Eco. Env. & Cons. 31 (4) : 2025; pp. (1699-1703)
Copyright@ EM International
ISSN 0971–765X

DOI No.: **http://doi.org/10.53550/EEC.2025.v31i04.055**
Website: www.envirobiotechjournals.com

Study of mono (2-ethylhexyl) phthalate as plasticizer

A.S. Jadhav[1], R.D. Nalawade[2] and D.P. Gaikwad[3]

[1]Department of Chemical Engineering, AISSMS College of Engineering, Pune, M.S., India
[2]Department of Civil Engineering, AISSMS College of Engg, Pune, M.S., India
[3]Department of Computer Engineering, AISSMS College of Engg, Pune, M.S., India

(Received 16 August, 2025; Accepted 11 October, 2025)

ABSTRACT

Kinetics of esterification has emerged as a field of growing interest and importance, in last three decades due to large number of powerful applications in many engineering fields. The commercial applications have demanded to generate the esters, in massive quantity. Thereby the research work has been started to fulfil the commercial need of one of such important ester viz. mono (2-ethylhexyl) phthalate or simply MEHP. Due to dielectric and plasticity nature, MEHP is predominantly used in massive quantity in electric and plastic industries along with wide number of other commercial applications. To have good commercial profit, it is the need of commercial market to generate such type of ester class which satisfy most of the applications in optimum cost. To fulfil this requirement, the properties, kinetics, easy & fast analysis method, use of programming methods like MATLAB for quick calculations becomes the prominent facts. Selection of route is also important for the formation of mono (2-ethylhexyl) phthalate in environment point of view. This also affect on operational cost. This paper is the serious attempt and partial fulfilment made to accomplish this goal.

Key words: *Esterification, MEHP, Dielectric, Plasticity*

Introduction

Kinetics of esterification has emerged as a field of growing interest and importance, in last three decades due to large number of powerful applications in many engineering fields. The commercial applications have demanded to generate the esters, in massive quantity. Thereby the research work has been started to fulfil the commercial need. Various types of esters as per their pertinent properties are required in commercial applications. The esters are broadly classified into their aliphatic, aromatic and cyclic compounds. Aliphatic hydrocarbon esters are normally required in formulation of dyes, compounding of the color along with plastics, pharmaceutical reagents, simple and branch- chain polymers etc. while as aromatic hydrocarbon esters are used as formulations in pharmaceutical industries, plasticizers, textile industries, detergents, complex dyes, engineering polymers, food additives, dielectric fluid in electrical industries, additive fluid in lubricating oils (it is used to reduce the friction in machine parts as well as to enhance the efficiency of the engine), coating agents etc. e.g. mono-octyl phthalate or maleate, dinonyl phthalate or maleate, monobutyl phthalate or maleate, mono-ethyl phthalateesters of its own family (comparison is with maleate). World consumption for phthalates is estimated at 3.25 X 106 Ton, of which MEHP accounts for 2.1 X 106 Ton (Gerhard *et al.,* 2025). Prognoses for the world market show an annual increasing demand of 2.5 % is recorded. Due to such large amount of world's requirement, China had made their separate technology to produce MOP/MEHP. This product can be made of by two ways –

1. By esterification of Phthalic anhydride along with 2-ethyl –1- hexanol or octanol.
2. By esterification of Phthalic acid along with2-ethyl –1- hexanol or Octanol (H. Scott Fogler. 2004).

But unfortunately China has not opened their door to give up this technology. The first route is adopted by many companies' like Henkel Ltd., Mitsubishi, DuPont, HoeChest etc. But still the first route is also new one to our technology.

The second one is not yet tried and is totally new one. Literatures suggest that the second route may prove to be the economical that is using the phthalic acid route. But the condition is that water should be withdrawn at fast rate, otherwise conditions may form the equilibrium. In the first route more cost is expended not only in formation of anhydride form from phthalic acid but also in handling, transportation and storage of it. Since phthalic anhydride is very much hygroscopic, it affects seriously on reaction kinetics and equilibrium conditions if contaminated. This affects on the environment and the product purity as well. Hence the modifications have been devised, but the system is fully automated with separate automation charges. In general, it has been concluded that it is better to adopt the second route which is the reaction between phthalic acid and 2-ethyl-1- hexanol. But unfortunately this route is not tried yet in India, and hence this is the first step and the serious attempt made to look in the New Horizon.

