

Formulation, Emulsion, and Thermal Stability of Emulsifiable Malathion Concentrate using Ethanol as a Solvent

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Abstract

This work considers the formulation, emulsion and thermal stability of malathion pesticide in the form of emulsifiable concentrate (E.C.). Ethanol as solvent and different types of emulsifiers is considered in the formulation using 50% emulsifiable malathion concentrate. Ethanol, which is polar solvent and miscible with water, is considered in this work instead of the nonpolar and immiscible aromatic solvents such as Dimethylbenzene. The target is to formulate emulsifiable environmentally safe pesticide using ethanol as a solvent. This solvent is selected because it is less harmful compared with aromatic solvents which often used. The emulsifiers are those that have a hydrophobic hydrophilic balance (HLB) value between eight and eighteen. Four samples conform to the criteria of the emulsion stability test for the formulation of 50% emulsifiable concentrate. These formulations contain the emulsifier concentration of 7, 8, 9, and 10-wt-%. Such samples also underwent a thermal stability tests. The degradation kinetics of the emulsifiable malathion concentrate follows a first order degradation rate. The shelf life of emulsifiable malathion concentrate was estimated using Arrhenius equation.

Keywords: Malathion, pesticides formulation, emulsion stability, degradation, thermal stability

1. INTRODUCTION

Pesticide formulation is the process of transforming a pesticidal chemical into a

product which can be applied, by practical methods, to permit their effective, safe and economical use [1]. Therefore, a pesticide formulation is a physical mixture composed of biologically active chemicals and inert ingredients that provides effective and economic control of pests. Majority of pesticide chemicals require formulations that are stable and economically and effectively used [2]. The continuing and increasing use of pesticides seems assured, provided due account is taken for the safety of the plant operator, the end-user and the environment [3].

Pesticide formulation is classified into two general types, according to the physical forms; namely, *liquid* and *dry* formulations. Liquid formulations are among the most popular formulation types. As a general group, recommended dosages of liquid formulations are easily computed and dispensed. When realistically conceived, emulsifiable and similar liquid concentrates are considered economic formulations, since they can be readily diluted with water and conveniently applied. It is worth mentioning that all liquid formulations have the same requirements, that is solvent or fluid diluents must be physically compatible with the active ingredient under all conditions of storage [4]. Recent developments of safer formulations of agrochemicals have been studied [5]. Knowles presented formulation for granular (GR), solution concentrate (SL), emulsifiable concentrate (EC), wettable powder (WP) and suspension concentrate (SC).

Emulsifiable concentrate consists of the toxicant, the solvent and the emulsifier [6]. The solvent and its concentration determine the solubility characteristics of the pesticidal chemical particularly for the purpose of storage conditions. In addition, at a given concentration, the physical nature of the combination of pesticidal chemical and the solvent determines the type of emulsifier and emulsifier balance to be used. Therefore, the selection of solvent and emulsifier is a critical issue representing the initial phase of emulsifiable concentrate development [7]. Organic solvents are used in pesticide formulations because most pesticidal chemicals are insoluble in water [8]; in this area solvents are conveniently classified as polar or non-polar [9].

This work aimed to formulate environmentally safe pesticide using ethanol as a solvent. This solvent is selected because it is less harmful compared with aromatic solvents which often used. The target is to formulate stable emulsifiable malathion. The study considered formulation of 50% malathion emulsifiable concentrate by mixing the active malathion ingredient, the emulsifier and the solvent. Different polar and non-polar solvents can be used, but the ones which form a stable phase solution with the malathion active ingredient are the most convenient. The solvents which match such criterion are then mixed with different types and concentrations of emulsifiers so that maximum emulsifier concentration of 10% can be achieved. The resulting products are subsequently tested for emulsion and thermal stability in order to obtain products that meet the specifications of the Food and Agriculture Organization of the United Nations (FAO) as well as the World Health Organization (WHO) for qualified pesticides. As a result, ethanol was used as solvent and different types of emulsifiers at different concentrations were tested; these emulsifiers are those having a hydrophobic hydrophilic balance (HLB) value between eight and eighteen.

