THE STABILITY STUDY OF MYRISTYL DIMETHYL AMINE OXIDE AS AN AMPHOTERIC SURFACTANT IN STRONG OXIDANT MEDIA CONTAINING 5 % M/M SODIUM HYPOCHLORITE THROUGH MEASUREMENT OF DECOMPOSING RATE USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AND TWO PHASE TITRATION

A. Gholami*, M. H. Taghriri

Department of Analytical Chemistry, Faculty of Chemistry, University of Kashan, Kashan P.O. Box 87317-51167, Iran

ABSTRACT

Myristyl dimethyl amine oxide is a surface-active agent (surfactant) that has been used in recent years widely in detergent industry as the foaming agent and a viscousing agent. Although this type of surfactants are very stable, however, in some specific chemical media such as strong acid and alkaline cleaners, oxidant media containing sodium hypochlorite may not have sufficient stability. In this study, we will study the effective variables on the decomposition of mirystyl dimethyl amine oxide surfactant with trading name of "Ammonyx" and obtain the rate constant and reaction order of decomposition reaction of the surfactant in specific chemical media for each of these variables and finally the rate law of decomposition. The results of this study show that the decomposition rate of the Ammonyx surfactant to the concentration of NaOH is first-order and the rate constants at three temperatures to 4, 20 and 47 degrees of Celsius are 1.8655×10^{-4}, 2.7548×10^{-4} and 4.3294×10^{-4} hr^{-1} respectively. The Ammonyx surfactants decomposition rate relative to the NaClO concentration is first-order and the rate constant in the three mentioned temperatures is 3.4682×10^{-4}, 4.9251×10^{-4} and 7.2582×10^{-4} hr^{-1} respectively.

Finally, the decomposition rate of Ammonyx relative to surfactant concentration (like other two variables) is first-order and the rate constant at above temperatures equal to 1.6892×10^{-4}, 3.2205×10^{-4} and 5.8045×10^{-4} hr^{-1} respectively.

The activation energy for the decomposition of Ammonyx in collision with NaOH, NaClO and the surfactant molecules equals to 14.3, 12.55, 20.85 kJ mol and Arrhenius constants for these molecules equals to 0.0975 hr^{-1}, 0.0823 hr^{-1} and 0.6542 hr^{-1} respectively.

In addition, for comparing the accuracy of the two-phase titration results, high performance liquid chromatography HPLC method has also been used. For this purpose, surfactant concentrations in some samples under study were also measured by using analytical HPLC system. The results showed that two-phase titration data have good agreement with HPLC data but chromatography has less accuracy and precision from two phase titration method.

Keywords: Myristyl dimethyl amine oxide, Two-phase titration, Reaction rate, Reaction order, surfactant analysis, Bleaching agents

1. INTRODUCTION

Analytical Chemistry deals with the procedures for determining the amount of a chemical compound in mixed samples. Qualitative methods present information about chemical species present in the sample. In contrast, quantitative methods provide numerical information about the species present in sample. Analytical methods are often classified into two groups: Classical analysis and Instrumental analysis. According to this classification, it is primarily historical.

In the classical methods, analysis often will be done with separating components in a sample through precipitating, extraction or distillation. Then in order to do qualitative analysis, the isolated components will react with specific reagents to recognize their products by color, melting and boiling points, solubility in a series of solvents, odors and chemical activity. For quantitative analysis, the amount of analyte will be determined by gravimetric or titrimetric measurements.

Around 1930, in order to solve analytical problems, chemists began to exploit the phenomena other than classical methods. Thus, the use of physico-chemical properties such as conductivity, electrode potential, absorption or emission of light, the mass-to-charge ratio and fluorescent for quantitative analysis of a variety of inorganic, organic and biological samples began. In addition, efficient chromatographic separation techniques began to replace distillation, extraction and

deposition to separate components of complex mixtures before their quantitative and qualitative determination. The newer methods for separating and measuring the amount of chemical species called the instrumental methods. Many phenomena that instrumental methods have been built based on them have been known for a century or more. However, use of these methods by chemists was delayed due to the lack of reliable and simple instruments. In fact, the development of new instrumentation analysis methods is done in parallel with the development of electronics industry and computers. Develop and improve the analytical methods to get the accurate analytical results and saving time and costs, are the main tasks of analytical chemists.

In analytical chemistry, instrumental methods act as catalyst that provides the possibility to communicate quickly between theoretical and applied principles [1].

Surface-active agents that called surfactant are the compounds that are widely used today, in abundance, in the production of detergents and both public and private hygiene products. When, surface-active molecule enters in water, the molecules orient in ways that their hydrocarbon chain disposed toward the top surface and the hydrophilic parts placed in an aqueous solution. Other molecules are dispersed among the water molecules. The specific structure of surface-active agents causes high solubility of these compounds in various solvents, and their unique properties, such as high tendency of these compounds to be at the intersection of liquid-liquid, solid-liquid, liquid-gas and the formation of an electric double layer at the interface the tendency to form a micelle, which provides high cleaning power[2,3].

Properties of surface-active agent will be determined in two parts of hydrophilic and hydrophobic of them, and any surface-active agent, according to the nature of the two parts, has properties and applications of its own. Properties such as solubility, reducing of surface tension, critical micelle concentration (CMC), cleansing power, wetting power and foaming capacity are including the properties that make a surface-active agent suitable for the specific application and unsuitable for other applications [4, 5].

Among the thousands of surfactants produced and used, Myristyl dimethyl amine oxide with trade name "Ammonyx" is a kind of amphoteric surfactants that has found wide application in detergents and personal hygiene today. This surfactant is used as a lubricant in the textile industry. Ammonyx structure is as follows: IUPAC name Ammonyx, N and -N dimethyl Tetradecane 1-amine oxide and it is also known as Tetradecane dimethyl amine oxide (TDAO). The structure is two ionic salt structures that in its natural form, it has more nonionic properties

of a material. There are varieties of applications of these surfactants in various industries. These compounds are used as wetting, anti-spark and softener in the textile industry and cleaner in detergent industry and many other uses [6-8].

In synthesizing of Ammonyx, first, the N and N - dimethyl dodecyl amine, t-butyl hydroperoxide and vanadium oxy-acetylacetone are placed adjacent to each other in a suitable reactor side by side. Then the reactor is heated up to a temperature 65-70 ^{0}C so that the exothermic reaction started. Then the heating is stopped so that highly exothermic reaction subsided. The reaction mixture in the distillation column will be distilled at 90 temperatures and the product obtained from the column is cooled to ambient temperature. The reason for distillation is removing excess t-butyl hydroperoxide. Then, it will be soft by anhydrous diethyl ether, and filtering operation is performed under conditions so that to avoid the exposure of the remaining amine oxide to air. Finally, it is washed with ether without water under vacuum and dried [9-12].

Ammonyx is used as a viscosing agent and foam booster in cosmetic-health products. This surfactant is very gentle, soft and non-toxic for the skin and does not cause allergies. To measure these amphoteric surfactants, various methods are used such as chromatography and two-phase titration [13, 14].