Experimental

A three neck round bottom flask of capacity 100 ml is used as reactor. A helical coil condenser is attached to it, to reflux the vapours. In the other neck rubber septum is placed to withdraw samples using a needle -syringe assembly. In the third neck temperature provision can be made. This reactor is placed in the oil bath heated with electrical coil. The temperature can also be set by calibration of heating coil assembly (Peter Sykes Kirk, 2004). The stirring of reaction mixture is done using magnetic needle. The reactor top is enclosed by condenser with cooling water assembly.

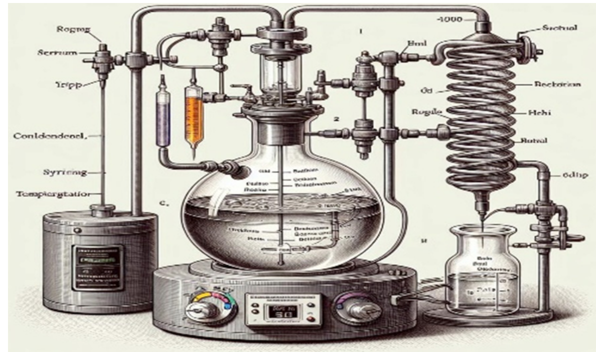


Fig. 1. Experimental Setup

Procedure: A glass reactor (borosilicate type) is kept in silicone oil bath having the boiling point above 400 °C. The surrounding oil is heated to predefine reaction condition, which gives the heat to reaction as soon as possible, and to reduce the reaction time. Hence the magnetic stirrer assembly is introduced in the system. To avoid leakage and the vapour losses the condenser with cooling water assembly (in glass) has been embedded on the top of the reactor (Kuehne and Horne, 1975). The reactor joined with condenser is checked whether it's airtight. If the vapour formation is there, they are refluxed into the reactor again and give rise to the increase in reaction heat annd rate. After sufficient time interval (reaction time), the system is switched off to carry out next product analysis or for the next batch.

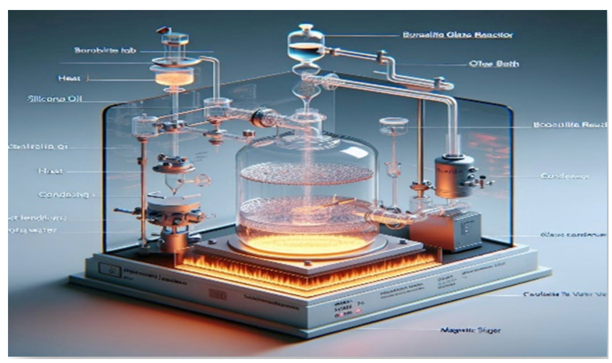


Fig. 2. Procedure set up

Analytical Characterization

Solubility: Where M = mono-octyl phthalate or mono (2- ehtyl hexyl phthalate) (Peter Sykes Kirk. 2004). The sample after the periodic instants can be analyzed by saponification with alkali. The concentration of reactant or product can be found out by volumetric analysis or by material balance

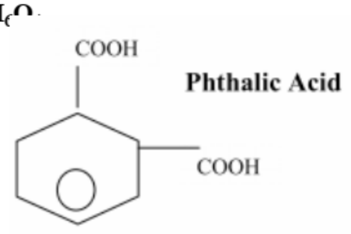
$$A + B \underset{}{\overset{Heat}{\rightleftharpoons}} M + W \quad .. (1)$$

Where M = mono-octyl phthalate or mono (2-ehtyl hexyl phthalate). The sample after the periodic instants can be analyzed by saponification with alkali. The concentration of reactant or product can be found out by volumetric analysis or by material balance techniques. In fact, it has been found out experimentally that the formation of mono-octyl phthalate does not require any catalyst

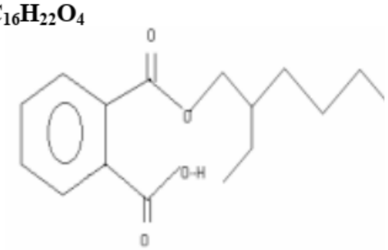
Structures of reactants, intermediates and products

Before carry out the main reaction we must know the important structure reactants, intermediates and products

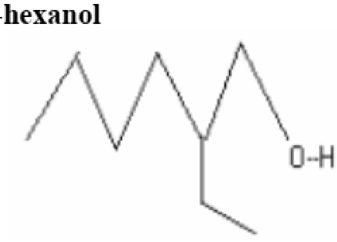
1. **Molecular Weight = 166.13**
   C_8H_6O



