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SYNTHESIS AND CHARACTERIZATION OF THE MONOETHANOLAMIDE FROM PALM OIL

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Palm monoethanolamide (PMEA) was synthesized by direct transamidation of palm oil with monoethanolamine at temperatures between 80-160°C. The maximum yield (85.5%) was achieved at a palm oil/ monoethanolamine mole ratio of 1:3, temperature of 160°C, reaction time of 3 hours and catalyst concentration of 0.6%. Recrystallization using a combination of hot hexane and warm water were the best conditions to purify the PMEA, as judged by its melting point and infrared (IR) spectrum. The PMEA was not soluble in water and most hydrocarbon solvents. However, about 60% of it dissolved in a microemulsion system containing 25% water at 50°C. The transamidation process proceeded via a first order reaction with an activation energy of 17.4kJ/mol.

INTRODUCTION

Fatty alkanolamides are nonionic surfactants of wide uses. Large quantities are used by the detergent, toiletry and cosmetic industries. Besides emulsifying properties, they can boost and stabilize foam. In some liquid formulations and lubricants, amides are used as a viscosity controller. In addition, alkanolamides are valued for their biodegradability. Some water-insoluble fatty alkanolamides such as lauric, myristic and stearic monoethanolamides (Burnette, 1966) are used as starting materials in the production of water-soluble polyoxyethylene amides (Jungermann and Taber, 1966). A number of reports on synthesis of fatty alkanolamides have been published (Farris, 1979; Knout and Richtler, 1985 and Fairheller *et al.*, 1994). In most studies, the alkanolamides were prepared by condensing fatty acids or fatty acid esters with various alkanolamines, namely mono- and

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diethanolamines. The yields varied with the mole ratios and reaction conditions used. Reaction temperatures of 150°-200°C and reaction times of 2 - 3 hours produced the highest yields (Shapiro, 1968). Various catalysts at different concentrations were used to improve the yield. Coconut oil was the most important feedstock studied, especially for the production of short and medium chain C_{8-14} fatty alkanolamides. In contrast, direct transamidation of palm oil, which contains long chain aliphatic acids, has not been investigated. The temptation of producing this surfactant from palm oil is great, considering the availability of palm oil as raw material. Furthermore, the coproduct, glycerol does not interfere with but acts as a desired liquifier for the alkanolamides.

In this study, we report the synthesis of nonionic surfactant, palm monoethanolamide, by direct transamidation of palm oil (PO) with monoethanolamine under various conditions using sodium methoxide as catalyst. Its solubility in pure solvents and microemulsion are also discussed.

EXPERIMENTAL PROCEDURES

Materials

Refined, bleached and deodorized (RBD) palm oil was obtained from Southern Edible Oil Industries, Klang, Malaysia. Sodium methoxide (1% solution) was prepared by dissolving 1.0 g sodium metal in 100 ml dry methanol. Monoethanolamine (MEA), sodium dodecyl sulphate (SDS), decane and hexanol were purchased from BDH. The water was deionised.

Preparation of Palm Monoethanolamide (PMEA)

Palm monoethanolamide (*i.e.* monoethanolamide derivative of palm fatty acids) was synthesized by reacting RBD palm oil with monoethanolamine under various conditions. The reaction was carried out in an oil bath under atmospheric pressure. The required amount of palm oil (10.0 g, 0.012 mole) was heated gradually to a desired temperature (from 80-160°C). After the temperature was reached, MEA (2.17ml, 0.036 mole) was added followed by the catalyst (3 ml, 0.3%). The reaction mixture was then refluxed in nitrogen to prevent the oil from oxidation. The completeness of the reaction was monitored by micro-TLC and IR spectra. During the reaction, samples of the mixture were taken every 30 minutes in the first 2 hours and every 60 minutes thereafter. For each sample, the infra-red spectrum, TLC chromatography and alkanolamide content were determined. The samples were spotted on TLC plates and developed in a mixture of n-hexane/ethyl acetate (85:15, v/v) plus one drop of acetic acid. The spots were visualized with iodine vapour. IR spectra were determined using a Perkin-Elmer 1600 spectrophotometer, either neat or in $CHCl_3$ solution. Disappearance of the palm oil carbonyl peak at 1734 cm^{-1} and appearance of an amide carbonyl peak at 1642 cm^{-1} were observed. The reaction was repeated by changing the following conditions: a) temperature, b) oil to MEA ratio, and c) catalyst concentration. The PMEA contents were determined after recrystallization of the crude product. Recrystalization was done by dissolving the crude monoethanolamide (3.0 g) in hot hexane (45°C, 100.0 cm^3) and the solution poured into warm water (45°C, 60.0 ml) and left overnight at room temperature. The crystals formed were filtered out, washed with cold hexane and dried in a desiccator under vacuum to a constant weight. The presence of monoethanolamide was confirmed by IR and ^{13}C -NMR spectroscopy.