High performance liquid chromatography HPLC is very popular method because of the sensitivity, easy adjustment for accurate quantitative measurements, and its suitability for separation of non-volatile or unstable thermal and foremost. It is widely used for materials that are very important in the industry, various fields of science and society. High performance liquid chromatography has been widely used to isolate and measure surfactants [15].

In the two-phase titration method, the measurement is based on the belief that anionic surfactants and soaps will combine with cationic surfactants to create an ions pair insoluble in water. The ions pair immediately is extracted into the organic solvent non-miscible with water. The fundamental reaction is the basis for the equivalent titration of ionic surfactants with a standard solution of the surfactant with opposite charge in the two-phase titration. This process will be completed with intense shaking of two water and organic phase mixture [16, 17].

Amphoteric surfactants Myristyl dimethyl amine oxide (Ammonyx) is a cationic surfactant in an acidic media and can be titrated by sodium dodecyl sulfate (SDS) 0.004 F. At the equivalence point, the color of chloroform organic phase will change from blue to opaque pink.

A large number of organic dyes are used as an indicator in the two-phase titration. Methylene blue is the most common cationic dye. This dye is in single form in water. In titration that methylene blue is used, end point detection is difficult. The chloride and other anions create nuisance. However, by methylene blue, anionic surfactants in sewage, soil and surface water (even Sediments) can be measured [18- 29].

In this study, the desired surfactant that is an amine oxide will be used in a very strong oxidizing sodium hypochlorite media, along with other influential variables. Experimental results show that some properties of formulated product such as viscosity, surfactant percent and the percentage of oxidant, change after the time. The main objective of this research is to determine whether the Myristyl dimethyl amine oxide decomposes in these particular products. In addition, if it decomposes, how fast does this occur and what effect do the environmental variables such as temperature, pH and concentration of oxidizing media have on the rate of decomposition? On the other hand, how are the reaction laws that represent the rate of decomposition of surfactant? As well as, how do the B-side environment variables appear in the decomposition rate equation?

2. EXPERIMENTAL

2.1 Apparatus and reagents

Table 1. Apparatus

Row	Device name	Model	Manufacturer	Manufacturing Country
1	High performance liquid chromatography	Crystal 200	ATI-UNICAM	England

Table 2. Characteristics of chemicals used in this study

Row	Chemical	Chemical formula	Purity	Manufacturer	Manufacturing Country
1	Myrystyl dimethyl amine oxide (Ammonyx)	$C_{16}H_{36}NO$	25%	Indigo phenomenon chemistry	Korea
2	Sodium hypochlorite	$NaOCl$	12%	lran	Iran
3	Sodium hydroxide	$NaOH$	99.9%	Merck	Germany
4	Concentrated sulfuric acid	H_2SO_4	98%	Merck	Germany
5	Dimidium bromide	$C_{20}H_{18}BrN_3$	95%	Merck	Germany
6	Disulfin Blu	$C_{27}H_{31}N_2NaO_6S_2$	99%	Merck	Germany
7	Chloroform	$CHCl_3$	99.9%	Merck	Iran
8	Hayamyn 1622	$C_{27}H_{42}ClNO_2$	99%	Merck	Germany
9	Sodium thiosulfate	$Na_2S_2O_3$	99%	Merck	Germany
10	Potassium iodate	KIO_3	99.9%	Merck	Germany
11	Acetic acid	HOAC	Glacial	Merck	Germany
12	Phenolphthalein	C H O	85%	Merck	Germany
13	Starch	$(C_6H_{12}O_6)_n$	99.9%	Merck	Germany
14	Methanol (HPLC grade)	CH_3OH	100%	Merck	Germany
15	Acetonitrile (HPLC grade)	CH_3CN	100%	Merck	Germany

2.2. Obtaining of reaction law for decomposion of Ammonyx surfactant

Since the intended media is formed of three different chemicals, including Ammonyx (Myristyl dimethyl amine oxide), sodium hypochlorite and sodium hydroxide, it is expected that Ammonyx decomposition reaction be as follows:

$$a \text{ Ammonyx } + \text{ b NaClO } + \text{ c NaOH} \rightleftharpoons \text{Pr}oduct$$

The general rate law, related to above reaction, is defined as follows:

$$\text{Rate} = K \text{ [Ammonyx]}^x.[\text{NaOCl}]^y.[\text{NaOH}]^Z$$

Now, to investigate the decomposition rate of Ammonyx, in the presence of variables of Ammonyx, sodium hypochlorite and sodium hydroxide and to obtain the reaction order compared to any of the influencing variables from the 3 influencing factors, the concentrations of the two variables will be fixed at high amount and the concentrations of third variable will be changed at low amounts. Then, the rate of reaction will be measured to the third variable concentrations and from the results, the rate constant and reaction order is calculated. Similarly, in the next steps, the concentration of the two variables will be kept in the fixed large quantities and the concentrations of third variable will be changed in less quantity.

2.3. Obtaining of reaction rate relative to sodium hydroxide

In this section, the concentration of sodium hypochlorite and Ammonyx variables held constant and concentration of NaOH is changed:

$$\text{Rate}_1 = K[\text{NaOH}]^Z.[\text{NaOCl}]^y.[\text{Am}]^x \qquad \text{(Equ= 1)}$$

$$\text{When: } [\text{NaClO}]= [\text{Am}]= \text{Constant, then } K_1= K [\text{NaClO}]\times[\text{Am}] \qquad \text{(Equ.= 2)}$$

$$\text{Rate}_1= K_1 \times [\text{NaOH}]^z \qquad \text{(Equ= 3)}$$

$$\text{Ln Rate}_1 = LnK_1 + zLn[\text{NaOH}] \qquad \text{(Equ= 4)}$$

According to equation (4), the $LnRate_1$ curve can be obtained in terms of $Ln[NaOH]$. Slope of the curve results z (the reaction order) and intercept show the LnK_1.

In this step, 5 solutions containing three variables of Ammonyx, sodium hypochlorite and sodium hydroxide will be prepared in which the concentration of Ammonyx and sodium hypochlorite is kept constant (both 5.0 % m/m) and sodium hydroxide concentrations will be considered 0.1, 0.2, 0.3, 0.4 and 0.5 % w/w, respectively.

After preparation of these solutions, decomposition rate of Ammonyx relative to [NaOH] is checked in three temperature: Fridge temperature (4 ^{0}C), room temperature (20 ^{0}C)) and oven

temperature (47 ^{0}C). Prepared solutions will be divided into three parts and will be placed in 3 listed temperatures. Then, the concentration of NaOH is measured at various time intervals.

For measuring the concentration of sodium hydroxide in samples, the following method is used. 2.00 grams of samples were weighted and dissolved in water in a 100.0 ml volumetric flask. Then, 10.0 ml of this solution transferred to a beaker and while stirring slowly, added 10 ml H_2O_2 30 % m/m. Hydrogen peroxide breaks down NaClO to the chlorine gas. Then the solution is boiled for decomposition of excess H_2O_2. The solution is cooled to ambient temperature. Then 15 ml of 20 % m/m $BaCl_2$ solution and 2.0 ml of 0.1 % m/m Phenolphthalein indicator solution is added to the beaker and it is titrated with 0.10 F standard solution of HCl until disappearance of the pink color [20].

