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Original Research Article

The Kinetic Study of Oleamide Synthesis: Effect of Oleic Acid Molar Ratio, Temperature and Catalyst Concentration

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ABSTRACT

Oleamide is amide derivative of oleic acid that is frequently used as slip agent in polymer industry. The present study explores the kinetic of oleamide synthesis by ammonolysis reaction between oleic acid and urea instead of ammonia gas at atmospheric pressure in the presence of AlCl_3 catalyst. The effect of oleic acid: urea molar ratio, temperature and catalyst concentration on the reaction kinetic was investigated and reaction rate constants were calculated. At low molar ratio of oleic acid:urea (i.e. up to 1:2), the reaction followed an overall second order kinetic and at higher molar ratio (i.e. 1:4 and 1:5), the pseudo first order dependence of rate respect to oleic acid was dominant at three examined temperatures and catalyst concentrations. The values of rate constant were increased by increasing the temperature and urea as well as AlCl_3 concentration in which the highest amount was attributed to the operational condition of oleic acid: urea molar ratio of 1:4, temperature of 200 °C and AlCl_3 catalyst concentration of 1 wt% that was selected as optimum condition for oleamide synthesis.

Keywords: Oleamide, Synthesis, Kinetic, Urea, Catalyst

Introduction

Primary fatty acid amides have numerous applications in industry as lubricant, detergent, corrosion inhibitor, anti-block and slip agent. These materials are used in polyolefin and polymeric films to decrease the coefficient of friction (CoF) or increase lubricity. Also, Fatty acid amides improve the scratch property of polymer surfaces by increasing the lubrication [1-4]. Oleamide (C-18, $C_{18}H_{35}NO$, amide of oleic acid) and erucamide (C-22, $C_{22}H_{43}NO$, amide of erucic acid) are two of the commonly used slip agents. Oleyl amide or 9-octadecenamide is another name of oleamide [5]. Each of oleamide and erucamide have unique property for industrial application. The melting point of erucamide is higher than that of oleamide and it has better thermal stability in application with higher temperature. On the other hand, oleamide is used in industries that need a low coefficient of friction in a short time [6-8].

There are several publications about the property and application of fatty acid amides in different industry [4,8,9-10]. Nevertheless, there is few studies about the synthesis of fatty acid amides in which most of them are based on the erucamide [11-13]. Moreover, the available results are not enough to investigate the reaction kinetic of other fatty acid amide, especially oleamide.

Oleamide is generally synthesized by ammonolysis reaction between oleic acid or its anhydride with ammonia gas at high temperature (200 °C) and pressure (345–690 kPa) [14-15]. Although, it can be biosynthesized from N-oleoylglycine [16].

The ammonolysis reaction has several drawbacks including low yield, harsh operation condition such as long reaction time and high pressure and temperature as well as high cost of raw material [17].

Hence, achieving to an appropriate synthesis method to overcome these drawbacks is necessary.

