STUDIES ON STABILITY OF WATER-IN-OIL EMULSIONS USING NON-IONIC SURFACTANTS

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In

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By

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DECLARATION

I hereby assure that the work presented in this project report entitled **“Studies on Stability of Water-in-Oil Emulsions Using Non-Ionic Surfactants**” is submitted towards completion of research project work in M.Tech (CAPPD) at the Indian Institute of Technology Roorkee, is an authentic record of my original work carried out under the guidance of **Dr. Vimal Kumar**, Assistant Professor. I have not submitted the matter embodied in this project report for the award of any other degree.

Place: Roorkee **Mahesh Prasad**

Date:

CERTIFICATE

This is to certify that Mr. Mahesh Prasad has completed the research project report entitled “**Studies on Stability of Water-in-Oil Emulsions Using Non-Ionic Surfactants**” under my supervision. This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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I thank all well-wishers who in any manner directly or indirectly have put hands in any part of this work.

Mahesh Prasad

ABSTRACT

In the present work the stabilization of water-in-oil emulsion prepared with water dispersed in a continuous diesel phase using two different non-ionic surfactants (Span 80 and Tween 80) has been studied. The emulsions were prepared such that their mixture HLB is 5.5. The water–in–oil emulsions have been prepared by ultrasonication. The stability of the emulsion has been studied by varying different parameters and determined on the basis of turbidity measurements at different wavelengths using UV Spectrophotometer. A mathematical model has been developed using Box Behnken Design (BBD) approach with Response Surface Methodology (RSM), to optimize the stable conditions for the emulsions. Four responses have been taken in consideration. The results shows that the experimental results best fits the mathematical model developed and can reasonably predict turbidity for a combination of input parameters other than the ones used for model prediction. Seven optimum results have been obtained for high desirability for stability of emulsion. From the present work it can be concluded that higher the turbidity, higher will be the stability of the emulsion.

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CHAPTER 1

INTRODUCTION

1.1 Background

The structure and stability of colloidal suspensions and emulsions have been of great interest for many years. The emulsion systems are widely used in the food, cosmetics, pharmaceuticals, etc. industries. One of the emerging application emulsion system is emulsified fuel for transportation and in the furnaces. The advantages of using emulsified fuels as an alternative for the fuel itself are environmental as well as economic benefits. Due to the rise in demand and usage of fosil fuels, and generating undesirable emissions during the combustion process, there is a need to reduce the usage fossil fuels. The pollutants (Cox, NO_x, unburnt hydrocarbons, etc.) that are exhausted from the internal combustion engines or diesel engines adversely affect the environment and cause problems such as global warming, smog, respiratory hazards, acid rain etc. Emulsion fuels are one of the alternatively for petroleum based diesel fuel.

Emulsified diesel fuel is prepared by mixing water in diesel fuel in the presence of an emulsifying agent/surfactant. There are various benefits to adding water to diesel. Vaporization of water increases fuel dispersion in sort of smaller droplets and the contact-surface between air and the fuel is increased which results in combustion that is more efficient. Since, the emulsion fuel reduces the combustion temperature inside the IC engine combustion chamber; there is a significant reduction in NO_x and PM formation.

Since the emulsions are inherently thermodynamically unstable, therefore the phase separation occurs eventually due to the instabilities present in the system. Emulsion type and stability are known to be associated with the equilibrium phase behavior in surfactant-oil-water systems and also with hydrophile-lipophile balance (HLB) of the system (as opposed to the empirical HLB number of the surfactant), which is related to the locus of aggregate formation in equilibrated mixtures **(Binks, 1999; Binks *et al.*, 2000)**: Macro-emulsions do not form spontaneously but rather require an input of energy. The process by which an emulsion completely breaks (coalescence) i.e. the system separates into bulk oil and water phases, is generally considered to be governed by four different droplet loss mechanisms i.e. Brownian flocculation, creaming, sedimentation flocculation and disproportion.

Sedimentation or creaming of drops might occur due to the density difference between the continuous and dispersed phases and can be intensified or restricted by flocculation. The thinning film between drops coming closer must reach a critical thickness for coalescence to occur. Ostwald ripening is the development of large droplets at the disbursement of smaller ones and relies on the solubility and transport of the dispersed phase in the continuous phase.