Solubility in pure solvents

The solubility of PMEA in pure solvents was determined by adding the solvents drop by drop to 10.0 mg of monoethanolamide until a clear solution was observed. The solutions were vortexed for mixing and centrifuged to confirm the solubility. The volume of added solvent was recorded and the solubility expressed as mg/ml solvent.

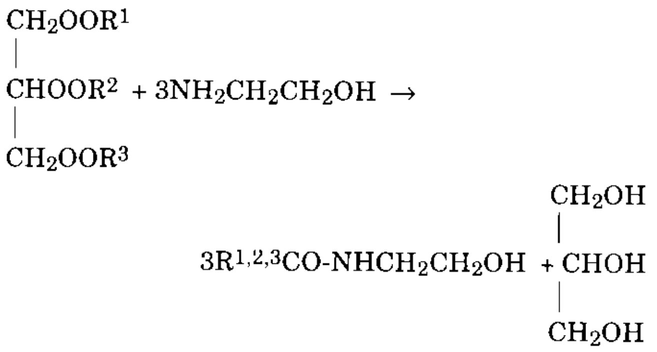
Solubility in microemulsion

Microemulsions are thermodynamically stable isotropic solutions containing a hydroacarbon and water, stabilized by either a single nonionic surfactant or by a combination of an ionic surfactant and cosurfactant. Microemulsions provide a large interfacial area between the hydrocarbon and water phases where solubilizates are dissolved. They are used as solvent for molecules weakly soluble or insoluble in pure solvents such as water. Among their applications are as solvents for dyes (Wortmuth *et al.*, 1990; Crower, 1987), carriers for flavours in vegetable oils (El-Nokaly, 1991) and solubility enhancers, for example, methanol in triglycerides (Dunn and Bagby, 1994) and water in alkanes (Aveyard *et al.*, 1992).

In this study, microemulsions were prepared by first mixing decanes with SDS/hexanol (65:35) mixtures to obtain solutions containing decane/SDS/hexanol (25:26:49 wt %). This ratio was found to incorporate the most water in a water/decane/SDS-hexanol system (Hamdan *et al.*, 1996). Subsequently, the required amounts of water were added to yield transparent isotropic solutions (microemulsions) of different water contents. The PMEA samples were then added to the microemulsions until permanent turbidity was observed.

RESULTS AND DISCUSSIONS

The transamidation reaction of palm oil with monoethanolamine was:



$$\begin{array}{l} CH_2OOR^1 \\ | \\ CHOOR^2 \\ | \\ CH_2OOR^3 \end{array} + 3NH_2CH_2CH_2OH \rightarrow 3R^{1,2,3}CO\text{-}NHCH_2CH_2OH + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

where R^1,R^2 and R^3 are the hydrocarbon moieties, varying from C_{12} - C_{18}. The progress of the reaction was followed by IR and micro-TLC. The IR spectrum was used to monitor the changes in the peaks at 1734 cm^{-1} (ester carbonyl) and 1642 cm^{-1} (amide carbonyl). The area ratio of the two carbonyls versus reaction time is shown in *Figure 1.* The ratio was almost constant after 3 hours of reaction. This suggests that formation of PMEA was at the maximum after 3 hours. *Figure 2* shows a typical result of TLC analysis of the reaction product. Traces of unreacted PO appeared on TLC even after 5 hours of reaction. Ethanolamine residue and glycerol were not separated and remained at the origin.