2. MATERIALS AND METHODS

2.1 Materials

The materials used in this study are the active ingredient malathion pesticide, ethanol as solvent, and emulsifiers with HLB values ranged from 8 to 18. Malathion technical grade was purchased from Cheminova, Denmark; its physical properties are listed in Table 1. The emulsifier alkylaryl ether sulfates (EM101) was used. The emulsifier is characterized by a HLB value ranging from 8 to 18. Surfactants reduce the interfacial tension between immiscible liquids or between liquids and solid surfaces [10]. In pesticide formulations, the surfactant characteristics of great interest are wetting and dispersing for water-dispersible powders and emulsifying for emulsifiable concentrates.

Table 1: Chemical and physical properties for malation

Empirical formula	C ₁₀ H ₁₉ O ₆ PS ₂
Molecular weight	330.4
Colour	Colourless to light amber
Melting point	2.85°C
Boiling point	156-157°C at 0.7 mmHg
Physical state	Liquid
Vapor pressure	40 mmHg at 30°C; 12.5 mmHg at 20°C
Density	1.23 g/ml at 25°C
Surface tension	37.1 Dynes/cm at 24°C
Solubility	145 ppm in water at 15°C, miscible with several organic solvents

2.2 Preparation of Solutions

The following agents were used in preparation of standard solution D; CaCO₃ (purity > 99 %), MgO (purity > 99 %), sodium hydrogen carbonate (purity > 99 %), ammonia solution (1.0 N), hydrochloric acid (1.0 N), sodium hydroxide (1.0 N) and methyl red-indicator. To prepare the standard solution D, which is used in this work, stock solutions of A, B, and C were initially prepared. Stock solutions of A, B and C were prepared as illustrated below.

2.2.1 Stock solution A:

This is composed of 0.04 M calcium carbonate ion solutions. It is prepared by weighing 4.0 g of calcium carbonate which are then transferred into a 500 ml conical flask with a minimum of distilled water. Hydrochloric acid (82 ml of 1.0 N solution) was slowly added to the flask, via the filter funnel, while swirling the contents continuously. When all calcium carbonate was dissolved, the solution was diluted to approximately 400 ml with distilled water and boiled to expel the excess carbon dioxide. The solution was then cooled and a solution of methyl red indicator (2 drops) was added and neutralized to an intermediate orange color with the ammonia solution. The solution was transferred into a 1000 ml volumetric flask and make up the difference in volume with distilled water; mixed and then stored in a polyethylene

container. One ml of this solution when diluted to 1000 ml would give a solution of 4 ppm. Hardness was expressed as calcium carbonate.

2.2.2 Stock solution B:

This is composed of 0.04 M magnesium ion solution. The procedure for preparation of this solution is similar to that used for solution A.

2.2.3 Stock solution C:

This is composed of 1.0 M sodium hydrogen carbonate solution. It is prepared by dissolving 84.01 g of sodium hydrogen carbonate in distilled water, which is then transferred into a 1000 ml volumetric flask and make up the volume with distilled water. One ml of this solution when diluted to 1000 ml would give a 23 ppm of sodium solution.

2.2.4 Standard solution D:

This is composed of 342 ppm hardness, pH 6.0-7.0, and 80:20 Ca:Mg ratio. It is prepared by pipetting 68.5 ml of solution A and 17.0 ml of solution B into a 1000 ml beaker which is then diluted to approximately 800 ml using de-ionized water. The solution pH was adjusted in the range of 6.0 to 7.0 using 0.1 N of sodium hydroxide. The solution was quantitatively transferred to a 1000 ml volumetric flask and make up to volume with de-ionized water [11].

2.3 Formulation of emulsifiable malathion concentrate

Four formulations of 50% emulsifiable malathion concentrate have been considered in this work depending on the concentration of the emulsifier; these are summarized in Table 2.

Table 2: Emulsifier malathion concentrate formulations

Emulsifier (EM101; HLB = 11.9) concentration	Contents
7%	Malathion : 52.57 gm/100ml. Emulsifier: 7 gm/100ml Ethanol : made up to 100 ml
8%	Malathion : 52.57 gm/100ml. Emulsifier: : 8 gm/100ml Ethanol : made up 100 ml
9%	Malathion : 52.57 gm/100ml. Emulsifier: : 9 gm/100ml Ethanol : made up 100 ml
10%	Malathion : 52.57 gm/100ml. Emulsifier: 10 gm/100ml Ethanol : made up 100 ml

2.3.1 Initial emulsification

A 100 ml graduated cylinder is filled with 95 ml of standard water D. Five milliliters of emulsifiable concentrate is gently poured into the remaining part of the 100 ml cylinders. The cylinders, which contain emulsifiable concentrate and water D are closed and then inverted once. After 30 seconds, spontaneous formation of emulsified mixture was examined visually.

