinetic studies performed out at 80°C, using SLES 2EO (20% by weight) solutions with added NaCl (2% by weight) showed 23% reduction in amount hydrolyzed compared to systems without any additives by 16 hours of reaction. The inhibition of rate of acidic degradation of SLES by the addition of metal salts can be qualitatively explained as the competition for binding sites on the micelles between the reactive hydrogen ion and other ions present in the system due to the addition of the metal salts. The decreased hydrogen ion binding to micelles results in decreased rate of acidic hydrolysis

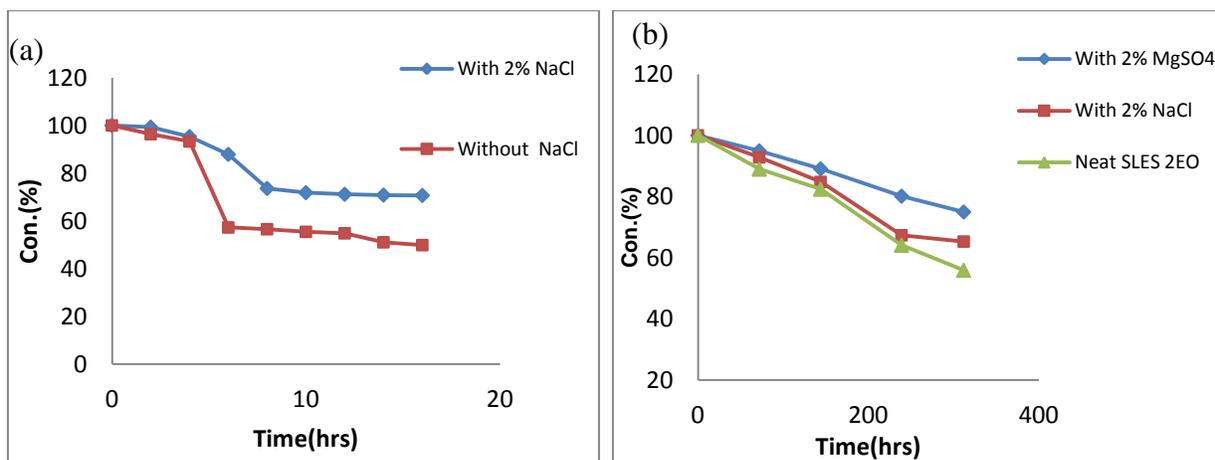


Fig:12 (a) Effect of added NaCl on rate of hydrolysis of SLES 2EO (20%, pH2) at 80°C :
 (b) Comparison of effect of added MgSO4 and NaCl on hydrolysis rate of SLES 2EO (20%, pH2) at 50°C

Inhibiting effect of different salts are different. Analysis of SLES hydrolysis in presence

of NaCl and MgSO₄ shows that inhibiting effect MgSO₄ is higher than NaCl. In absence any added salts 20% SLES 2EO solution (initial p^H2) undergone about 44%hydrolysis at 50⁰C by 312 hours. Percentage of surfactant hydrolyzed decreased to 35% in presence of NaCl and 25% in presence of MgSO₄ under same reaction condition. The extent of the inhibition is a reflection of the strength of the binding of the added counter ion to the micelle. The higher hindrance of hydrolysis in the presence of MgSO₄ compared to NaCl can be attributed to higher binding ability of Mg²⁺ to the micelle. This is due to the fact that ions of more charge density will be strongly attracted to micelles and hence more likely to displace reactive ion bound to micelle and hence inhibits reaction rate. Mg²⁺ ions have high charge density compared to Na⁺ ions. Higher charge and smaller size of Mg²⁺ ions compared to Na⁺ ions resulted in higher charge density.