The emulsion stability can be explained with the help of DLVO theory. This theory explains the accumulation of aqueous dispersions quantitatively and explains the force between charged surfaces interacting through a liquid medium. It combines the effects of the electrostatic repulsion which is the sum of Maxwell's electric field stress and the osmotic pressure and the van der Waals attraction due to the double layer of counter-ions. The osmotic pressure is usually repulsive whereas Maxwell's stress and the van der Waals force are always attractive **(Verway and Overbeek, 1948)**.

1.2 Surfactants and Emulsions

This section explains about surfactants and emulsions and also the thermodynamic aspects related with emulsion formation. The various classes of surfactants and their role as 'surface active agents' are covered. Brief explanation of design and analysis of experiments is given.

1.2.1 Interfacial tension

It is an obvious statement that water and oil don't mix and upon vigorous shaking will eventually separate to achieve a minimum surface area between the two distinct phases (the same can be said of any two immiscible bulk liquids). Interfacial tension exists in the boundary region between the two bulk liquid phases. Interfacial tension is the property of a liquid/liquid interface exhibiting the characteristics of thin elastic membrane acting along the interface in such a way as to reduce the total interfacial area by an apparent contraction process (**Myers, 1992**).

Thermodynamically, interfacial tension is the excess of free energy resulting from an imbalance of forces acting upon the molecules of each phase. Atoms or molecules at an interface between two immiscible liquids generally have a higher potential energy than those in the bulk of the two phases. For two immiscible liquid phases, surface molecules interact more strongly with those in the bulk rather than those in the adjacent phase. Interfacial tension is normally defined in units of dyne/cm or mN/m as a force per unit length which is equal to energy per unit area.

1.2.2 Surfactants

Surfactants are materials which exhibit the characteristic of reducing the interfacial tension between two immiscible liquids by way of enhanced adsorption at the interface. Surfactants or 'surface active agents' or ‘emulsifying agents’ are usually amphiphilic organic compounds, i.e., possessing in the same molecule two distinct groups which greatly in their solubility relationships. Generally surfactants possess a hydrophobic tail group and a hydrophilic head group. The hydrophobic tail is usually a long chain hydrocarbon and the hydrophilic head is an ionic or highly polar group that imparts water solubility to the molecule. The unique amphiphilic structure of surfactants gives rise to some characteristic properties which fall into two broad categories;

a) Adsorption: the tendency of a surfactant molecule to collect at an interface. The adsorption properties of surfactants means these molecules are usually found at the interface between oil and water phases with the hydrophilic head groups favoring inclusion in the water phase and the hydrophobic tails favoring inclusion in the oil phase see Figure 1.1.

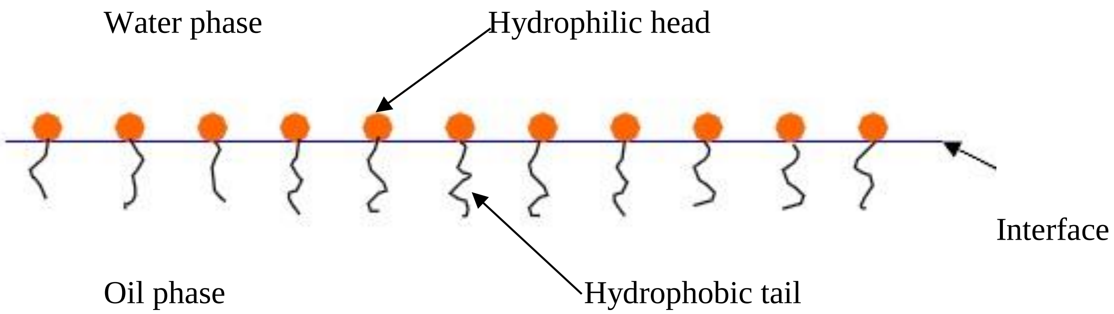


Figure 1.1 Adsorption of surfactant molecules at an oil/water interface.

b) Self-assembly: the property of surfactants where they arrange themselves into organized structures in aqueous solutions once a certain concentration is reached, usually referred as the critical micelle concentration (CMC). At low concentrations surfactant molecules form solutions in water but some molecules will be adsorbed at the air/solution interface and onto the walls of the containing vessel. As the concentration increases the surfaces become covered with a monolayer of surfactant molecules. Further increases in concentration causes normal dissolution processes to cease and the molecules in solution begin to aggregate into organized micelles, which form at a precisely defined concentration (**Hunter, 1993**). Figure 1.2 shows a schematic representation of a surfactant micelle in aqueous solution.