2.4. Obtaining of reaction rate relative to sodium hypochlorite

In this part of study, the Ammonyx surfactant and sodium hydroxide concentrations are kept constant and sodium hypochlorite concentration is changed:

$$\text{Rate}_2 = K[NaOH]^Z.[NaOCl]^y.[Am]^x \qquad \text{(Equ= 5)}$$

$$\text{When: } [NaOH]= [Am]= \text{Constant, then } K_2= K [NaOH]\times[Am] \qquad \text{(Equ.= 6)}$$

$$\text{Rate}_2= K_2 \times [NaClO]^y \qquad \text{(Equ= 7)}$$

$$\text{LnRate}_2= \text{LnK}_2 +y\text{Ln}[NaClO] \qquad \text{(Equ= 8)}$$

According to equation (8), the LnRate_2 curve can be obtained in terms of Ln[NaClO]. Slope of the curve results y (the reaction order) and intercept show LnK_2.

In the following, 5 solutions containing three variables of Ammonyx, sodium hypochlorite and sodium hydroxide will be prepared in which the concentration of Ammonyx and sodium hydroxide is kept constant (both 5.0 % m/m) and sodium hypochlorite concentrations will be considered 0.1, 0.2, 0.3, 0.4 and 0.5 % w/w, respectively.

After preparation of these solutions, decomposition rate of Ammonyx relative to [NaClO] is checked in three temperatures: Fridge temperature (4 ^{0}C), room temperature (20 ^{0}C)) and oven temperature (47 ^{0}C). Prepared solutions will be divided into three parts and will be placed in 3 listed temperatures. Then, the concentration of NaClO is measured at various time intervals. The sodium hypochlorite measuring method is as follows:

2-3 grams of potassium iodide KI, are dissolved in 50 ml distilled water in a beaker and 10 ml Concentrated acetic acid (glacial) is added. Now 10 ± 0.1 ml of sample solution is added to the beaker. Then, the resulting solution is kept for 15 minutes in a dark place and titrated with a 0.1

N standard solution of sodium thiosulfate $Na_2S_2O_3$, until create a light yellow color. At this stage, 1.0 ml of starch solution (freshly Prepared) was added to the solution and titration continues to disappearance of the blue color [25].

2.5. Obtaining of reaction rate relative to Ammonyx surfactant

In this part, the concentrations of sodium hypochlorite and sodium, hydroxide is kept constant and Ammonyx concentration is changed:

$$Rate_3 = K[NaOH]^Z.[NaOCl]^y.[Am]^x \qquad (Equ= 9)$$

When: $[NaOH]= [NaClO]=$ Constant, then $K_3= K [NaOH]\times[NaClO]$ $\qquad$ (Equ.= 10)

$$Rate_3= K_3\times [Am]^x \qquad (Equ= 11)$$

$$LnRat_3= LnK_3 +xLn[Am] \qquad (Equ= 12)$$

According to equation (12), the $LnRate_3$ curve can be drawn in terms of $Ln[Am]$. As a result, the slope of the curve x, (the reaction rate to Ammonyx) and intercept give the LnK_3.

In the following, 5 solutions will be prepared in which the concentration of sodium hypochlorite and sodium hydroxide is kept constant in 5.0 % m/m and the Ammonyx concentrations will be considered 0.1, 0.2, 0.3, 0.4 and 0.5% m/m, respectively.

After preparation of these solutions, decomposition rate of Ammonyx is checked in three temperatures: Fridge temperature (4 ^{0}C), room temperature (20 ^{0}C)) and oven temperature (47 ^{0}C). Prepared solutions will be divided into three parts and will be placed in 3 listed temperatures. Then, the concentration of Ammonyx surfactant is measured at various time intervals. The method for surfactant measurement is as follows:

2.5.1. Measurement of Ammonyx concentration with two-phase titration method

To measure Ammonyx in the sample solution, 5.00 grams of the sample are weighted and is reached to 100.0 ml in a volumetric flask with distilled water. Then, 10.0 ml of this solution is reached to 100.0 ml in another flask. Now, 30.0 ml of this solution is added to a graduated cylinder with lid. Then, about 15 to 20 drops of sulfuric acid 2.0 N are added. After adding sulfuric acid, 10 ml of chloroform and 10 ml of mixed indicator solution is added and shaked well until the organic phase be blue. Then, it is titrated with a 0.004 F standard solution of sodium dodecyl sulfate, SDS surfactant [17].

After each adding of SDS solution, the mixture is shaken vigorously so that the reaction products are extracted into the organic phase. The endpoint of titration is the color changes of organic phase from blue to gray.

2.5.2. Measurement of Ammonyx concentration with high-performance liquid chromatography

To separation and measurement of molecules by high-performance liquid chromatography, the instrumental parameter must be determined and optimized. HPLC solvents that are used for mobile phase must be from HPLC grade. In this study, the mobile phase for separation of Ammonyx as an amphoteric surfactant is acetonitrile solvent that buffered with ammonium acetate 0.1 M at pH= 6.5. In the preparation of buffers, after dissolving Ammonium acetate in acetonitrile, the organic solvents should be passed through 0.45 micron filters, until they have no insoluble particles. After filtering, the mobile phase should be degassed, so that no air bubbles form under the working pressure. Otherwise, the retention time of peaks will not be the same. Although for the separation of surfactant compounds, the special column must be used, but due to the unavailability of the column, a non-polar column was used. The used column is a C-18 reverse phase column. The detector used is UV detector. For determining the wavelength of maximum absorbance ($_{max}$), a solution of Ammonyx will be placed in UV cell of spectrometer and absorption spectrum is obtained. $_{max}$ of the spectrum is equal to 220 nm. A suitable flow rate of 1000 μl/min has been selected that leads to a good separation in reasonable time [7].

2.5.2.1. Sample preparation for measuring with HPLC

For measuring the concentration of Ammonyx with HPLC technique, after injecting of sample into column and recording the chromatogram, the calibration curve will be plated. For this purpose, standard solutions of ammonyx with concentrations of 10, 20, 40, 60 and 80 ppm will be prepared from its commercial samples (with a concentration of 25 % m/m) and the pH will be set to 6.5 by ammonium acetate buffer. After setting the optimal instrument conditions, 10 μl of each standard solution is injected through loop of a 6-way valve and the chromatogram is obtained. The software calculates the peak area. Before injecting of sample, because the sample contain a strong oxidant (sodium hypochlorite) and may be damage column, the oxidant must be removed from the sample media.