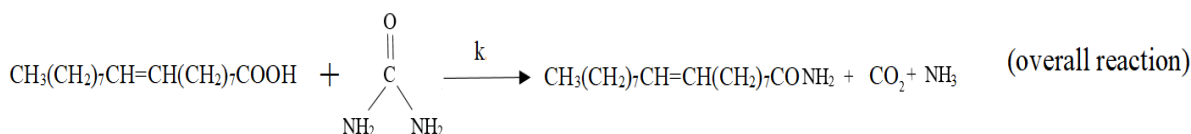
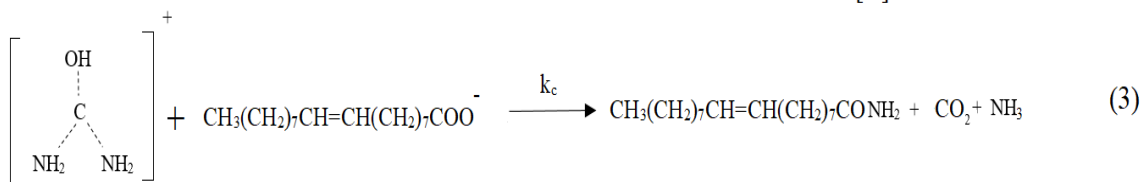
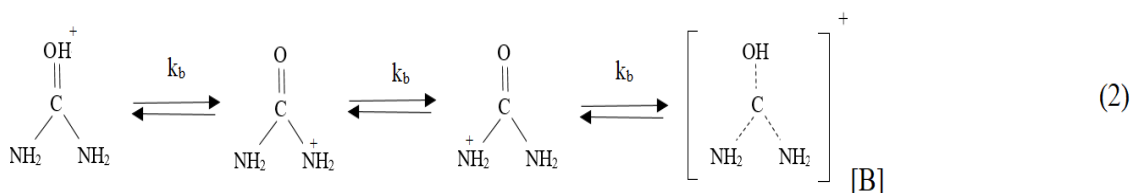
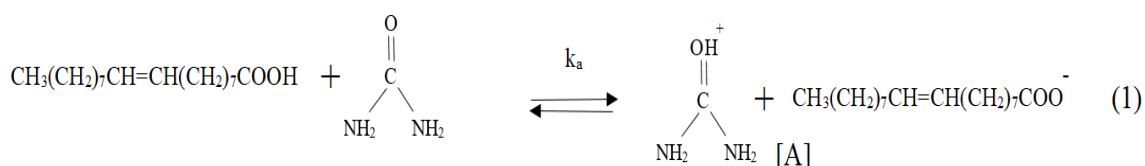
On the other hand, *reaction kinetics* studies are a main step of *research* and development for material production in *industries*. Kinetic investigation is crucial to understand the reaction rates and the parameters affect the speed of chemical reaction [18]. Consequently, it can help to select the optimized condition for achieving a maximum reaction yield.

In this paper, the ammonolysis reaction for oleamide synthesis is performed by oleic acid and urea instead of ammonia gas with $AlCl_3$ catalyst. The presence of urea and $AlCl_3$ catalyst allows the oleamide synthesis at mild operational condition (i.e., atmospheric pressure and short reaction time) with low cost that is attractive for industrial production. The aim of this work is to investigate the reaction kinetic of oleamide synthesis in the presence of catalyst. This paper

explains the effect of oleic acid:urea molar ratio, temperature and catalyst concentration on the kinetic of oleamide synthesis for the first time. It deals specially with kinetic data and furthermore gives some recommendations for the selection of the operation condition.

Theoretical: Kinetic studies

The synthesis reaction of oleamide from oleic acid and urea can be written as following reactions in scheme 1. As seen, urea is protonated by oleic acid [A] followed by rearrangement to intermediate structure of [B]. Then the reaction between oleic acid anion and [B] led to oleamide synthesis [19-20].



Scheme 1. The proposed mechanism for oleamide synthesis

Based on the proposed mechanism, the rate law can be defined as:

$$-\frac{d[\text{Oleic acid}]}{dt} = k_c [\text{RCOO}^-][\text{B}] \quad (1)$$

in which, the concentration of $[\text{RCOO}^-]$ is obtained from the first reaction in mechanism scheme:

$$k_a = \frac{[\text{RCOO}^-][\text{A}]}{[\text{oleic acid}][\text{urea}]} \rightarrow [\text{RCOO}^-] = \frac{K_a [\text{oleic acid}][\text{urea}]}{[\text{A}]} \quad (2)$$

Also, the concentration of [B] is calculated as following by using the second reaction in mechanism:

$$[B] = k_b [A] \quad (3)$$

Hence, by substituting the [RCOO⁻] and [B] in Eq. 1:

$$-\frac{d[\text{Oleic acid}]}{dt} = k_a k_b k_c [\text{oleic acid}][\text{urea}] = k[\text{oleic acid}][\text{urea}] \quad (4)$$