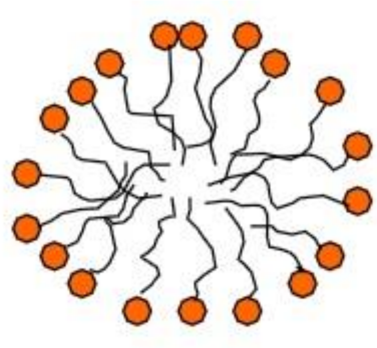


Figure 1.2 Spherical surfactant micelle.

Micelles are often globular and roughly spherical in shape but ellipsoids, cylinders, and bilayers or vesicles are also possible. The shape and size of a micelle depends on the molecular geometry of its surfactant molecules and solution conditions (such as surfactant concentration, temperature, pH and ionic strength). Surfactants can be classified in a number of ways but the most useful classification method is based on the nature of their hydrophilic head groups

1.2.2.1 Anionic surfactants

Anionic surfactants have a head group composed of highly electronegative atoms, which make these groups strongly polar, with a small counter ion, which is usually a small cation such as a sodium ion. This class of surfactant can be divided into subgroups such as alkali carboxylates or soaps ($RCOO^-M^+$); sulphates ($ROSO_3^-M^+$) such as sulphate ester surfactants, fatty alcohol sulphates and sulphated fats and oils; sulphonates ($RSO_3^-M^+$) such as aliphatic and alkylarylsulphonates and to a lesser degree phosphates (**Myers, 1992**). Figure 1.3 and 1.4 illustrate sodium dodecyl sulphate (SDS), a very commonly used anionic surfactant and a novel anionic surfactant (alkylarylsulphonate), which is used in enhanced oil recovery, respectively.

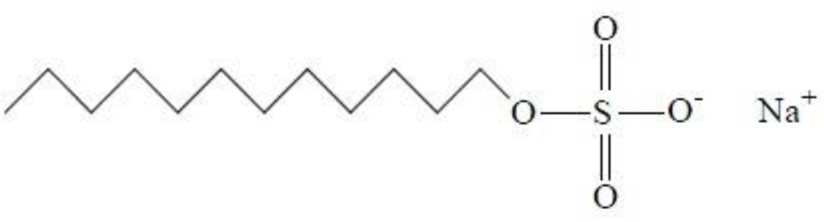


Figure 1.3 Sodium dodecyl sulphate (SDS).

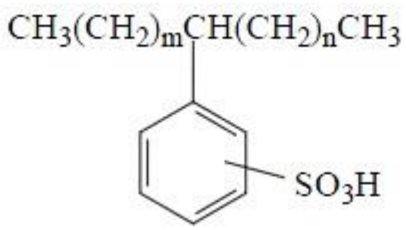
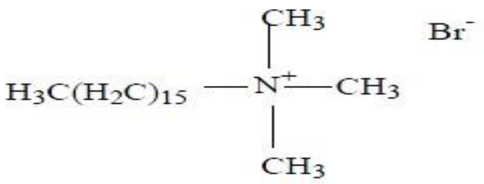


Figure 1.4 Alkylarylsulphonate.

1.2.2.2 Cationic surfactants

Cationic surfactants as the name suggests, possess positively charged head groups which is usually contain a nitrogen atom or an amide group. There are two important categories of cationic surfactants which differ mainly in the nature of the nitrogen containing group (**Myers, 1992**). The first consists of alkyl group, with halide, sulphate or acetate counter-ions. An example is cetyltrimethylammonium bromide (CTAB) shown in Figure 1.5.



$$\mathrm{H_3C(H_2C)_{15}-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_3\quad Br^-}$$

Figure 1.5 Cetyltrimethylammonium bromide (CTAB)

The second category contains heterocyclic components within which are an amino group or a nitrogen atom. An example of this type is alkyl substituted pyridine salts shown in figure 1.6. Other cationic functionalities are possible but are less common.