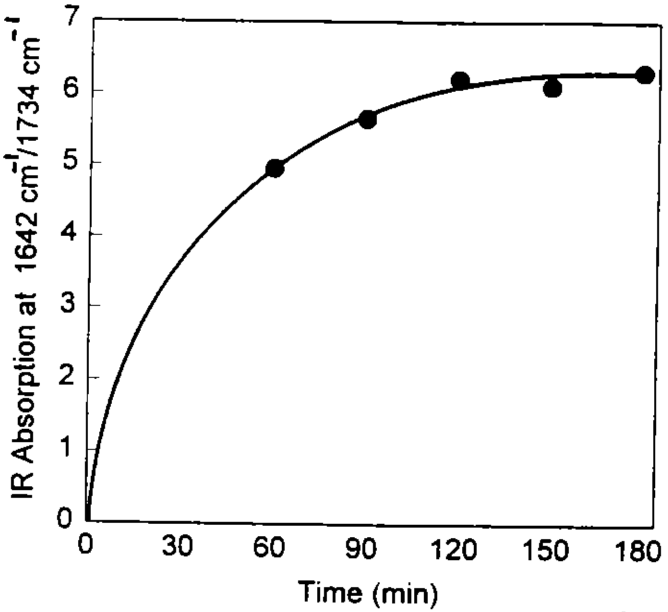


Figure 1. Ratio of IR absorption at 1642 cm^{-1}/ 1734cm^{-1} for the formation of palm monoethanolamides at 100°C

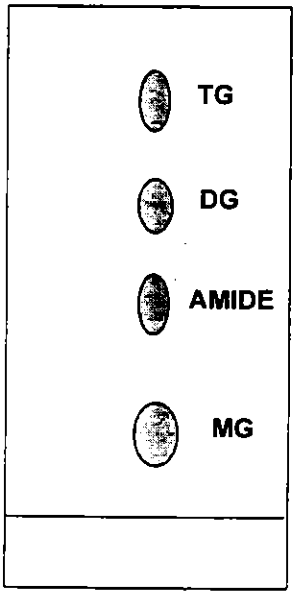


Figure 2. Analysis of reaction products by TLC. Triglyceride (TG), diglyceride (DG) and monoglyceride (MG) were from PO residue. Solvent: hexane/ethyl acetate/acetic acid (85:15:1 drop, v/v).

Crude PMEA is a yellowish waxy solid. After recrystallization with hot hexane and warm water, a white waxy solid was obtained. When only hot hexane was used, the IR spectrum of the PMEA showed a broad absorption band at 3200-3500 cm^{-1} due to the O-H, glycerol and N-H amine *(Figure 3B)*, and the PMEA had a wider melting point range, 78.3-79.9°C. Using a combination of hot hexane and warm water for recrystallization gave PMEA with a narrower melting point range, 84.5-85.4°C, and IR spectrum with a sharp peak in the above regions *(Figure 3C)*. This result suggests that using hot water may remove traces of unreacted MEA and the coproduct glycerol. The crystallization can be repeated to increase purity. The presence of PMEA was confirmed by infrared (IR) and ^{13}C-NMR spectroscopy. Both IR and NMR spectra of PMEA showed characteristic peaks at 1642 cm^{-1} and at 173 ppm respectively that were indicative of an amide carbonyl carbon (CONH). Other IR peaks were: N-H (3294 cm^{-1}, 1558 cm^{-1}), and O-H (3100 cm^{-1}, 3400 cm^{-1}). The ^{13}C-NMR peaks were: 14.1 ppm (CH_3), 22.7-34.0 ppm (CH_2) and 62.2 ppm (CH_2OH).