2.3.2 Emulsion stability

The cylinder is inverted 10 times, and is allowed to stand undisturbed in a constant water bath at $30 \pm 1^\circ\text{C}$ for 24 hours. After that formation of any cream or oil phases have been examined in each system after standing for 30 seconds, 30 minutes, 1 hr, 2 hrs, 3 hrs, 4 hrs, 8 hrs, and 24 hrs. After standing for 24 hours, the cylinder was again inverted 10 times; and then formation of any cream or oil phase was examined after standing for another 24 hrs. The later test is check for re-emulsification. Final stability test was followed by allowing the cylinder to stand undisturbed for a further period of 30 minutes, and cream free oil formation was examined at the end of the 30 minutes period.

2.3.3 Thermal stability test

Fifty milliliters of the 50% emusifiable malathion concentrate is stored in screw capped bottles in an incubator at different pre-specified temperatures of 25, 35, 45 and 55°C for different periods of times, namely 7, 14, 21, 28 and 35 days [11]. After that, the cap was removed and the content was allowed to cool naturally to room temperature.

2.4 Analysis of malathion

The concentration of malathion was determined as follows. Malathion was dissolved in absolute ethanol and its concentration was determined by HPLC using RP-18 column and acetonitrile-water mixture as a mobile phase. Quantification was achieved by comparing the peak area for the sample solution with that for a standard solution of malathion [12]. The concentration of malathion (C_A) was calculated using equation 1:

$$C_A = \frac{w_2 \times A_1}{w_1 \times A_2} \quad (1)$$

Where w_1 and w_2 are the weight of the standard and the sample solutions, respectively; A_1 and A_2 are the average areas of the standard and sample solutions, respectively.

3. RESULTS AND DISCUSSION

3.1 Stability of ethanol emulsion

The stability of a pesticidal chemical is measured by its ability to withstand (a) the degradative effects encountered during storage formulation and (b) the environment to which it is subjected after application [13]. Emulsion stability tests were conducted for

the 50% emulsifiable malathion concentrate formulation. Four formulations were considered which meet the criteria of the FAO emulsion stability test for emulsifiable malathion concentrate. These formulations are illustrated in Table 2. The results for stability tests, as of the sequence described above, are shown in Table 3. It is seen that the emulsion is stable after 2 hours in which cream or oil phase levels are below the standard specifications set by both FAO and WHO organizations. For the case of 10% emulsifier concentration, the emulsion is completely clear up to 4 hours period, i.e. without any phase precipitation. It is also seen (Table 3) that the re-emulsification test after 24 hours passed the specifications; where the level of oil or cream is below the specified standards. The optimum emulsion stability using ethanol is obtained at an HLB value equal to 11.9. At an HLB below or above 11.9, the emulsion was less stable.

Table 3: Emulsion stability for 50% emulsifiables malathion concentrates using ethanol as a solvent

Time	Emulsifier Concentration EM101 (HLB = 11.9)							
	7 %		8 %		9 %		10%	
	Cream/ml	Oil/ml	Cream/ml	Oil/ml	Cream/ml	Oil/ml	Cream/ml	Oil/ml
30 Seconds	0	0	0	0	0	0	0	0
30 Minutes	1.5	0	1	0	1	0	0	0
1 Hour	1.5	0	1	0	1	0	0	0
2 Hour	1.5	0	1.5	0	1	0	0	0
3 Hour	2	0	1.5	0	1	0	0	0
4 Hour	2	0	1.5	0	1	0	0	0
8 Hour	2	0	2	0	1.5	0	0.5	1
24 Hour	2	0	2	0	1.5	0	1	0
24 Hr & 30 Sec Re-Emulsification	0	0	0	0	0	0	0	0
24.5 Hour	1.5	0	1	0	1	0	0.5	0

In order to compare ethanol stability with dimethylbenzene, similar tests were performed using dimethylbenzene as a solvent. The stability tests results for this solvent are shown in Table 4. Comparing the data in Table 4 with that in Table 3 indicates that precipitation of oil or cream phases using ethanol solvent occurs at earlier periods than that when using dimethylbenzene solvent. Also, the amounts of oil or cream precipitate are higher when dimethylbenzene is used than that when ethanol is used; i.e. in the case of dimethylbenzene, the precipitate reached a level as high as 6 ml, while in the case of ethanol the maximum level of precipitation was around 3 ml. This is due to the fact that ethanol is polar solvent, which is miscible in water and the 3 ml precipitation is due to the malathion, which is immiscible in water. The 6 ml precipitation of dimethylbenzene formulation is due to the fact that both dimethylbenzene and malathion are immiscible in water.