The reaction rate is overall second order. Also, it is first order with respect to each oleic acid and urea concentration. At low concentration of urea and with assumption of [urea] = n [oleic acid], the reaction rate can be rewritten as:

$$-\frac{d[\text{Oleic acid}]}{dt} = -\frac{d[\text{Urea}]}{dt} = k[\text{oleic acid}][\text{urea}] = kn [\text{oleic acid}]^2 \quad (5)$$

Hence, the reaction is second order respect to oleic acid concentration. By solving the Eq. 5, the time dependence of oleic acid concentration is obtained as:

$$\frac{1}{[\text{oleic acid}]} = knt + \frac{1}{[\text{oleic acid}]_0} \quad (6)$$

According to this equation a plot of 1/[oleic acid] versus time is linear.

However, at higher concentration of urea, (i.e. [urea] >> [oleic acid]), the overall reaction rate becomes first order and independent of urea concentration according to Eq. 7.

$$-\frac{d[\text{oleic acid}]}{dt} = -\frac{d[\text{urea}]}{dt} = k[\text{oleic acid}] \quad (7)$$

$$\log[\text{oleic acid}] = -kt + \log[\text{oleic acid}]_0 \quad (8)$$

At this condition the plot of log [oleic acid] versus time is linear with a negative slope.

Experimental

The synthesis of oleamide was carried out with different amount of oleic acid, urea and AlCl₃ catalyst in the reactor under stirring at 160, 180 and 200 °C for 3 h. The urea was decomposed to CO₂ and NH₃ gases at 140 °C and reacted with oleic acid to produce oleamide. Then, crude product was subjected to solvent extraction with chloroform subsequently purified with hexane, ethanol and acetonitrile.

To study the kinetic of reaction, several samples were withdrawn from the reaction mixture at different time and their acid values (AV) were measured. The acid value (AV) of the reaction

mixture was defined as the amount of KOH (mg) needed to neutralize of free acid in 1 g of sample.

$$AV = \frac{V_{eq} \times N \times 56.1}{W} \quad (9)$$

in which, N, V_{eq} , W and 56.1 are normality of KOH, titrant value, mass of the sample and molecular weight of KOH, respectively.

The kinetic of reaction was investigated at different oleic acid / urea molar ratio, temperature and catalyst concentration according to Table 1.

Table 1. operational condition for the synthesis of oleamide

Experiment number	Oleic acid / urea molar ratio	Temperature (°C)	Catalyst concentration (wt%)
1	1:1	200	1
2	1:2	200	1
3	1:4	200	1
4	1:5	200	1
5	1:4	160	1
6	1:4	180	1
7	1:4	200	0.4
8	1:4	200	0.8
9	1:4	200	1.2

Results and discussion

Effect of oleic acid: urea molar ratio

The plot of 1/acid value versus time for reaction mixture with oleic acid:urea molar ratio of 1:1 and 1:2 and log (acid value) versus time with oleic acid:urea molar ratio of 1:4 and 1:5 at 200 °C in the presence of 1wt% of $AlCl_3$ catalyst is shown in figure 1 and 2, respectively. As seen, at

oleic acid:urea molar ratio of 1:1 and 1:2, the plot of $1/\text{acid}$ value versus time is linear that confirmed the reaction has second order kinetic according to Eq. 6.

However, at higher oleic acid:urea molar ratio (i.e. 1:4 and 1:5), according to kinetic studies section and Eq. 8, the plot of $\log(\text{AV})$ versus time is linear (figure 2). These data indicate the pseudo-first order kinetic is dominant when $[\text{urea}] \gg [\text{fatty acid}]$.