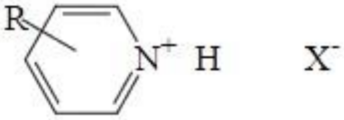


Figure 1.6 Alkyl substituted pyridine salt

1.2.2.3 Non-ionic surfactants

The two previously mentioned surfactants dissociate in water to produce a net charge on the head group of the molecule. This is not a necessary requirement for the existence of surface activity and non-ionic surfactants can offer advantages over ionic surfactants i.e. the effect of solution pH is lessened and the degree of water solubility can be controlled by controlling the polarity and size of the head group. Non-ionic surfactants can be further divided into sub-groups such as block copolymer non-ionic surfactants; derivatives of polyglycerols and other polyols; and polyoxyethylene based surfactants like polyoxyethylene 23 lauryl ether ($CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_{23}OH$) which are the most numerous and widely used.

An example of Non-ionic surfactant is Span 80 shown in figure 1.7

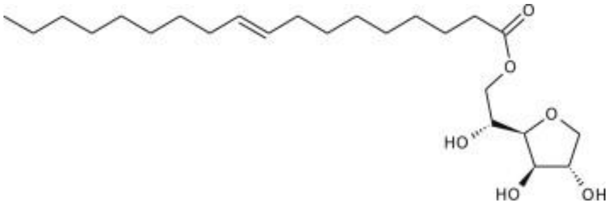


Figure 1.7 Span 80

1.2.2.4 Zwitterionic surfactants

Zwitterionic surfactants contain or have the potential to form both positive and negative functional groups under specified conditions. The Zwitterionic nature of these surfactants makes them very much compatible with other forms of surfactants. There are in general four classes of functionalities with potential for producing Zwitterionic surfactants; imidazole derivatives such as fatty acid/aminoethylethanolamine condensates ($RCONHCH_2CH_2NR^{'}R^{''}$), betaines and sulphobetaines such as dodecylbetaine ($C_{12}H_{25}(CH_3)_2N^+CH_2COO^-$), amino acid derivatives, and lecithins.

1.2.2.5 Aqueous surfactant structures

Surfactant molecules in solution exhibit unusual physical properties. In dilute solutions the surfactant acts as a normal solute but upon reaching a well defined concentration, abrupt changes in physical properties are observed. These properties include; osmotic pressure, turbidity, electrical conductance, and surface tension. This concentration as mentioned in precious Section is called the CMC where at and above this concentration micellisation occurs. The formation of micelles is an alternative mechanism to adsorption at the interface by which a surfactant solution may decrease its interfacial energy. The CMC of a surfactant can be affected by a number of factors outlined on the following page.

- The length of the hydrocarbon chain. In aqueous solutions, the CMC of ionic surfactants can be halved by the addition of each CH_2 group. For non-ionic surfactants the CMC may be reduced by up to a factor of 10 for each CH_2 group added.
- Temperature. Above certain temperatures, micelle forming surfactants show a rapid increase in their solubility. This temperature is known as the *Kraft point.* Below this point the solubility of a surfactant is insufficient for micelle formation.
- The addition of salts in the case of ionic surfactants. The repulsion between charged head groups is reduced by the addition of counter ions (**Shaw, 1980**).

1.2.2.5.1 Micelle structures

There are a number of different micellar structures possible and the structure obtained for a particular surfactant system depends on a number of factors. Figure illustrates a spherical micelle which is generally referred to when considering the application of micelles to separation science techniques. A generalization of temperature and concentration effects on surfactant systems is that spherical micelles usually form when a surfactants concentration is near its CMC and temperature is near its Kraft point. Higher surfactant concentrations (>50%) and higher temperatures will lead to the formation of liquid crystals in solution. Other factors influencing the structure of micelles include the nature of the surfactant and the surfactant *Packing Factor*.

$$Packing\ factor = v_t/(a_h l_{c,t}) \qquad \textbf{(1.1)}$$

where v_t = volume of the tail group

a_h = optimal head group area

$l_{c,t}$ = critical tail length

The packing factor along with surfactant characteristics such as the size of the head group, number of hydrocarbon chains and the charge on the head group, number of hydrocarbon chains and the charge on the head group will determine the type of micellar structure formed. Table 1.1 illustrates this point.