To neutralize NaClO in the samples, H_2O_2 solution (30% m/m) is added to the sample solution. Hydrogen peroxide breaks down sodium hypochlorite into chlorine gas. For removing excess

hydrogen peroxide, samples boil for a few minutes to remove excess hydrogen peroxide [12]. To neutralize the alkality of the sample, a diluted solution of HCl will be used. Acid solution is added drop by drop to be neutralized. Neutral point is controlled by the pH meter [20].

After passing solvent with appropriate follow rate and adjustment of instrumental variables on the optimal values, each time 10 μl of sample is injected into the column and the chromatogram is obtained.

3. EXPERIMENTAL RESULTS

3.1. Obtaining of decomposition rate Law of Ammonyx relative to sodium hydroxide

The concentration of NaOH in samples placed in 3 temperatures was measured at 10 day intervals. Each measurement repeated 3 times. The results have been reported in Tables 3(4 ° C), Table 4 (20 ° C) and Table 5 (47 ° C):

Table 3. Change of NaOH concentration versus time at 4 °C

% m/m NaOH	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[NaOH]	Ln[Rate]
0.1	2.7604×10^{-5}	-2.3026	-10.4975
0.2	3.8750×10^{-5}	-1.6094	-10.1584
0.3	5.4167×10^{-5}	-1.2040	-9.8234
0.4	8.2390×10^{-5}	-0.9163	-9.4039
0.5	1.1250×10^{-4}	-0.6931	-9.0925

Table 4. Change of NaOH concentration versus time at 20 °C

% m/m NaOH	Decomposition rate (C_2-C_1/T_2-T_1)	Ln [NaOH]	Ln [Rate]
0.1	3.1345×10^{-5}	-2.3026	-10.3702
0.2	6.4175×10^{-5}	-1.6094	-9.6539
0.3	9.1650×10^{-5}	-1.2040	-9.2975
0.4	1.1469×10^{-4}	-0.9163	-9.0733
0.5	1.4250×10^{-4}	-0.6931	-8.8562

Table 5. Change of NaOH concentration versus time at 47 °C

% m/m NaOH	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[NaOH]	Ln[Rate]
0.1	4.3333×10^{-5}	-2.3026	-10.0466
0.2	8.6771×10^{-5}	-1.6094	-9.3522
0.3	1.1698×10^{-4}	-1.2040	-9.0535
0.4	1.8146×10^{-4}	-0.9163	-8.6145
0.5	2.1875×10^{-4}	-0.6931	-8.4276

Since the NaOCl and Ammonyx concentration is high, therefore concentration variation is negligible relative to [NaOH] and can be assumed to be constant in the reaction law.

Now, to obtain the reaction order and the rate constant K_1 relative to NaOH, following equation will be used.

$$\text{Ln Rate}_1 = \text{Ln}K_1 + z\,\text{Ln[NaOH]}$$

With drawing LnRate_1 in terms of Ln[NaOH], K_1 and z can be obtained. According to this equation, the slope of the plot is z and $\ln K_1$ is the intercept.

According to the data of Tables 3, 4 and 5, the plot of $\ln \text{Rate}_1$ based on Ln[NaOH] is obtained:
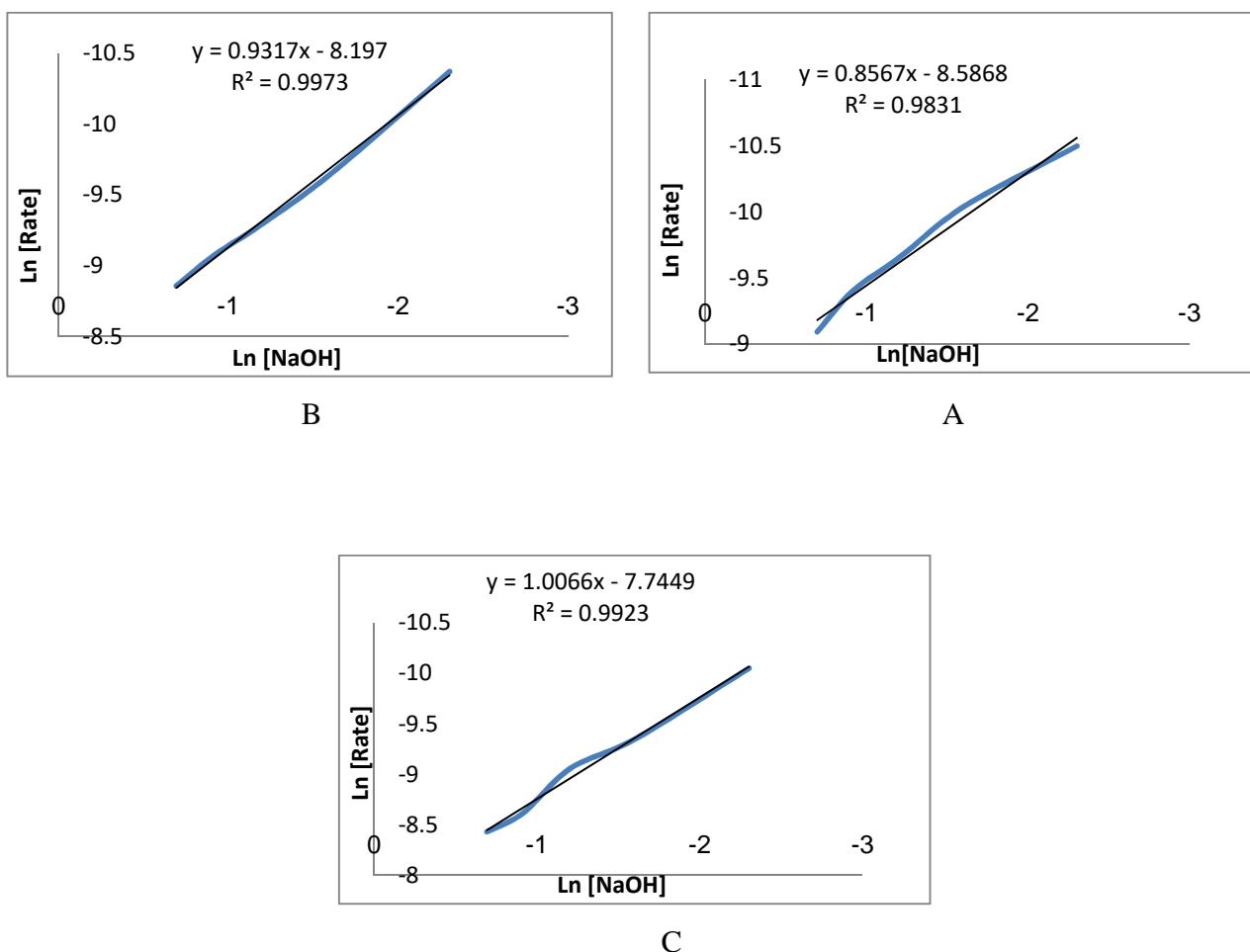
Fig.1. Plot Ln[Rate] in terms of Ln[NaOH] at three temperatures: A: fridge (4 ^{0}C), B: room temperature (20 ^{0}C) and C: oven temperature (47 ^{0}C)

As the results show, the reaction order z, in temperatures of 4, 20 and 47 ^{0}C is equal to 0.8567, 0.9317 and 1.0016. Since the order of reaction is independent of temperature and other laboratory variables, the differences in results are due to random error. The average number for reaction order relative to NaOH" equals to 0.93 and according to the rounding rules, the order of reaction will be approximately equal to 1 and this number is consistent with theoretical expectations that the order of reaction is an integer.