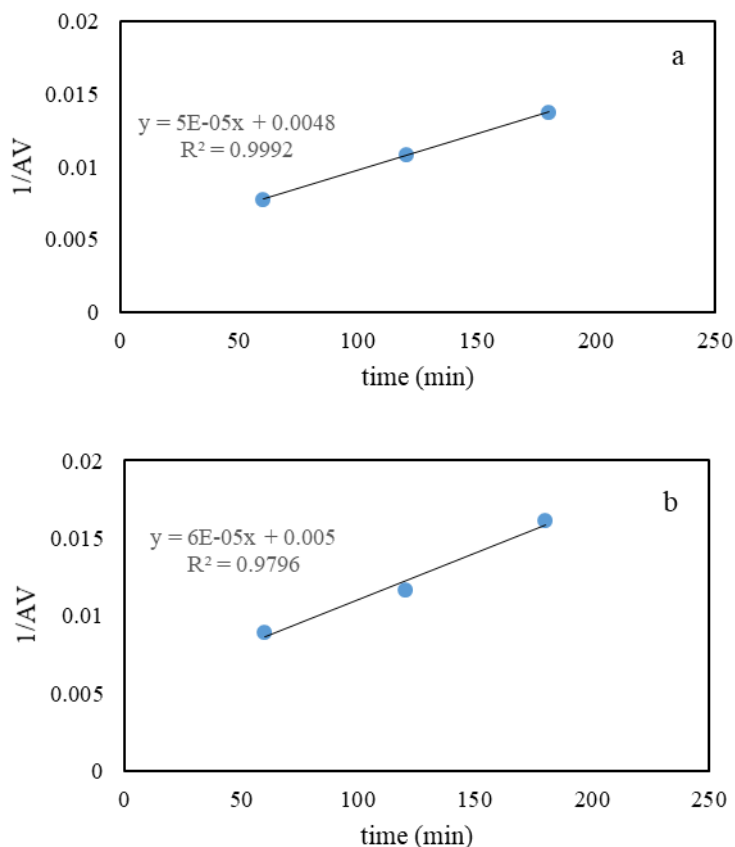


Figure 1. Plot of $1/\text{AV}$ versus time at 200 °C for reaction mixture with (a) 1:1 molar ratio of oleic acid:urea (b) 1:2 molar ratio of oleic acid:urea at 200 °C in the presence of 1 wt% AlCl_3

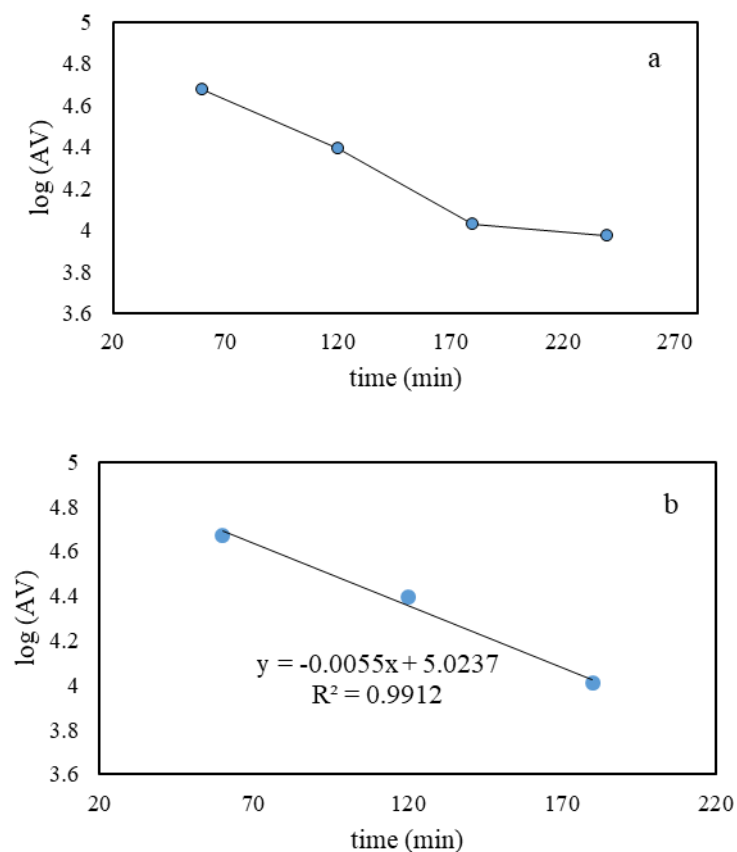


Figure 2. Plot of log (AV) versus time for reaction mixture with (a) 1:4 molar ratio of oleic acid:urea (b) 1:5 molar ratio of oleic acid:urea at 200 °C in the presence of 1 wt% AlCl₃

The rate constant values for oleamide synthesis were obtained from the slope of linear plot of $1/AV$ versus time for oleic acid/urea molar ratio of 1:1 and 1:2 (figure 1). Also, at higher molar ratio (i.e. 1:4 and 1:5), rate constants were calculated from the slope of linear plot of log (AV) versus time that are reported in table 2.