3.5 Effect of initially added Dodecanol on hydrolysis of 20% SLES2EO solutions

As one of the products of the hydrolysis of SLES is dodecanol, we were interested to find the effects of the alcohol on the rate of reaction. Variation of concentration with time for solutions with different initial dodecanol/SLES mole ratio at 50⁰C is shown in fig 13a. For samples with initial Dodecanol/SLES mole ratio equals to 0.1 and 0.2 rate of hydrolysis is smaller than SLES 2EO neat samples. Hydrolysis about 400 hours at 50⁰C of samples with Dodecanol/SLES mole ratio equal to 0.3 showed ~5%percentage increase in quantity hydrolyzed compared to neat SLES samples under same reaction conditions.

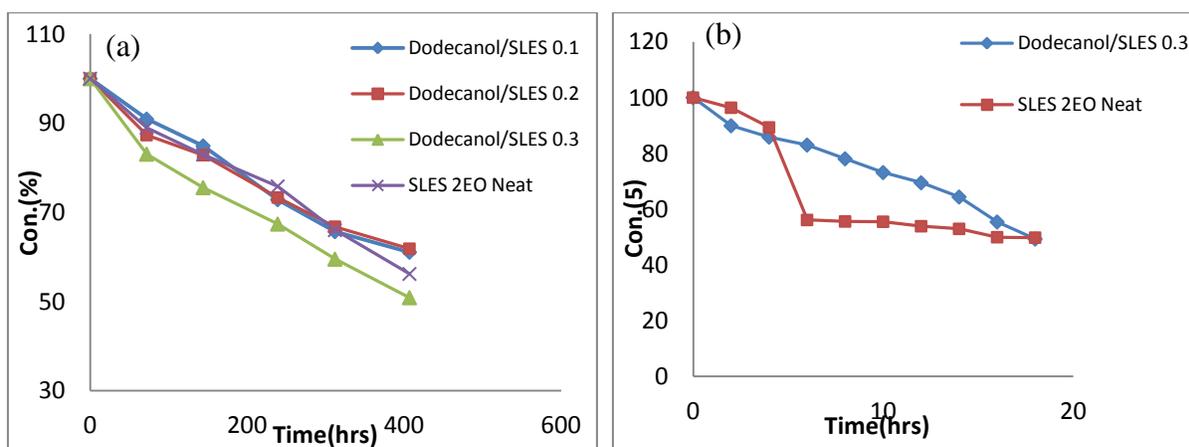


Fig 13 (a) Variation of concentration of SLES samples (20% by weight), initial p^H2 with different amount of added dodecanol at 50⁰(stagnant) **(b)** 80⁰C (stirred)

Solubilization limit of dodecanol in SLES solutions are determined to be around dodecanol/SLES mole ratio of 0.25. at 80⁰C. It has been obtained from section 3.1 that the rate of hydrolysis is inhibited in presence of dodecanol at concentrations below the solubilization limit in the micelle. The decrease in the reaction rate is considered to be caused by the decrease in hydrogen ion concentration at the surface of micelle as a result of the reduction of the negative charge density at the surface by the addition of hydrophobic dodecanol. The results obtained are in accordance with Masayuknia Nagaland and Shoko Yokoyama's ^[8] published work on acidic degradation of sodium dodecyl sulfate in presence of dodecanol. Furthermore, the hydrolysis of SLES 2EO with dodecanol concentration above the solubilization limit (dodecanol/SLES mole ratio-0.3) is increased. This might be due to the increased hydrogen ion concentration on micellar surface arises from electrostatic interactions between micelles and dodecanol

Difference in kinetics of acidic hydrolysis of SLES 2EO solutions (without dodecanol) and solutions with dodecanol can be clearly identified from fig 13 b. In presence of initially added dodecanol (dodecanol/SLES 2EO ratio 0.3) SLES exhibited a nearly linear variation of concentration with time. Different trend of variation might be due to change in phase behavior of SLES. Even though neat SLES also hydrolyzed to produce dodecanol amount dodecanol present is very less.