3.2. Obtaining the decomposition rate of Ammonyx relative to sodium hypochlorite

The concentration of NaClO in samples placed in 3 temperatures was measured at 10 day intervals. Each measurement repeated 3 times. The results have been reported in Tables 6 (4 ° C), Table 7 (20 ° C) and Table 8 (47 ° C):

Table 6. Change of NaOCl concentration versus time at 4 ° C

| % m/m NaOCl	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[NaOCl]	Ln[Rate$_2$]
0.1	7.0015×10^{-5}	-2.3026	-9.5668
0.2	1.0446×10^{-4}	-1.6094	-9.1667
0.3	1.3985×10^{-4}	-1.2040	-8.8749
0.4	1.8187×10^{-4}	-0.9163	-8.6122
0.5	2.2187×10^{-4}	-0.6931	-8.4134

Table 7. Change of NaOCl concentration versus time at 20 ° C

% m/m NaOCl	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[NaOCl]	Ln[Rate$_2$]
0.1	3.9364×10^{-5}	-2.3026	-10.1427
0.2	7.9875×10^{-5}	-1.6094	-9.4350
0.3	1.1521×10^{-4}	-1.2040	-9.0686
0.4	1.5646×10^{-4}	-0.9163	-8.7631
0.5	1.8896×10^{-4}	-0.6931	-8.5740

Table 8. Change of NaOCl concentration versus time at 47 ° C

% m/m NaOCl	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[NaOCl]	Ln[Rate$_2$]
0.1	8.8465×10^{-5}	-2.3026	-9.3329
0.2	1.2176×10^{-4}	-1.6094	-9.0134
0.3	1.9397×10^{-4}	-1.2040	-8.5478
0.4	2.7088×10^{-4}	-0.9163	-8.2138
0.5	4.6867×10^{-4}	-0.6931	-7.6656

Since the NaOH and Ammonyx concentration is high, therefore the variation of concentrations is negligible relative to variation of [NaClO] and can be assumed to be constant in the reaction law.

$$LnRate_2 = LnK_2 + yLn[NaClO]$$

According to the data of Tables 6, 7 and 8, the plot of $LnRate_2$ based on $Ln[NaClO]$ is obtained:
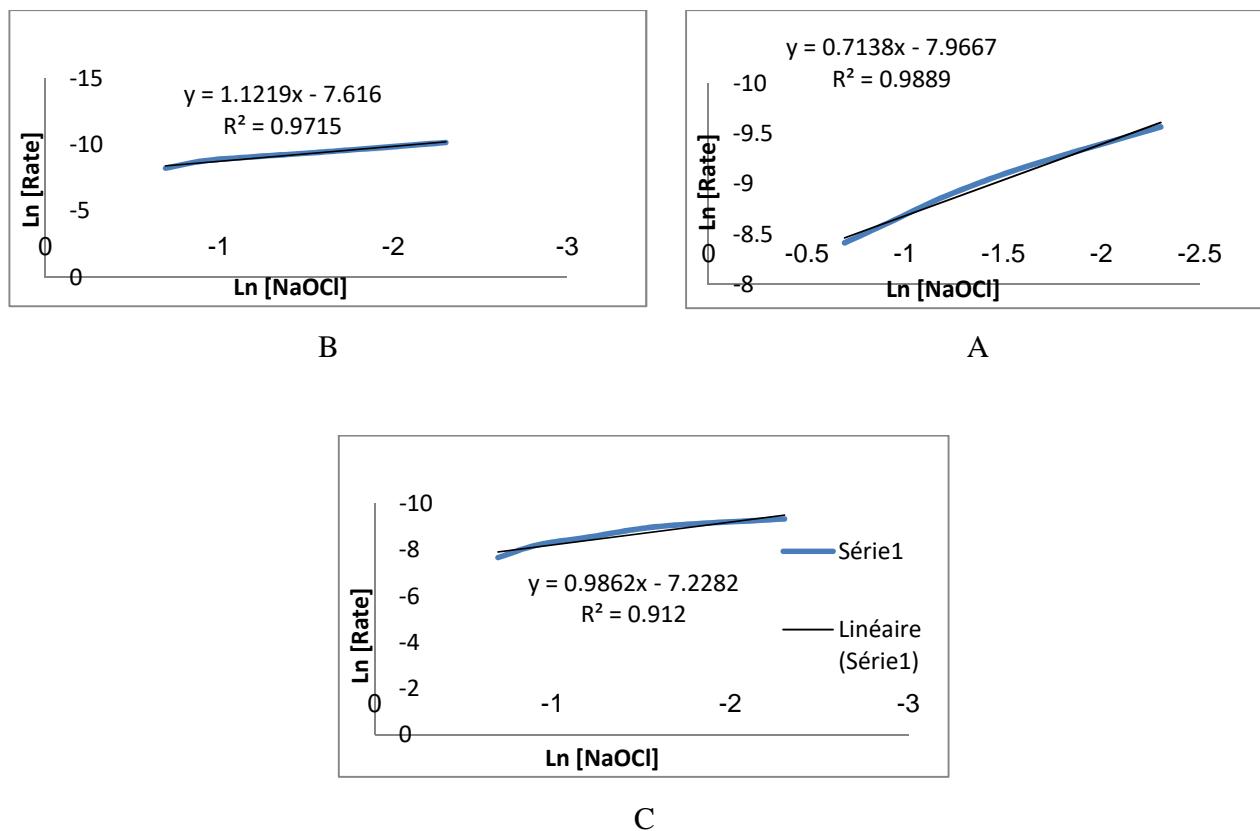
Fig.2. Plot of $Ln[Rate_2]$ in terms of $Ln[NaClO]$ at three temperatures: A: fridge (4 ^{0}C), B: room temperature (20 ^{0}C) and C: oven temperature (47 ^{0}C)

As experimental results show, the reaction order in three temperatures of 4, 20 and 47 ^{0}C is equal to 0.7138, 1.1219 and 0.9862. Since the order of reaction is independent from temperature and other laboratory variables, the differences in results are due to random errors. The average order of reaction compared to NaOH equals to 0.94 and according to the rounding rules, the order of reaction will be approximately equal to 1 and this number is consistent with theoretical expectations that the order of reaction is an integer.