As seen by increasing the oleic acid:urea molar ratio from 1:1 up to 1:4, rate constant values were increased from 5×10^{-5} to 0.0054 min^{-1} that provide the reaction has faster rate at higher molar ratio. Although, further increase in oleic acid:urea molar ratio to 1:5 had no significant effect on the k value. Consequently, the 1:4 molar ratio was selected as optimum condition for oleamide synthesis.

Table 2. The rate constant value (k) of reaction at different oleic acid:urea molar ratio at 200 °C

Oleic acid : urea molar ratio	1:1	1:2	1:4	1:5
k (min ⁻¹)	5×10 ⁻⁵	6×10 ⁻⁵	0.0054	0.0055

Effect of temperature

The effect of temperature on the reaction kinetic of oleamide synthesis was studied at 160, 180 and 200 °C with optimum oleic acid:urea molar ratio of 1:4 in the presence of 1 wt% of AlCl₃ catalyst. Plot of log (AV) versus time at 160 and 180 °C is shown in figure 3. Also, the plot at 200°C was indicated at previous section (figure 2).

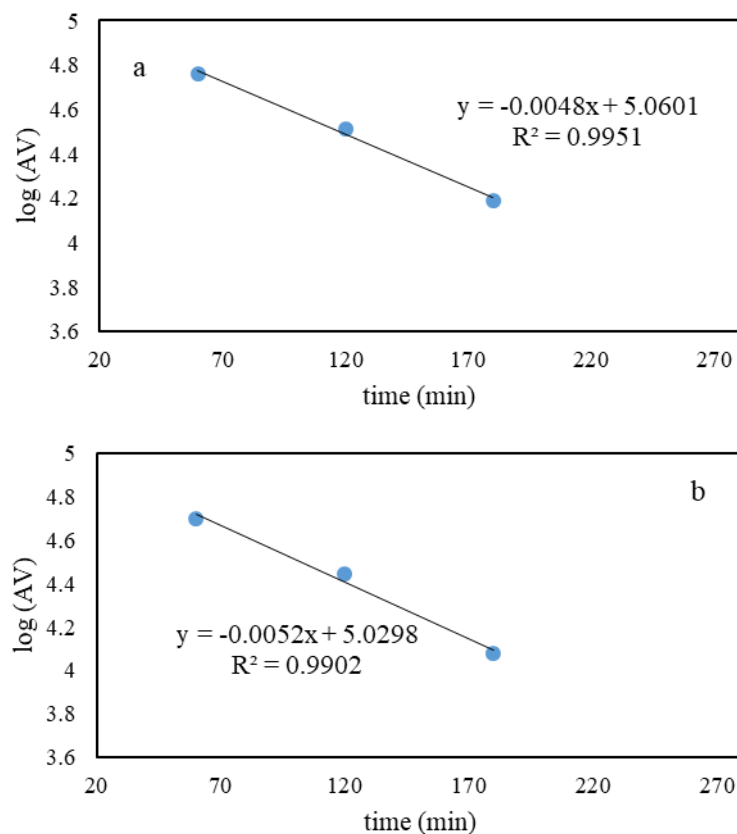


Figure 3. Plot of log (AV) versus time at (a) 160 °C and (b) 180 °C with 1:4 molar ratio of oleic acid:urea in the presence of 1 wt% of AlCl₃

As seen, the plots are linear with a negative slope. Consequently, based on the kinetic studies and Eq. 8, the reaction follows the pseudo first-order kinetic rate. k values were calculated from the slope of $\log(AV)$ versus time at different conditions of figure 3 and is reported in figure 4. As seen, the rate constant values of reaction are increased by increasing the temperature and reached to a maximum value of 0.0054 min^{-1} at $200 \text{ }^\circ\text{C}$.