Table 4: Emulsion stability for 50% emulsifiable malathion concentrates using Dimethylbenzene as a solvent

Time	Emulsifier Concentration EM101 (HLB = 11.9)							
	7 %		8 %		9 %		10%	
	Cream/ml	Oil/ml	Cream/ml	Oil/ml	Cream/ml	Oil/ml	Cream/ml	Oil/ml
30 Seconds	0	0	0	0	0	0	0	0
30 Minutes	0	0	0	0	0	0	0	0
1 Hour	0	0	0	0	0	0	0	0
2 Hour	0	0.5	0	0	0	0	0	0
3 Hour	0	1	0	0.5	0	0	0	0
4 Hour	0	2	0	1	0	0	0	0
8 Hour	0	5	0	2	0	1	0	1
24 Hour	0	5	0	4.5	0	4	0	4
24 Hr & 30 Sec Re-Emulsification	0	0	0	0	0	0	0	0
24.5 Hour	0	0	0	0	0	0	0	0

3.2 Thermal stability

Thermal stability tests are conducted using samples that conform to the criteria of the FAO emulsion stability test. These samples are placed in four different incubators at temperatures of 35, 45 and 55°C for 35 days. The thermal stability tests data demonstrates the performance of the emulsifiable malathion concentrate at different climate temperatures. It was shown that high temperatures changed in the chemical structure of malathion; this is due to the rupture of the weak bonds of malathion.

The kinetics model allows prediction of the level of degradation at different temperatures and times. For such purpose, the following simple degradation model was proposed:



In order to avoid side reaction or oxidation during the thermal tests, the samples were placed in a closed vessel at a controlled temperature. Only the samples that passed the FAO and WHO emulsion stability test were subjected to thermal stability test.

The kinetics was considered in this work at different temperatures and times. This was performed by determining malathion concentration using HPLC after 7, 14, 21, 28 and 35 days of storage in these incubators. Kinetics of malathion at different emulsifier concentrations and temperatures of 35, 45 and 55°C are shown in Figures 1-3, respectively. The experimental data at different temperatures were analyzed using first-order degradation models ($-r_A = kC_A$). Where k is the degradation rate constant and was determined for each sample at the given temperature. For a first order reaction a plot of $\ln C_A/C_{A0}$ vs time should be linear where C_{A0} is the initial malathion concentration. As shown in Figures 1-3, this model fit the experimental data reasonably well with R^2 above 0.980. The reaction rate constant (k) is determined from the slope of the line.