3.6 Effect of initial Concentration on hydrolysis of 20% SLES solutions

Hydrolysis of SLES 2EO solutions with different initial concentrations well above CMC has been investigated. Variation of concentration of SLES 2EO with time for 20%, 15%, 10% SLES 2EO solutions with same initial p^H (p^H 2) at 50⁰C under stagnant conditions is plotted in Fig 14a. All the three chosen concentrations are well above CMC. Amount of SLES being hydrolyzed by 400 hours at 50⁰C is 44.08%, 46.13% and 46.89% respectively for initial concentration of 20%, 15% and 10% respectively. It can be seen from plots that trend of degradation is similar for 10% and 20% solutions. But 15% SLES 2EO solutions exhibited a slightly different trend. Initial concentration well above CMC was found to have no considerable effect on rate of hydrolysis. Almost similar acidic degradation SLES 2EO solutions in above mentioned concentration point to existence of region of reasonably constant size and shape of micelles well above CMC

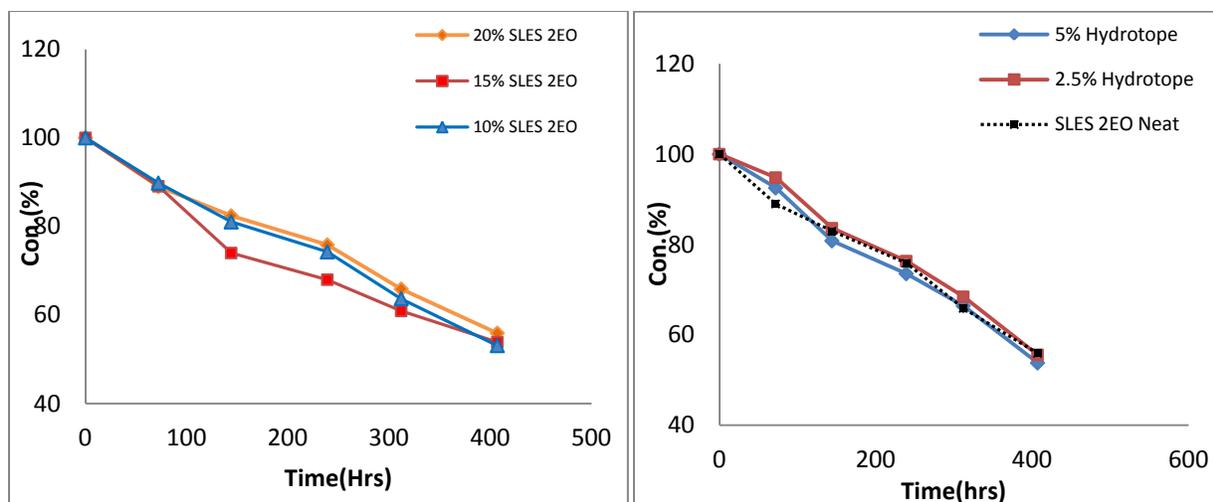


Fig14: Variation of concentration of SLES 2EO(at 50°C, initial pH2)(a) at three different concentrations(b) in presence of propane-1,2- diol

3.7 Effect of propane-1,2-diol on acidic degradation of SLES 2EO

Propane 1, 2 diol is used as a hydrotope in detergent formulations. To identify effect of propane-1,2- diol degradation kinetics of SLES 2EO solutions in presence of initially added propane -1,2 -diol has been analyzed. Kinetics of variation of concentration for SLES 2EO solutions with 2.5% and 5 % hydrotope by weight has been shown in fig 14b. It has been found that hydrotope has no considerable effect on rate of hydrolysis of SLES. About 44% hydrolysis had occurred in presence of 2.5% propane-1,2-diol, which is same as the quantity hydrolyzed by same concentration of SLES 2EO without any additives. In presence of 5% propane-1,2-diol hydrolysis proceeds to 46%. Slight enhancement on rate at high concentration of propane-1,2- diol might be due to the interaction of polar hydroxyl groups of the molecule with sulfate group of micelles. Lesser influence specifies its weak interaction with SLES micelles.