The temperature dependency of rate constant can be studied by Arrhenius equation. This equation is a simple and accurate equation for the chemical reaction rate constant [21].

$$k = k_0 \exp\left(\frac{E_a}{RT}\right) \quad (10)$$

For this purpose, the activation energy (E_a) for oleamide synthesis was obtained from the Arrhenius equation by using the linear slope of the $\log(k)$ versus $1/T$ to be 95 KJ.mol^{-1} . This E_a value can be used for prediction the rate constant at other temperature in the ranges of $160\text{--}200^\circ\text{C}$.

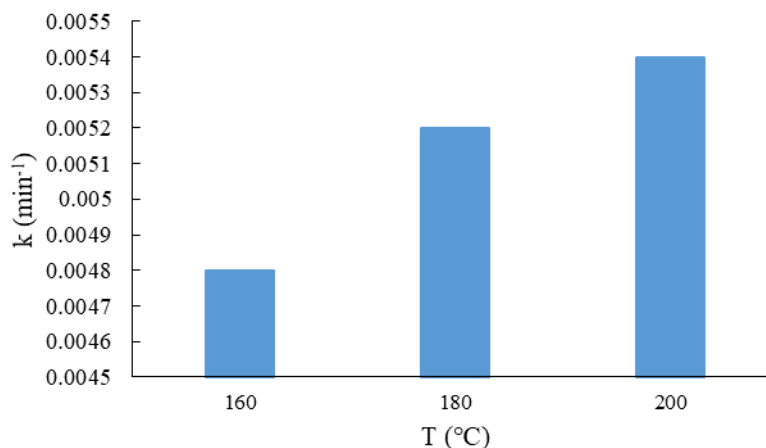


Figure 4. The effect of temperature on the rate constant (k) of reaction with 1:4 molar ratio of oleic acid:urea in the presence of 1 wt% AlCl_3

The effect of AlCl_3 catalyst concentration

The influence of AlCl_3 catalyst concentration on the reaction rate constant was evaluated by the oleamide synthesis at four different concentrations of AlCl_3 with 1:4 molar ratio of oleic acid:urea and temperature of $200 \text{ }^\circ\text{C}$. The plot of $\log(AV)$ versus time for 0.4, 0.8 and 1.2 wt% AlCl_3 concentration is shown in figure 5. Also, the plot for reaction mixture with 1 wt% AlCl_3 was

indicated at previous section (figure 2). As seen, the figures are linear and follow the pseudo first order kinetic based on the Eq. 8.