The effect of temperature and mole ratio on the yield of PMEA are shown in *Figures 4* and *5* respectively. All values are in percentage by weight (wt %). The yield of PMEA was higher

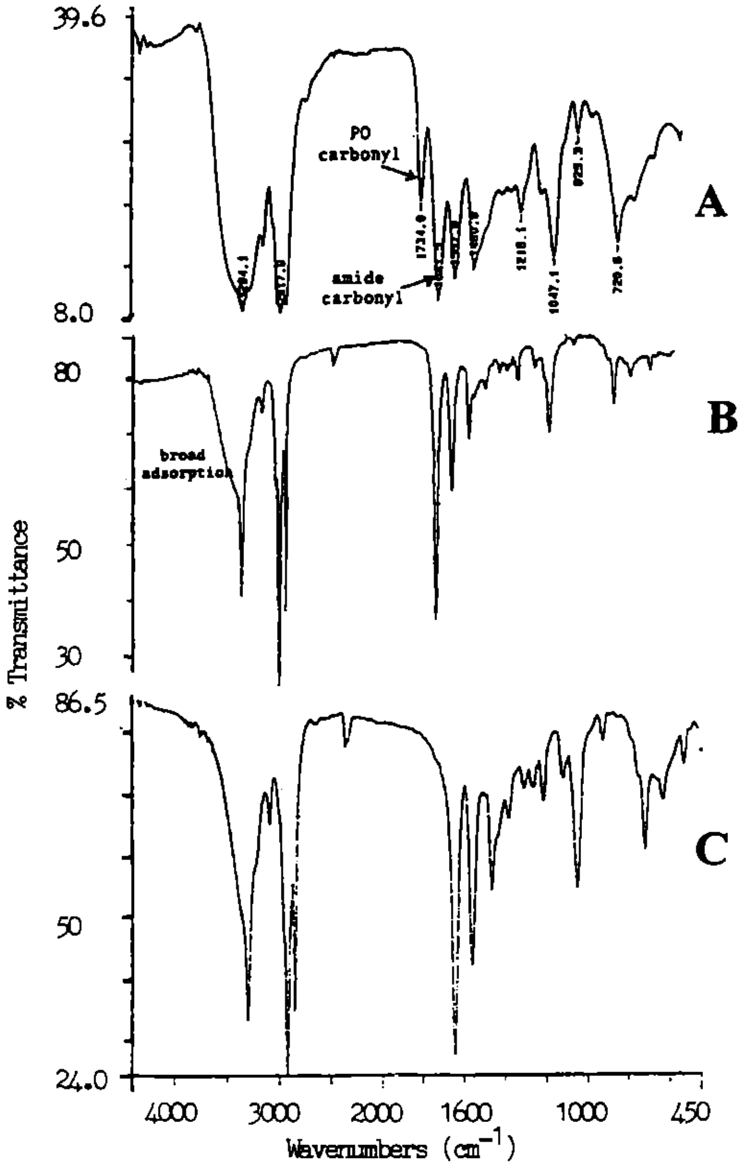


Figure 3. Infra-red spectra of crude (A) and crystallised palm monoethanolamides: (B), with hot hexane and (C), with a combination hot hexane and warm water.

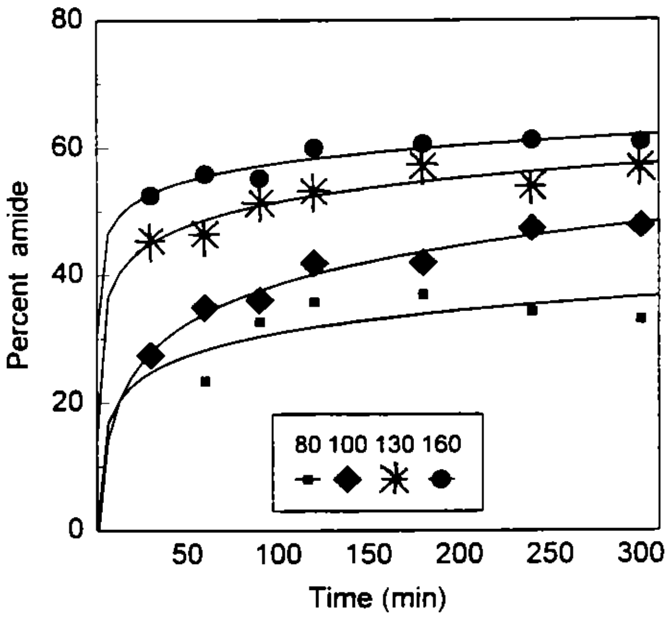


Figure 4. Effect of temperature on the formation of palm monoethanolamides. Mole ratio 1.0:3