2. **Mono-octyl Phthalate**
   Molecular Weight = 278 . 3474
   $C_{16}H_{22}O_4$



3. **Molecular Weight = 130. 23**
   $C_8H_{18}O$
   2-ethyl-1-hexanol



Structures of reactants, intermediates & products

Gas Chromatography: It is the easiest technique to analyze the components in the mixture. But if we are using the components which are having higher boiling points, it results in chocking of columns using in chromatographic method. Phthalic acid has the boiling point 215 ^{0}C, mono (2-ehtyl hexyl) phthalate has the boiling point 278 ^{0}C, 2-ethyl-1-hexyl alcohol has 183 ^{0}C and di (2-ethyl hexyl) phthalate has the boiling point 231 ^{0}C. If the mixture is tried on the GC, the column may get chock and the results will be erroneous. If we use higher range of temperature the ester, i.e. the mono-octyl/ 2-ethylhexyl phthalate gets decompose over a temperature range of 210 ^{0}C and instead of true peak values we get the apparent values which cannot match with our product. Hence it has been also found out in many research papers that chromatographic techniques are avoided and researchers have followed the simple and optimistic way either saponification experiment, colorimetric method or Acid value test. Hence this method cannot be suitable for the analysis of the ester sample.

Saponification Test: Analytical testing has to be carried out first by Saponification Experiment. The saponification value of an ester is defined as the number of mg. of KOH required to neutralize the free acids obtained from the hydrolysis of 1 gram of ester and named as the saponification value or saponification number. The saponification number is inversely proportional to the relative molecular masses of the fatty acids obtained from the esters.

Saponification Experiment Apparatus: Water bath with shaking and heating assembly, 25 ml pipette, 25 ml burette, N/2 alcoholic KOH solution, 250 ml flask fitted with reflux condenser, distilled water, Syringe, phenolphthalein indicator, two conical flask of 250 ml capacity (Arabi *et al.,* 2003). In Saponification and the titration needed afterwards, traces the following reaction (Kunichika Nakamiya *et al.,* 2005).

Monoester + H_2O + Unreacted PA ——— KOH Saponification + Unreacted KOH + Unreacted Alcohol ($C_8H_{17}OH$)

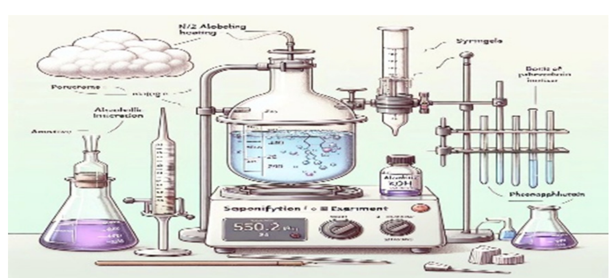


Fig. 3. Saponification Experiment Apparatus

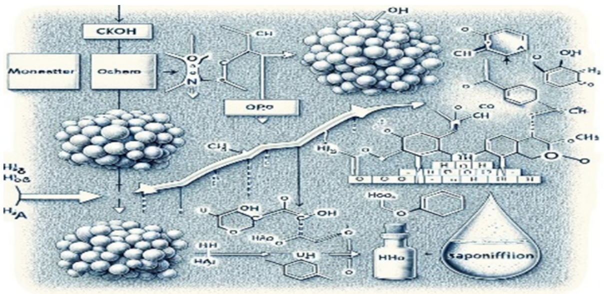


Fig. 4. Graphical Representation of Reaction

Acid value Test: All the mentioned tests are not able to give the sufficient data so as to enable the kinetics. Hence the acid value test has been tried.

Acid value Test Procedure: Take 0. 5 g of sample in a conical flask with the help of syringe. To this, add 20 ml of benzene and 20 ml of methanol. Then swirl the sample completely in the solvent. Methanol acts dually, that is to prevent the polymerization and provide the neutral base for detecting the end point. After the addition of methanol some sample may get polymerize since they have tendency to get polymerize at an elevated temperature. In our case we are using the pure limiting reactant, i.e. Phthalic acid and hence addition of benzene is not required. Add few drops of phenolphthalein indicator and titrate the contents against the 0.1 N KOH. The end point is colourless to pink. Check the normality of alc. KOH daily at least one time since there are chances to change its normality due to the storage Suppose, Normality of alc. KOH = 0.112 N Weight of the sample in the flask = 0.5336 g Burette reading for sample, M = 1.6 ml.