Table 1.1 Packing parameter and micelle structure.

Surfactant type	**Critical packing parameter**	**Micelle structure formed**
Single hydrocarbon tail with large head group	<1/3	Spherical
Single tail with small head group	1/3 – 1/2	Cylindrical
Double tail with large head group	½ - 1	Flexible bilayers
Double tail with small head group (anionic)	~1	Planar bilayers
Double tail with small head group (nonionic)	>1	Inverted micelles

1.2.3 Emulsions

It is a heterogeneous system consisting of at least one immiscible liquid dispersed in another in the form of droplets. The emulsions with diameter more than 0.1 μm possess a minimal stability, which may be accentuated by such additives as surface- active agents, finely divided solids etc. (**Becher, 1966**). Emulsions are generally opaque or milky in appearance due to relatively large droplets which scatter white light.

The formation of emulsion requires the generation of a very large amount of interfacial area between two immiscible phases which in turn requires work to be done on the system i.e.

vigorous shaking of two immiscible liquids in a closed container. The work required to generate one cm^3 of new interface is given by the following formula;

$$W = \sigma_i \Delta A \tag{1.2}$$

where W is work done; $\sigma_i$is the interfacial tension between two immiscible phases and ΔA is the change in interfacial area. Since work done on the system remains as potential energy, the system will be thermodynamically unstable and will undergo transformations to reduce the interfacial area to a minimum and so achieve minimum potential energy. These energetically favourable transformations are summarized as follows,

a) *Coalescence,* the joining of two or more drops to form a single large drop of larger volume;
b) *Flocculation,* the mutual attraction of individual drops to form loose assemblies of particles in which the identity of each is maintained;
c) *Breaking* of an emulsion where gross separation of the two phases occurs and the physical and chemical properties of the emulsion are lost;
d) *Creaming* is related to flocculation and will occur over time with almost all emulsions where there is a difference in the density of the two phases.

Upon the addition of a surfactant (emulsifying agent) to the system, a number of factors will contribute to enhance the emulsion stability:

a) A saturated monolayer of surfactant molecules is adsorbed at the oil-water interface, lowering the interfacial tension between the two phases resulting in less work being required to increase the surface area (Equation)
b) Mechanical stabilization of the interfacial film. By combined use of water-soluble and oil-soluble surfactants, the interfacial film is stronger and more elastic which retards coalescence
c) If the surfactant is ionic and imparts a charged atmosphere which can slow down the rate at which particles come together
d) High viscosity. The addition of a surfactant to an oil-water mixture can have a profound effect on the resulting emulsion viscosity depending on the type and concentration of surfactant used. High viscosities retard the rate of coalescence, creaming etc.

Another factor which effects emulsion stability is the ratio of oil and water phases. A relatively small volume of the dispersed phase will favour emulsion stability. The relative ratios of the oil and water phases and surfactant will also determine the type of emulsion if any that will form. The two most important types for the purposes of this research are oil-in water (O/W) and water-in-oil (W/O) emulsions.

Emulsions are divided into two broad classes based on if there is a single emulsion or a double or multiple emulsion groups. Those classes could be explained with the help of pairing of typical oil (O) and water (W) immiscible fluid. Single emulsions can further be divided into two different categories. A surfactant is used for creating a buffer like stabilizing layer between the two layers of oil and water in a single emulsion. First one of the categories is oil-in-water emulsions (O/W) which involves oil droplets finely dispersed in water. The other one is water-in-oil emulsion (W/O) in which water droplets are dispersed in oil. Except the separation of immiscible phases by at least two surfactant thin films , double or multiple emulsion classes is same as that of single emulsion classification. In a W/O/W (water-in-oil-in-water) emulsion group, the immiscible oil phase separates two different water phases while in an O/W/O (oil-in-water-in-oil) emulsion group a immiscible water phase exists between two separate oil phases. Emulsion classification is shown in figure 1.8.