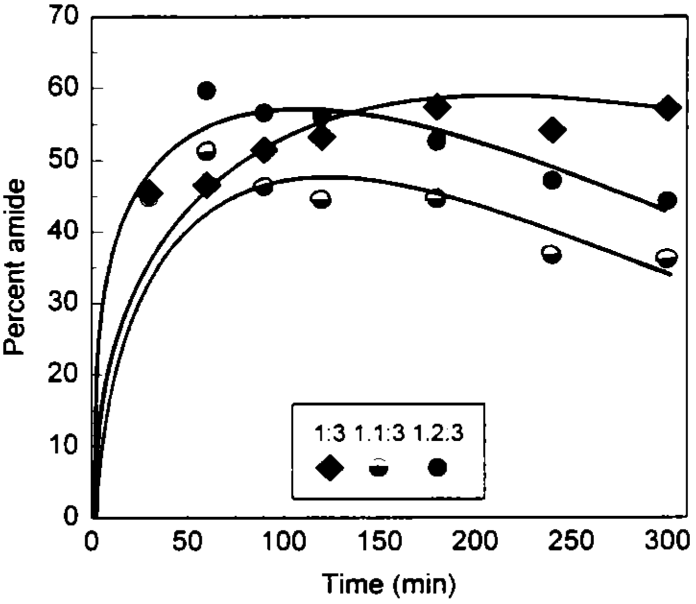


Figure 5. Effect of mole ratio (PO:MEA) on the formation of palm monoethanolamides. Temperature 130°C; catalyst 0.3%.

when the reaction was carried out at high temperature (160°C) than at low temperatures. The highest yield was achieved with 2-3 hours reaction and 60% of PMEA in the mixture. On the contrary, at low temperature (100°C), the amount of PMEA produced increased very slowly and became high only after 5 hours.

When the ratio of PO to MEA was increased (to 1.1:3 and 1.2:3) the yield was maximum within an hour of reaction and then declined slowly. The reason for this decline is not known. Presumably, excess PO and prolonged reaction time might have increased the side products and lowered the conversion to PMEA. The highest conversion of PO to PMEA was achieved at a PO to MEA mole ratio of 1:3. At this ratio, the yield increased steadily to a maximum after 2-3 hours reaction *(Figure 5)*. The effect of the catalyst on the yield of PMEA is shown in *Table 1*. The yield increased with catalyst concentration. Without catalyst, the yield was low, about 31%-35%. Higher yields (more than 80%) were obtained when the reactions were carried out for 2-3 hours with a catalyst concentration of 0.6%. The results from this study showed that the maximum yield (85.5%) was obtained after 3 hours reaction at 160°C with 0.6% catalyst.

TABLE 1. EFFECT OF CATALYST (CH_3ONA) CONCENTRATIONS ON THE FORMATION OF PALM MONOETHANOLAMIDE: MOLE RATIO 1:3; TEMPERATURE 130°C.

Time (min)	Concentration of catalyst			
	0%	0.1%	0.3%	0.6%
60	31.5	37.0	46.5	52.5
120	33.3	48.6	53.3	84.8
180	35.5	58.2	57.4	85.5

Table 2 shows the solubility of PMEA in various solvents. The compound was most soluble in chloroform followed by medium chain alcohols (hexanol and octanol). It, however, was not soluble in water and most hydrocarbon solvents. Despite its insolubility in water, it was possible to incorporate PMEA into a system containing water. *Figure 6* shows the amount of solubilised PMEA in microemulsions with different water contents. The solubility of PMEA increased with the water content of the microemulsion. It was found that as much as 60% PMEA was solubilised in a microemulsion containing 25% water at 50°C. However, the amount solubilised was lower at room tempera-