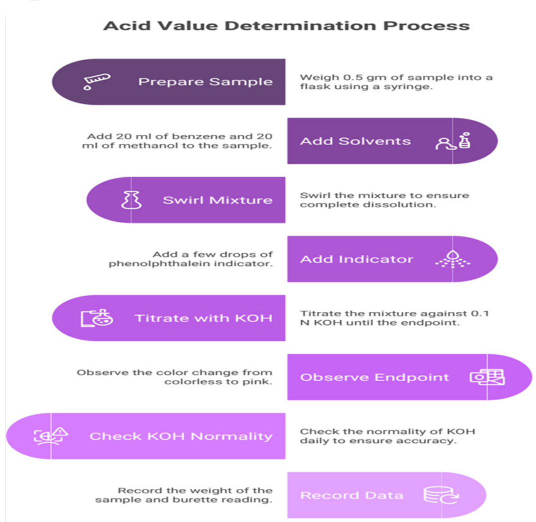


Fig. 5. Acid value Test Procedure

Acid Value = 56.1xNormality of alc. KOH x M / Weight of sample

=18.840 mg of KOH/g of sample.

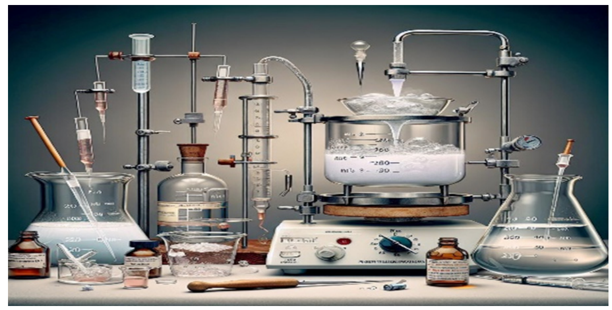


Fig. 6. Acid value Test Experiment Setup

Results and Discussions

Solubility: Where M = mono-octal phthalate or mono (2- ethyl hexyl phthalate) (Thorat *et al.*, 1992). The sample after the periodic instants can be analysed by saponification with alkali. The concentration of reactant or product can be found out by volumetric analysis or by material balance

Table 1. Solubility Data

Temperature °C	Solubility pHA (MG)/Octanol(ml)
27	10.2
48	12.26
78	18.08
110	54.45
125	151.92
150	412.04

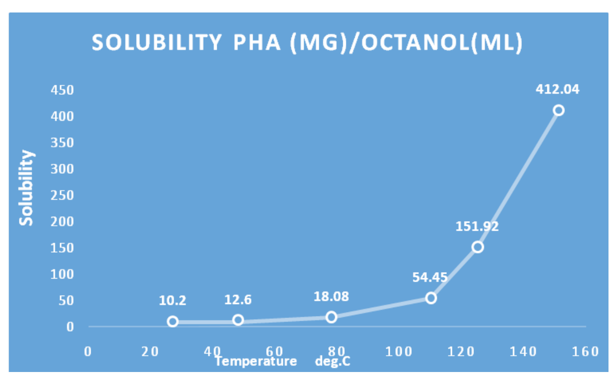


Fig. 7. Solubility of PHA/Octanol (ml)

Acid Value Test

The previously employed analytical techniques did not provide adequate data to facilitate kinetic modelling of the reaction. Consequently, the acid value test was explored as an alternative, given its ability to monitor changes in free fatty acid concentration, which can serve as a reliable indicator of reaction progress. The trend shows acid is increasing after 50min. The significance of the acid value test for phthalate plasticizers is to monitor plasticizer purity and to assess its degradation by quantifying the amount of free carboxylic acids present. A low acid value is crucial, as high levels indicate impurity from the manufacturing process or degradation due to hydrolysis, which can lead to reduced performance, leaching, and potential health and environmental concerns (ASTM D1639-90.1996).