3.8 Comparison of hydrolysis in presence of organic acid and inorganic acid

Acidic degradation of SLES 2EO in presence of organic acid showed a much slower kinetics compared to inorganic acid under same initial pH conditions. Rate constant, k_2 , obs of SLES 2EO hydrolysis, at 50°C in presence of inorganic acid (Hydrochloric acid) found to be $4.321 \times 10^{-06} \text{ Lmol}^{-1} \text{ s}^{-1}$. While the k_2 , obs in presence of citric acid under same reaction conditions is equal to $3.60 \times 10^{-07} \text{ Lmol}^{-1} \text{ s}^{-1}$. Even though rate constant showed a huge difference, SLES 2EO exhibited same trend of degradation for both

organic as well as inorganic acid catalysed reaction. Concentration vs. time plots of both acid catalysed reactions showed a steady decrease up to 144 hours and plateau region between 144 hrs and 288 hrs. Slower rate of hydrolysis in presence of citric acid results from its buffering action. Since its weak acid it undergoes partial hydrolysis in aqueous solution. Smaller changes in acidic concentration can be resisted by maintaining equilibrium between citrate ions and undissociated citric acid. As can be seen from fig 15b pH values of Hydrochloric acid catalysed reaction decreases at a faster rate compared to citric acid catalysed reaction.

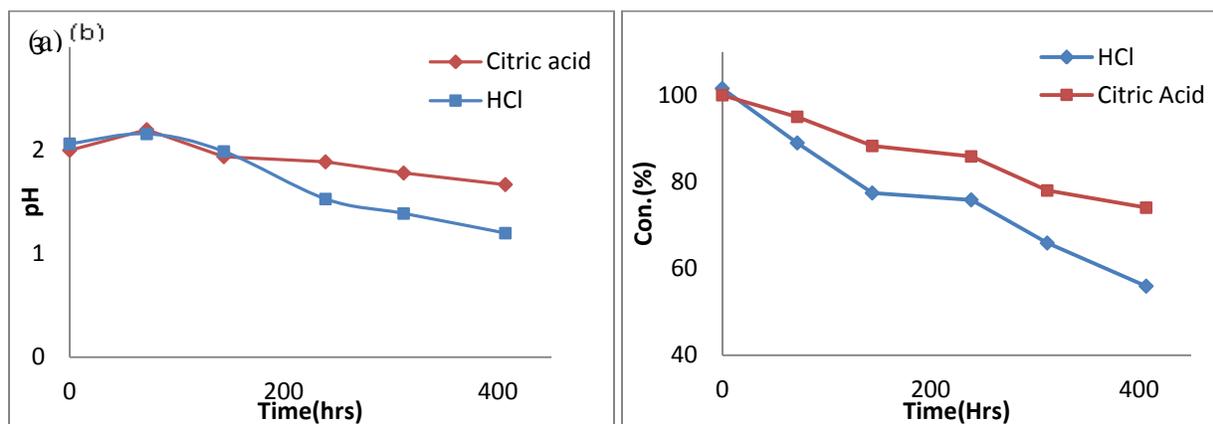


Fig15: (a) Concentration vs. time plot of SLES 2EO solutions with initial p^H 2 adjusted using citric acid and Hydrochloric acid. (b) Variation of pH with time Temperature =50°C