3.3. Obtaining of decomposition rate law for Ammonyx surfactant

The concentration of Ammonyx in samples placed in 3 temperature was measured at 10 day intervals. Each measurement repeated 3 times. The results have been reported in Tables 9 (4 ° C), Table 10 (20 ° C) and Table11 (47 ° C):

Table 9. Change of Surfactant concentration versus time at 4 °C

| % m/m surfactant	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[Am]	Ln[Rate$_3$]
0.1	1.7604×10^{-5}	-2.3026	-10.9474
0.2	3.2917×10^{-5}	-1.6094	-10.3215
0.3	5.1032×10^{-5}	-1.2040	-9.8831
0.4	6.8229×10^{-5}	-0.9163	-9.5926
0.5	8.6354×10^{-5}	-0.6931	-9.3570

Table 10. Change of Surfactant concentration versus time at 20 °C

% m/m surfactant	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[Am]	Ln[Rate$_3$]
0.1	3.0417×10^{-5}	-2.3026	-10.4005
0.2	4.9375×10^{-5}	-1.6094	-9.9161
0.3	9.2083×10^{-5}	-1.2040	-9.2928
0.4	1.2344×10^{-4}	-0.9163	-8.9997
0.5	1.6094×10^{-4}	-0.6931	-8.7345

Table 11. Change of Surfactant concentration versus time at 47 °C

% m/m surfactant	Decomposition rate (C_2-C_1/T_2-T_1)	Ln[Am]	Ln[Rate$_3$]
0.1	2.3542×10^{-5}	-2.3026	-10.6567
0.2	5.4375×10^{-5}	-1.6094	-9.8196
0.3	8.6667×10^{-5}	-1.2040	-9.3534
0.4	1.1510×10^{-4}	-0.9163	-9.0697
0.5	1.3656×10^{-4}	-0.6931	-8.8987

Since NaOH and NaOCl concentration is high, in rate equation can be assumed to be constant:

$$LnRat_3 = LnK_3 + xLn[Am]$$

With drawing $LnRate_3$ in terms of Ln[Am], x and K_3 can be obtained. According to the data of Tables 9, 10 and 11, the curve $LnRate_3$ based on Ln[Am] is obtained:

B

A

C
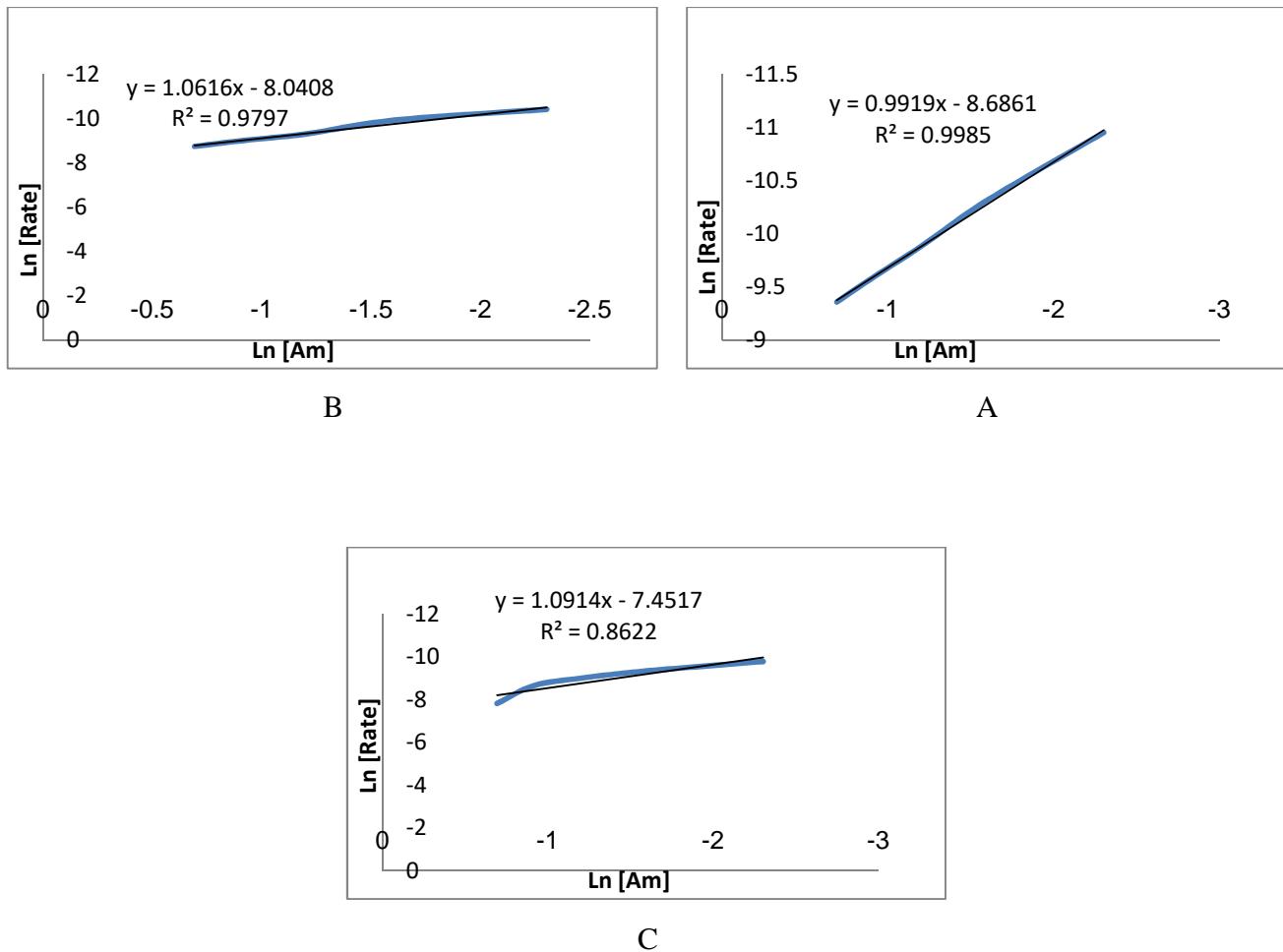
Fig.3. Plot of $LnRate_3$ in terms of Ln[Am] at three temperatures: A: fridge (4 ^{0}C), B: room temperature (20 ^{0}C) and C: oven temperature (47 ^{0}C)

As experimental results show, the reaction order in three temperatures of 4, 20 and 47 ^{0}C equal to 0.9919, 1.0616 and 1.0914. Since the order of reaction is independent from temperature and other laboratory variables, the differences in results are due to Random errors. The average order of reaction compared to Ammonyx equals to 1.045 and according to the rounding rules, the order of

reaction will be approximately equal to 1 and this number is consistent with theoretical expectations that the order of reaction is an integer.

3.4. Obtaining of Ammonyx concentration by high performance liquid chromatography

In HPLC analysis to prevent column saturation, the concentration of injected sample should not be high. Therefore, the unknown samples must be diluted to the necessary extent according to preliminary information that has been obtained from other methods. In this study, the surfactant concentration in real samples obtained by two-phase titration. Then, the sample was neutralized in accordance with the instructions in the paragraph 2-5-2-1 and with appropriate dilution; they are prepared for injection into the HPLC column. A certain volume (10 µl) of samples and then, standard solutions was injected into the column by a special syringe and the chromatogram obtained. Each injection is repeated three times.