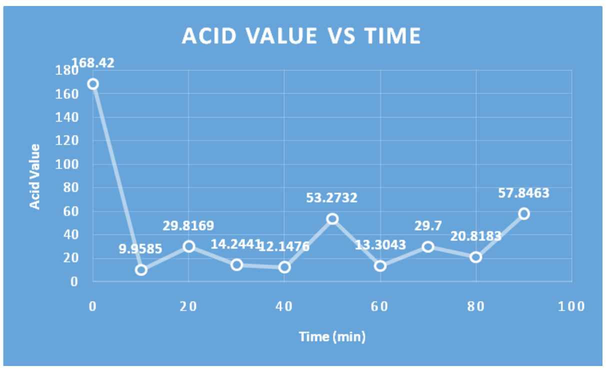


Fig. 8. Acid value Test

Conversion with respect to time is varying as it is concluded that monoester formation occurs in first 15 minutes. This is also mentioned in literature. Hence this method finds correct. As the normality of alc.KOH daily at least one time since there are chances to change its normality due to the storage (Jerzy Skrzypek *et al*., 1994).

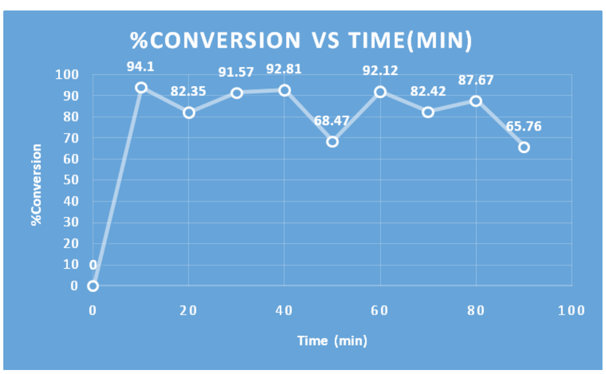


Fig. 9. % Conversion vs Time

Conclusion

It has been concluded that estimation of phthalic acid can be confirmed by Acid Value Test. Chromatographic method is not useful to higher boiling range compounds. Saponification method is traditional one, but takes longer time for the estimation. Colorimetric test needs lot of preparation of chemicals and reagents. It is need to get quick estimation in less time duration. This can be achieved by acid value test. It is tested for monoester formation of phthalic acid. The formation of monoester is within 15 minutes to 20 minutes. The graph of Acid Value versus time fluctuates after 15 min to 20 min time interval because reaction starts to form equilibrium. If water can be drawn-off, formation of monoester is irreversible but when reaction proceeds, after 25 minutes the peak again rises. Here there is formation of water molecule during the reaction. It enables the reaction in reverse mode. This ester is predominantly used as plasticizer in many chemical industries as well as good di-electric fluid for capacitors in most of the electrical industries. The usage is on massive scale. The method is eco-friendly to the environment and can be used for commercial applications.

Conflict of Interest- None

References

American Society for Testing and Materials. ASTM D1639-90.1996**.** Standard Test Method for Acid Value of Organic Coating Materials.

Arabi, M. 2003. Esterification of phthalic anhydride with 1-butanol and 2- ethylhexanolcatalyzed by heteropoly acids. *Health & Environmental Research Online* (*HERO*). 200(1-2): 105-110.

Gerhard Mestl, 2025. Phthalic acid, derivatives of phthalic acids. *Ullman Encyclopaedia*, 1 Organic Chemistry, Vol. 1, Students international edition, page 246 – I.L.

Jerzy Skrzypek, 1994. Kinetics of the esterification of phthalic anhydride with 2-ethylhexanol. I. Sulfuric acid as a catalyst. Chemical Engineering and Processing - Process Intensification. 33(6): 413-418.

Kuehne, M. E. and Horne, D.A. 1975. Photochemical cyclization of olefininc N-chloroamides. *J. Org. Chem*. 40: 1287-1292.

Kunichika Nakamiya, 2005. Microbial Production and Vaporization of Mono-(2-ethylhexyl) Phthalate from di-(2-ethylhexyl) Phthalate by Microorganisms Inside Houses. *Archives of Environmental and Occupational Health.* 60(6): 321-325.

Peter Sykes Kirk. 2004. Reaction Mechanism in Organic Chemistry. *Othmer Encyclopaedia.* A-9: 565-585.

Scott Fogler, H. 2004. *Finar Elements of Chemical Reaction Engineering*, 3nd edition, page 171, 2004.

Thorat, T.S., Yadav, V.M. and Yadav, G.D. 1992. Esterification of phthalic anhydride with 2-ethylhexanol by solid superacidic catalyst. *Applied Catalysis A: General*. 90(2): 73-96.