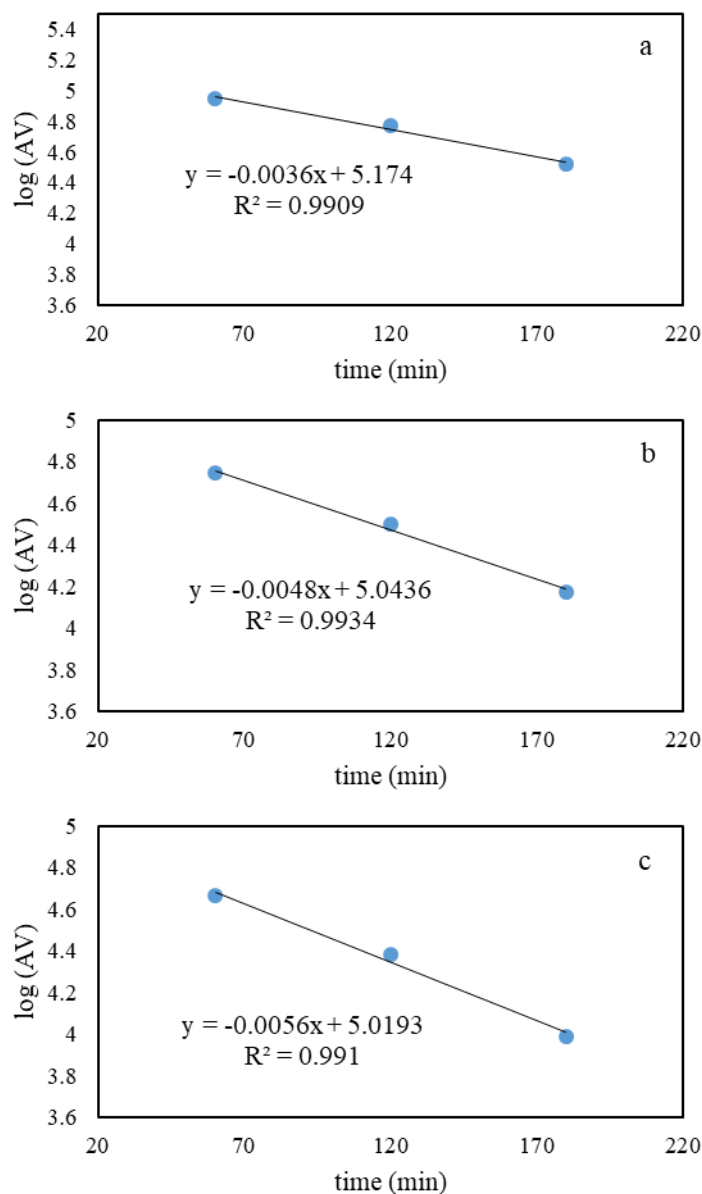


Figure 5. Plot of $\log(AV)$ versus time at (a) 0.4 wt%, (b) 0.8 wt% and (c) 1.2 wt% with 1:4 molar ratio of oleic acid:urea at 200 °C

The values of rate constant were obtained from the slop of $\log(AV)$ versus time at different catalyst concentration. The obtained rate constants are reported in figure 6. As seen, k values are increased by increasing the catalyst concentration up to 0.0054 min^{-1} for AlCl_3 concentration of 1

wt% and after that, further increase in AlCl_3 amount had no significant effect on the rate constant. Therefore, the AlCl_3 concentration of 1 wt% was considered as optimum value for oleamide synthesis.

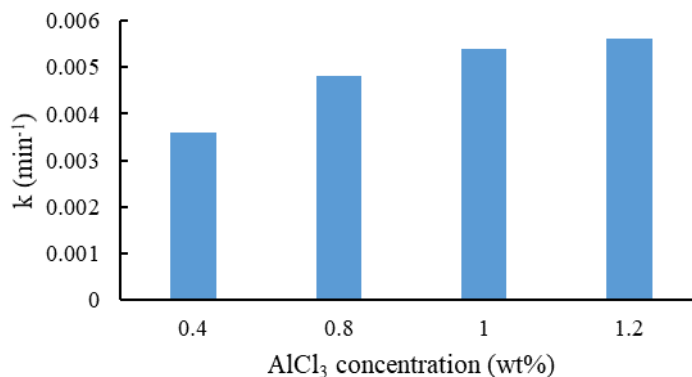


Figure 6. The effect of catalyst concentration on the rate constant (k) of reaction with 1:4 molar ratio of oleic acid:urea at 200 °C

Conclusion

Oleamide was synthesized by ammolytic process of oleic acid with urea in the presence of AlCl_3 catalyst. The effect of oleic acid:urea molar ratio, temperature and catalyst concentration on the reaction kinetic was studied and rate constants were calculated. It was found, at low oleic acid:urea molar ratio, the reaction rate followed the second order kinetic with first order dependence respect to urea and oleic acid concentration. However, by increasing the oleic acid:urea molar ratio to 1:4 in the reaction, the kinetic changed to pseudo-first-order at different time and catalyst concentration. The highest amount of rate constant was attributed to the operational condition of oleic acid: urea molar ratio of 1:4, temperature of 200 °C and AlCl_3 catalyst concentration of 1 wt% as optimum condition for oleamide synthesis.

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