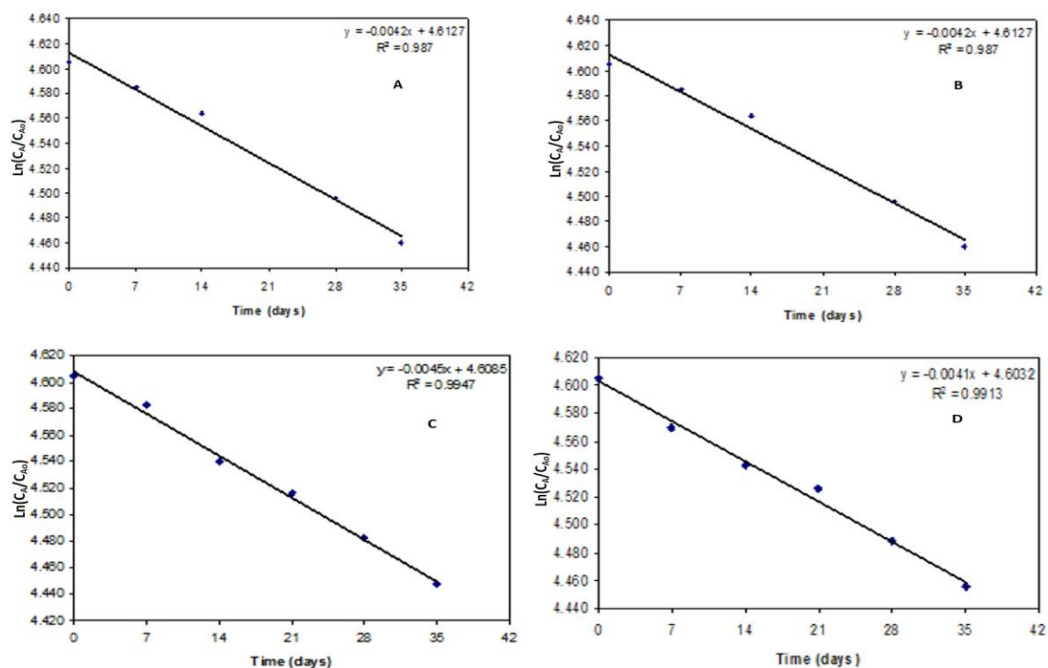


Figure 1: Kinetics of malathion degradation at 35°C using 50% emulsifiable malathion concentrate with ethanol solvent at different emulsifier (EM101 – HLB 11.9) concentrations; A: 7%; B: 8%; C: 9%; D: 10%.

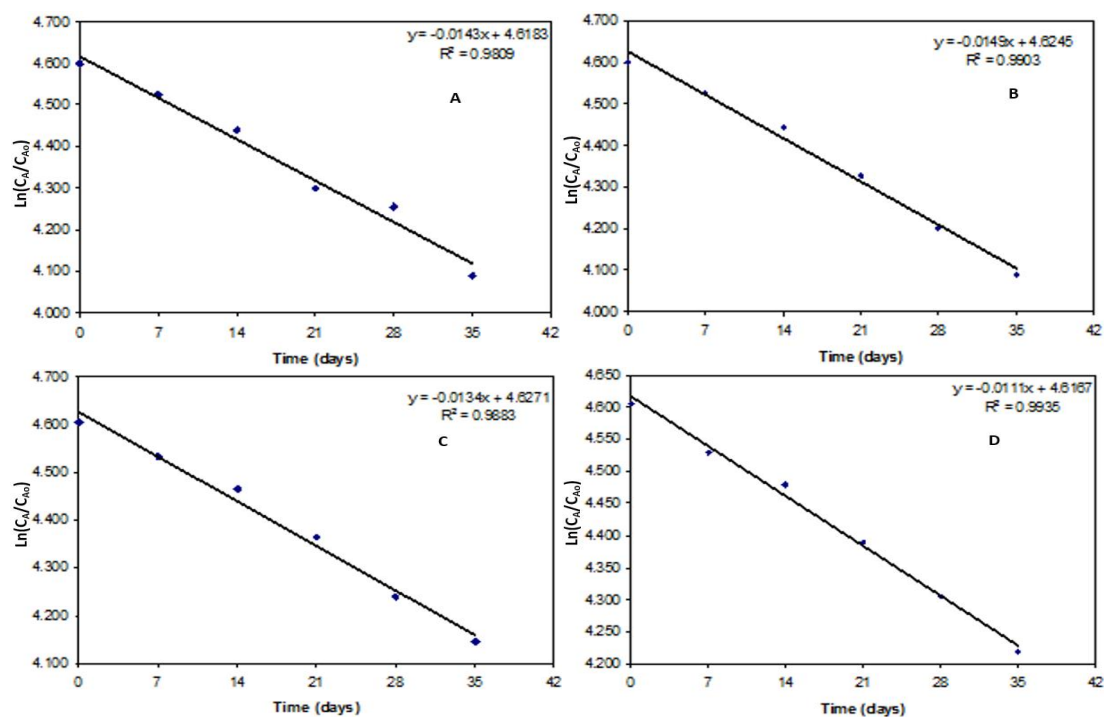


Figure 2: Kinetics of malathion degradation at 45°C using 50% emulsifiable malathion concentrate with ethanol solvent at different emulsifier (EM101 – HLB 11.9) concentrations; A: 7%; B: 8%; C: 9%; D: 10%..