TABLE 2. SOLUBILITY OF PALM MONOETHANOLAMIDE IN VARIOUS SOLVENTS

Solvents		Solubility (mg/ml)
1.	Ethanol	1.12
2.	Hexanol	2.92
3.	Octanol	2.26
4.	Chloroform	8.03
5.	Dichlomethane	2.43
6.	Acetic acid	1.58
7.	Water	Not Soluble
8.	Hexane	Not Soluble
9.	Octane	Not Soluble
10.	Decane	Not Soluble
11.	Dodecane	Not Soluble
12.	Tetradecane	Not Soluble
13.	Decanol	Not Soluble
14.	Glycerol	Not Soluble
15.	Xylene	Not Soluble
16.	Sulphuric acid	Not Soluble
17.	Hydrochloric acid	Not Soluble

ture, about 15%. A microemulsion with 25% water was the best to solubilize PMEA, although the solubility can slowly decrease because of phase inversion (the forming of o/w-microemulsion). Similar results were observed by previous workers (Hamdan *et al.*, 1995; Shah and Hamlin, 1971) suggesting the formation of inverse micelles when water became the continuous phase. The solubilization of PMEA in microemulsion is due to the formation of association structures, known as mixed micelles, between the surfactant and other molecules in the system. The PMEA molecules are incorporated into a space between surfactant molecules that form a spherical structure of mixed micelles. The amount of PMEA 'dissolved' becomes less when phase inversion occurs and water becomes the continuous phase.

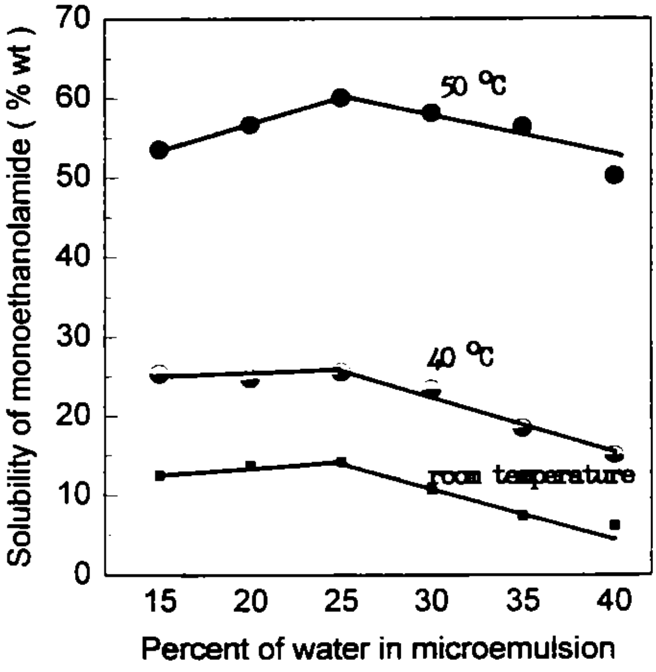


Figure 6. Solubility of palm monoethanolamides in microemulsion at various temperatures.

Kinetic and Activation Energy of Transamidation

The transamidation of PO with MEA may be written as;

$$PO + 3MEA \rightarrow 3\ Amide + Glycerol$$

The rate of disappearance of PO is

$$-d(PO)/dt = k' [PO]^x [MEA]^y \quad (1)$$

As MEA is in excess for the reaction, equation (1) becomes,

$$-d(PO)/dt = k\ [PO]^x \quad (2)$$

where k is the rate constant. Integration of the above equation, assuming a first order reaction, gives

$$\ln[PO]_t = \ln[PO]_0 - kt. \quad (3)$$

Assuming that the initial concentration of PO is 100%, or $[PO]_0 = 100\%$, therefore $[PO]_t = ([PO]_0 - 1/3\ \%Amide)$. Substituting this expression into equation (3) gives,

$$\ln([PO]_0 - 1/3\ \%Amide) = \ln[PO]_0 - kt \quad (4)$$

A plot of $\ln([PO]_0 - 1/3\ \%Amide)$ versus reaction time (t) gave a straight line with a negative slope *(Figure 7)*. This shows that the transamidation of palm oil with MEA is a first order reaction. The rate constants for each of the reaction temperatures, calculated from the slopes of the graphs, were $2.6 \times 10^{-4}\ s^{-1}$ (100°C), $1.7 \times 10^{-4}\ s^{-1}$ (130°C) and $1.2 \times 10^{-4}\ s^{-1}$ (160°C). The activation energy, E_a, expressed by Arrhenius's equation,