3.9 Effect of hydrolysis on surface properties of Sodium lauryl ether sulfates

Surface tension as well as CMC values of SLES solutions decreases with increase in extent of hydrolysis reaction. CMC values of SLES 2EO samples with initial p^H 2, p^H 3 and p^H 4 (Kept at 50°C) after 300 hours of hydrolysis has been estimated from surface tension vs. con plots (Fig 16.) p^H 2, p^H 3 and p^H 4 samples undergone 51%, 48% and 9% hydrolysis under given conditions. By comparing variation of surface tension with concentration of unhydrolysed SLES 2EO and SLES 2EO with an initial pH of 4 we can say that about 9% degradation has only smaller effects on surface properties .9% hydrolysis lead to slight decrease in surface tension values but CMC remained the same .A considerable variation in surface properties can be observed for approximately 50% hydrolyzed p^H 2 and p^H 3 sample solutions.CMC as well as surface tension reduces with hydrolysis. Variation in surface activity is caused by products of hydrolysis

such as dodecanol and dodecyl ethers. Generally presence of lesser surface active components do not affect equilibrium surface tension measurements. However presence of components highly surface active than major surfactant can greatly influence surface tension measurements. SLES hydrolyzed to produce dodecanol and other alcohols. Higher hydrophobicity of dodecanol compared to SLES made it more surface active than SLES. Because of high rate of degradation at pH2, pH3 conditions higher amount of dodecanol produced. This leads to significant variation in surface properties compared to neat SLES solution. Occupation of dodecanol molecules on the surface leads to reduction in surface tension. Interactions between hydroxyl group of dodecanol and sulfate group of SLES molecules causes reduction in electrostatic repulsion between individual SLES molecules. This facilitates micellar formation at lower concentration thereby decreases CMC.

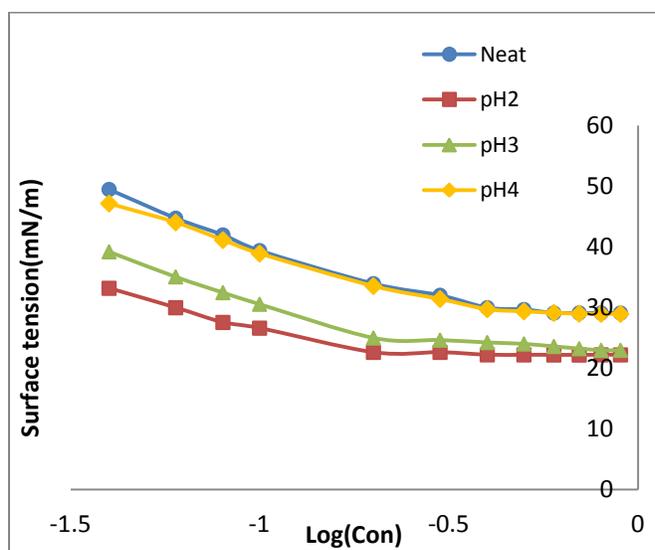


Table 3. CMC values of SLES 2EO after hydrolysis about 300hrs, at 50°C

Sample	CMC (mM)	Surface Tension at CMC(mN/m)
Neat SLES	0.4	30.01
pH4	0.4	22.93
pH3	0.2	24.66
pH2	0.2	29.45

Fig 16: Plot of surface tension vs. Log (Concentration)

3.10 Effect of Hydrolysis on the phase behavior of surfactants

Hydrolysis leads to changes in phase behavior of surfactants system. Most of surfactant systems could not proceed to complete hydrolysis, because of the phase change of the surfactant systems to liquid-crystalline phase, induced by the reaction product such as dodecanol and dodecyl ethers. We make some general observations concerning the optical microscope technique. Before hydrolysis all surfactants systems