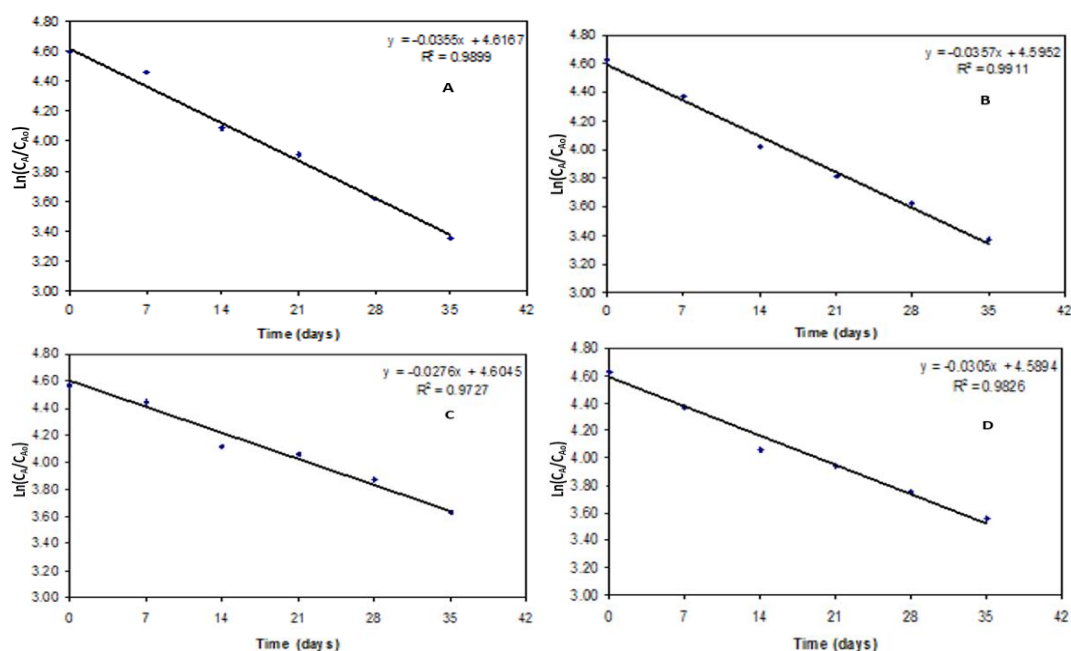


Figure 3: Kinetics of malathion degradation at 55°C using 50% emulsifiable malathion concentrate with ethanol solvent at different emulsifier (EM101 – HLB 11.9) concentrations; A: 7%; B: 8%; C: 9%; D: 10%.

In order to predict malathion concentration at the required time and temperature, k dependency on temperature was obtained by plotting natural logarithmic of the degradation rate constant ($\ln k$) versus the temperature reciprocal ($1/T$) where

$k = k_0 \exp \left[\frac{-E_a}{RT} \right]$ or use the decade method based on two data points [14]. Where E_a is the activation energy. Accordingly, the constants k_0 and E_a can be obtained from the intercept and slope, respectively, of the linear plot of $\ln k$ versus $1/T$. Figure 4 shows the plot of $\ln k$ vs $1/T$ for for 50% emulsifiable concentrate malathion with ethanol and 9% EM101. Values of k_0 of 4.19×10^{10} (day^{-1}) and E_a/R of 9431 (K).

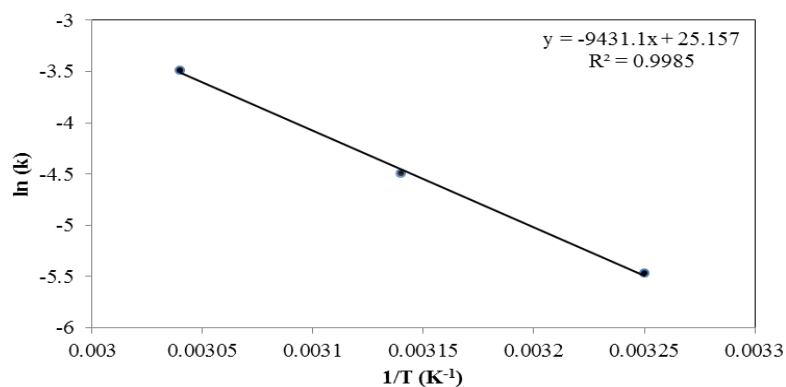


Figure 4: $\ln k$ vs $1/T$ for 50% emulsifiable concentrate malathion with ethanol and 9% EM101.

CONCLUSION

The following conclusion remarks can be drawn from the experimental data collected in this work:

1. Ethanol, which is less harmful to the environment and humans than other aromatic solvents, forms a stable emulsion with 7%, 8%, 9%, 10% emulsifier EM101(HLB=11.9).
2. Manufacturing of 50% emulsifiable malathion concentrate is controlled by the solvent type, emulsifier type and emulsifier concentration.
3. The degradation kinetics of emulsifiable malathion concentrate follows a first order degradation rate.

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