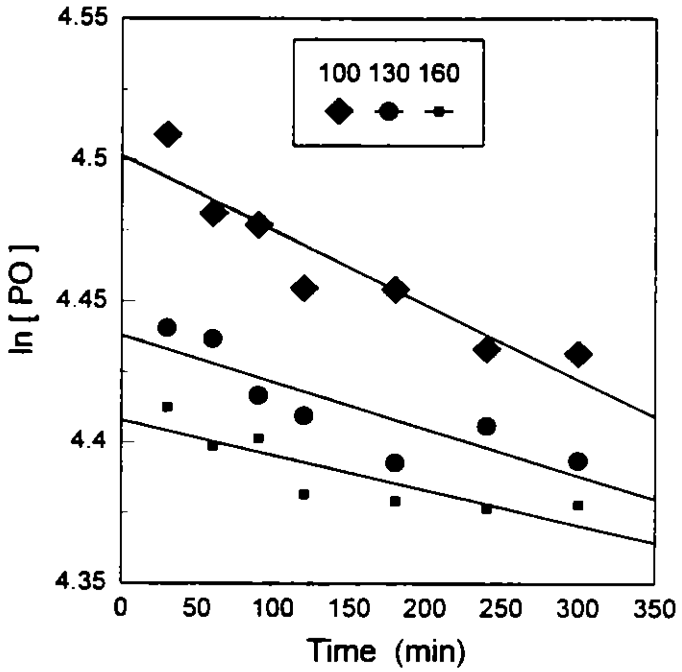


Figure 7. First-order plot for the transamidation of PO with MEA at various reaction temperatures.

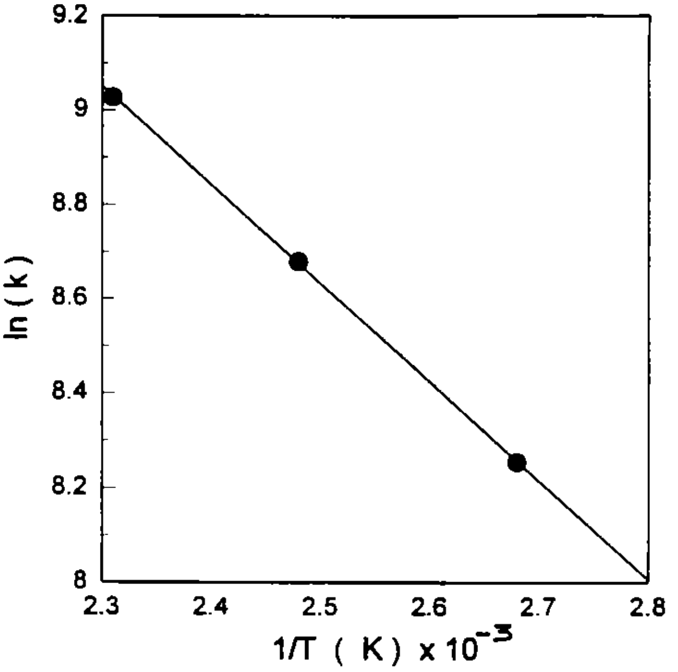


Figure 8. Arrhenius plot of rate constant at various reaction temperatures.

$$\ln k = -E_a/RT + \text{constant} \qquad (5)$$

was then calculated from a graph of ln k versus 1/T (^{0}K) *(Figure 8)*. The value was 17.4 kJ/mol. The low activation energy obtained showed that the transamidation reaction proceeded very easily with a catalyst.

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