were in concentrated micellar state exhibiting viscous isotropic mesophases. Upon hydrolysis a regular increase in viscosity of sample solutions has observed. This is due to increase in dodecanol concentration with hydrolysis. Presence of dodecanol leads to phase change to lamellar phase at water concentration higher than normal. Optical microscopic images of SLS, SLES1EO and SLES 2EO sample solutions collected after 324 hrs of hydrolysis under same reaction conditions (Initial p^H 2, temperature $50^{\circ}C$) are shown in fig 17. Initially all the surfactant solutions were in isotropic phase .Microscopic images of hydrolyzed SLS samples exhibited crystalline phase where as SLES 1EO and SLES 2EO samples displayed lamellar phase . Dodecanol concentration in of SLES 1EO and SLES 2EO samples hydrolyzed under above mentioned conditions is 0.219M and 0.209 M respectively. In presence of approximately same amount of dodecanol SLES1EO and SLES 2O displayed prominent lamellar phase. SLES showed an increase in lamellar arrangements with increase in percentage hydrolysis Even though hydrolyzed SLS samples have almost same dodecanol concentration (0.26 M) as SLES samples, they exhibited crystal structures under microscope. This might be due to the difference in degradation products of SLS and SLES.

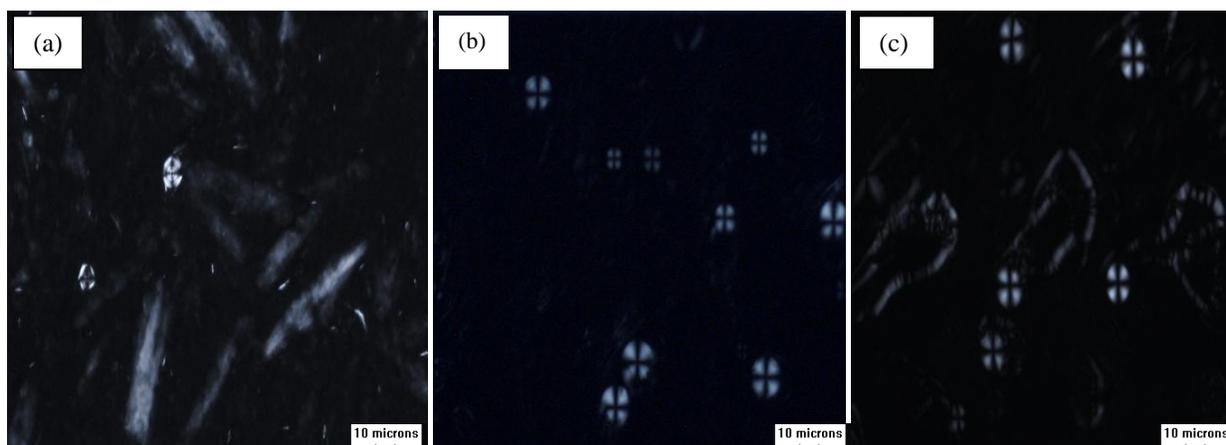


Fig 17 Microscopic images of partially hydrolyzed surfactant solutions (initial p^H 2, Temperature $50^{\circ}C$,Time 324 hrs, (a)SLS(crystalline) (b) SLES 1EO(lamellar) (c) SLES 2EO(lamellar)

4. Conclusions

Based on the above work, the following conclusions can be made.

1. The kinetics of hydrolysis of SLES is a function of pH and the kinetics of degradation is really slow above pH 4. The rate constants for hydrolysis at various pHs have been determined.
2. Number of ethoxylate groups influences the rate of hydrolysis, especially at low temperatures. Higher ethoxylation leads to faster hydrolysis.
3. Hydrolysis of SLES slows down after a certain degree of hydrolysis as the viscosity of the reaction mass increases due to phase changes in the surfactant system.
4. Buffers help in reducing the kinetics of hydrolysis in SLES. Low molecular weight organic acids like citric acid were found to reduce the kinetics of hydrolysis due to its buffering action. Added electrolytes also help in reducing the kinetics of hydrolysis. No significant influence of the hydrotope was observed on the degradation kinetics.
5. The hydrolysis of SLES leads to generation of dodecanol or dodecanol ethers leading to change interfacial properties. Lower surface tension is observed due to the presence of dodecanol at the interface.
6. The hydrolysis leads to phase change in SLES. The isotropic solution transforms to lamellar phase and increases in viscosity.

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