From recorded chromatograms, the software obtains the peak area of each standard solutions ic obtained by softwear. The calibration curve that represents the peak area dependence in terms of surfactant concentration is shown in Figure 5.
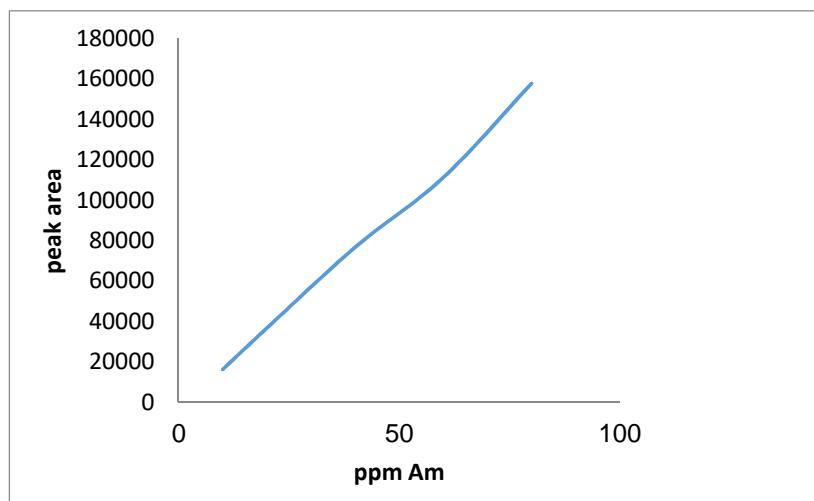
Fig.4. The Calibration curve for standard solution of Ammony

The equation:

$$Y= 1985.3X – 3763.5$$

Is best line for this plot. The correlation coefficient r, for the plot is 0.998 and shows that the curve follows the desired degree of linearity.

Peak area related to Ammonyx surfactant in one of the samples is as table 12:

Table 12. Peak area of Ammonyx in real sample

Repeat 1	Repeat 2	Repeat 3	Average
68055	68120	68355	68176.7

According to Equation:

$$Y=1985.3X – 3763.5$$

The average concentration of Ammonyx surfactant in real sample is 36.24 ppm

Determinations of surfactant concentration in one of the prepared samples (after 40 days) by two-phase titration show 0.3689 % m/m. The measurement of Ammonyx surfactant concentrations in the same sample, by HPLC method is 0.3624 % m/m. The results from two different methods are close together. By comparing the two measurements, one can conclude that the two-phase titration method can compete with the HPLC method because of its speed and accuracy.

3.5. Overall reaction order of Ammonyx decomposition

Before, the order of reaction and the rate constant of Ammonyx decomposition were obtained to the variables sodium hydroxide, sodium hypochlorite and Ammonyx at different temperatures. By using this information, the overall rate law of Ammonyx surfactant decomposition can be reported compared to all affecting variables in this environment:

$$\text{Rate}= K_1 \times K_2 \times K_3 \, [\text{Ammonyx}]^1 \times [\text{NaOH}]^1 \times [\text{NaClO}]^1$$

At three temperatures, 4, 20 and 47 °C, the decomposition rate of the surfactant Ammonyx obeys the following mathematical relationship compared to variables of the solution:

$$\text{Rate}_1 = 1.1 \times 10^{-11} \, [\text{Ammonyx}]^1 \times [\text{NaOH}]^1 \times [\text{NaClO}]^1 \quad (\text{at } 4 \,^0\text{C})$$

$$\text{Rate}_2 = 4.4 \times 10^{-11} \, [\text{Ammonyx}]^1 \times [\text{NaOH}]^1 \times [\text{NaClO}]^1 \quad (\text{at } 20 \,^0\text{C})$$

$$\text{Rate}_3 = 1.8 \times 10^{-10} \, [\text{Ammonyx}]^1 \times [\text{NaOH}]^1 \times [\text{NaClO}]^1 \quad (\text{at } 47 \,^0\text{C})$$

As expected, with increasing temperature, the rate constants increase. Now, by using these relationships, we can calculate the concentration of surfactant after a specified time.

3.6. Calculation of kinetical parameter such as activation energy and Arrhenius constant

Chemical reaction rate is a function of temperature and concentration. In most reactions, with increasing temperature, the rate increases, so the rate constants are strongly dependent on the temperature. This dependency is different in the various reactions. The best and the most

appropriate relationship between the rate constant of a reaction to temperature is presented by Arrhenius equation:

$$K = A. \exp(-E_a/RT)$$

K= Rate constant of reaction, hr^{-1}

A = Reaction frequency factor, hr^{-1}

E_a = Activation energy, $j.mol^{-1}$

R = Gas constant, $j.mol^{-1}.K^{-1}$

With plotting LnK versus 1/T, linear graph obtains that $-E_a/R$ is its slope and LnA is its intercept and E_a and A values can be calculated.

From the perspective of the kinetic theory, the activation energy (collision and transition state) is the energy barrier of reactant to product that the amount of energy depends on the type of reaction. In the decomposition reaction of Ammoyx in the presence of sodium hydroxide and sodium hypochlorite, as the temperature increases, the reaction rate constant increases with respect to each of the variables. With temperatures and rate constants, the activation energy of any of the three Ammoyx variables, sodium hypochlorite and sodium hydroxide is obtained.
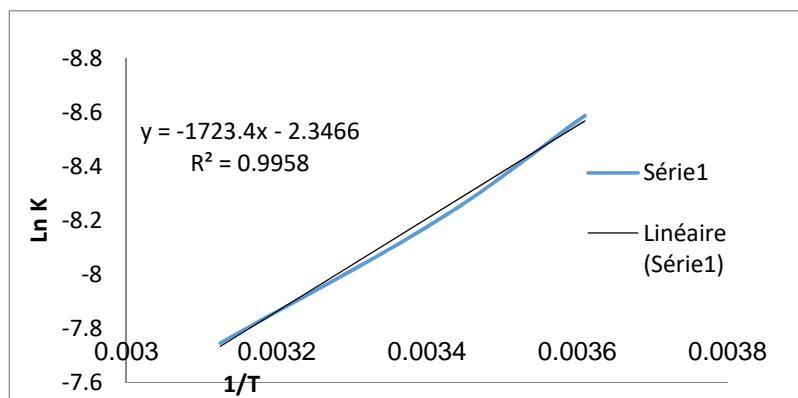
3.6.1 Kinetical parameters of the reaction caused by the collision with surfactant and sodium hydroxide

Given the rate constants obtained in the previous sections, the following table 13. can be adjusted:

Table 13. Rate constant and temperature of sodium hydroxide measurements

Temperature, ^0C	Rate constant, K_1	1/T, K^{-1}	LnK_1
4	1.8655×10^{-4}	3.6101×10^{-3}	-8.5868
20	2.7548×10^{-4}	3.4130×10^{-3}	-8.1970
47	4.3294×10^{-4}	3.125×10^{-3}	-7.7449

Based on above data, LnK_1 curves versus 1/T can be obtained:

Fig.5. LnK curves versus 1/T

According to Figure 5, the slope equal to -1723.4 that is the same $-E_a/R$ and the intercept is -2.3466 that are equal to LnA. According to the data, E_{a1} and A_1 is obtained:

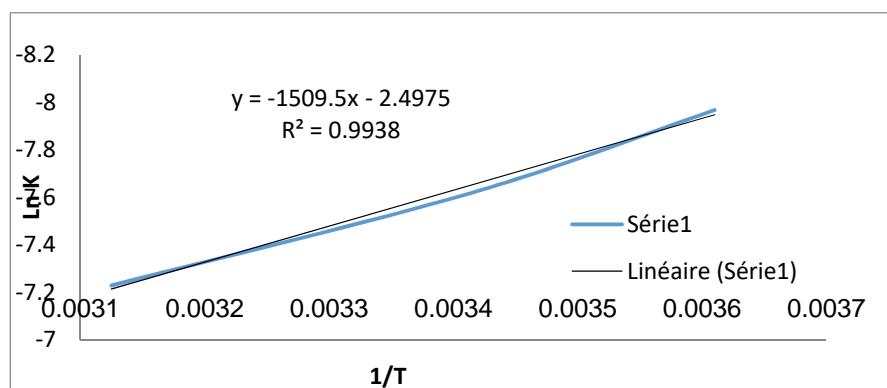$E_{a1} = 14328.35$ j.mol^{-1}

$A_1 = 2.66 \times 10^{-5}$ sec^{-1}

3.6.2. Kinetical parameters of the reaction caused by collision of surfactant with sodium hypochlorite

Given the rate constants obtained in the previous sections, the following table 14. can be adjusted:

Table 14. Rate constant and temperature of sodium hypochlorite measurements

Temperature, ^{0}C	Rate constant, K_2	1/T, K^{-1}	LnK$_2$
4	3.4682×10^{-4}	3.6101×10^{-3}	-7.9667
20	4.9251×10^{-4}	3.4130×10^{-3}	-7.6160
47	7.2582×10^{-4}	3.1250×10^{-3}	-7.2282

Based on the above data, LnK$_2$ curves versus 1/T can be obtained:

Fig.6. plot of LnK versus 1/T

According to Figure 6, the slope equal to -1509.5 that is the same $-E_a/R$ and the intercept is -2.4975 that are equal to LnA. According to the data, E_a and A is obtained:

$$E_{a2}= 12550 \text{ J.mol}^{-1}$$

$$A_2= 2.3\times10^{-5} \text{ sec}^{-1}$$

3.6.3. Kinetical parameters of the reaction caused by collision of surfactant with surfactant

Given the rate constants obtained in the previous sections, the following table 15. can be adjusted:

Table 15. Rate constant and temperature of Ammonyx

Temperature, ^{0}C	Rate constant, K_3	1/T, K^{-1}	LnK_3
4	1.6892×10^{-4}	3.6101×10^{-3}	-8.6861
20	3.2205×10^{-4}	3.4130×10^{-3}	-8.0408
47	5.8045×10^{-4}	3.125×10^{-3}	-7.4517

Based on the above data, LnK_3 curves versus 1/T can be obtained:
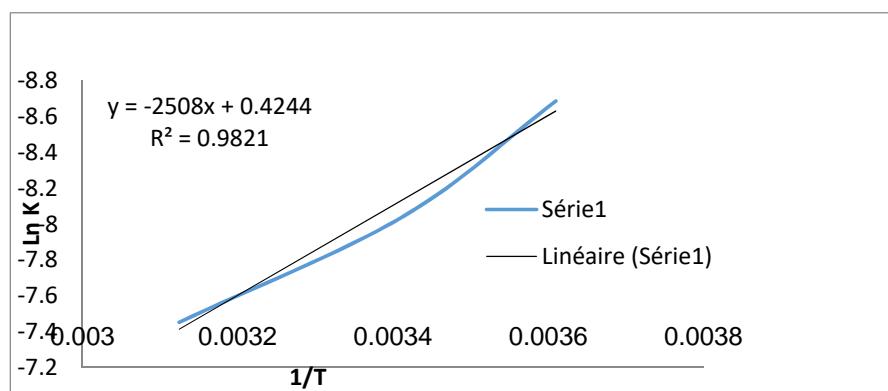
Fig.7. Ln K curves versus 1/T

According to Figure 7, the slope equal to -2508 that is the same $-E_a/R$ and the intercept is -0.4244 that are equal to LnA. According to the data, E_a and A is obtained:

$E_{a3} = 20851$ j.mol^{-1}

$A_3 = 1.8 \times 10^{-4}$ sec^{-1}

4. CONCLUSION

Obtaining the decomposition rate order of Mrystyl dimethyl amine oxide (Ammonyx) at different temperatures is important. With having the decomposition rate at different temperatures, the concentration of this substance in formulate products can be calculated versus time. In some products such as bleaching agents when the concentration of active ingredient will be lesser than an extent, the product loses its effectiveness property. For example, in medical products, when the concentration of active ingredient is less than the critical value, the medicine will be expired and these medications should not be consumed. By knowing the rate of destruction of a substance in a certain media, by adjusting the concentration, a certain life span can be determined for that product.

In this study, the rate of decomposition of a useful surfactant with chemical name Myristyl dimethyl amine oxide (Ammonyx) in a certain Home Care product that contains sodium hydroxide and sodium hypochlorite is studied. Since this product is exposed to different temperatures in winter and summer, the rate of decomposition of surfactant was examined in three different temperature 4 ^{0}C (Fridge temperature), 20 ^{0}C (room temperature) and 47 ^{0}C (oven temperature).

Experimental results show that the decomposition of the Ammonyx surfactant to NaOH is the first-order and the decomposition rate constant relative to the NaOH at mentioned temperatures are 1.8655×10^{-4}, 2.7548×10^{-4} and 4.3294×10^{-4} hr^{-1} respectively. The decomposition of Ammoyx surfactant to NaClO is first-order and the decomposition rate constant at mentioned temperatures are 3.4682×10^{-4}, 4.9251×10^{-4} and 7.2582×10^{-4} hr^{-1} respectively. Also, the decomposition of Ammonyx to the surfactant concentration is first-order and the decomposition rate constant at above temperatures are 1.6892×10^{-4}, 3.2205×10^{-4} and 5.8045×10^{-4} hr^{-1} respectively.

Since the measurement of rate constants is done in three different temperatures, by using the Arrhenius equation, chemical parameters such as activation energy and Arrhenius constant A can be obtained. The activation energy for decomposition of Ammonyx to NaOH and NaClO and the molecule are 14.3, 12.55, 20.85 kJ/mol and Arrhenius constant for the above are respectively 0.0957,0.0823 and 0.6542 hr^{-1} respectively,

By using high performance liquid chromatography, the Ammonyx concentration in the samples containing 0.5 % m/m was measured. By comparing the results of measurements by chromatography and two-phase titration, it was concluded that Ammonyx does not break into another surfactant, as well as the results of two phase titration are very close to the results of chromatography.

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