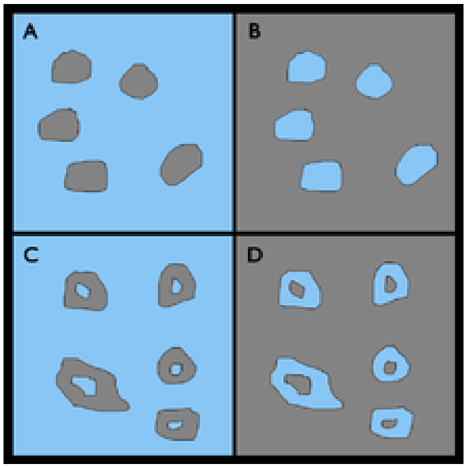


Figure 1.8 (a) oil in water emulsion, (b) water in oil emulsion, (c) water-oil-water multiple emulsion group and (d) oil-water-oil multiple emulsion group.

1.2.4 Applications

Emulsions are widely utilized in industrial, scientific and household applications. Emulsions are now a part of daily life as they have nearly endless uses in beauty, fabric, automotive and cleaning products. They are also used in manufacturing and biotechnological fields.

Soluble oil lubricants are helpful for low pressure and high speed operations and thus are widely used for metal working and friction reducing works (**Totten, 2003**). These lubricants are oil (mineral or fatty) in water emulsions.

There are variety of products that are prepared from silicone emulsions such as sun screens, skin care products, and fabric softeners. The reason for choosing silicon is because of its lubricating and non-irritating properties. Different amalgamation of surfactants and emulsion has been the key subject for a wide range of biological research, especially in the area of cell cultures (**Stefan *et al.*, 2003 and Cinelli *et al.*, 2006**). Some of the examples are shown in Table 1.2.

Table 1.2: Examples of Emulsions and their applications

Emulsion	**Continuous Phase**	**Dispersed Phase**	**Application**	**Surfactant**
Diesel Fuel and Water	Diesel	Water	Reducing fuel emissions	Nonionic surfactants based on aliphatic hydrocarbon tails (examples: alcohol ethoxylates, fatty acid ethoxylates, sugar esters of fatty acids)
Silicone and Water	Water	Silicon	Fabric Softener, Cosmetics	Nonionic surfactants (example: silicone copolyol)
Alcohol and Water	Water	Alcohol	Purifying contaminated ground water	Food or pharmaceutical quality agents similar to those used in whipped toppings and shampoos (examples: Polysorbate-20, Tween or Span)
Isooctane and Water	isooctane	water	Housing cell cultures	Have bactericide or bacteriostatic properties (example: Lecithin, a phospholipid found in many animals naturally)

1.2.5 Design and analysis of Experiments

Experiments often involve several factors and the general approach to planning and conducting the experiment is called the strategy of experimentation. There are several strategies that an experimenter could perform. Some of are as follows:

- *Best guess approach*: It is used frequently in practice by engineers and scientists. There are, however, at least two disadvantages of this approach. First, suppose the initial best-guess does not produce the desired results. Now, the experimenter has to take another guess at the correct combination of factor levels and this could continue for a long time, without any guarantee of success. Second, suppose the initial best-guess produces an acceptable result. Now the experimenter is tempted to stop testing, although there is no guarantee that the best solution has been found.
- *One factor at a time approach*: This method consists of selecting a starting point, or baseline set of levels, for each factor, then successively varying each factor over its range with the other factors held constant at the baseline level. The major disadvantage of the one factor at a time strategy is that it fails to consider any possible interaction between the factors.
- *Factorial experiment*: This is an experimental strategy in which factors are varied together, instead of one at time. An important and useful feature of factorials is that it makes the most efficient use of the experimental data.
- *Fractional factorial experiment*: It is a variance of the basic factorial design in which only a subset of the runs are made.

Response surface methodology (RSM) consists of a group of statistical techniques which includes Box–Behnken design (BBD) model for model building and model exploitation. By proper experimental design and analysis, the BBD relates the responses or output variables to a number of input variables that affect it. It also allows the calculations for finding out the response at intermediate levels which were not experimentally studied and shows the path on which to move by changing the input levels (**Montgomery, 2004 and Lataye *et al.*, 2008**). The optimization process involves the study of the responses of the statistically designed combinations of parameters, estimating the coefficients by fitting it in a mathematical model that best fits the experimental data, predicting the response of the fitted model and checking the adequacy and accuracy of the model (**Kumar *et al.*, 2008**).

BBD are formed by combining 2^k factorials with incomplete block designs. The resulting designs are usually very efficient in terms of the number of required runs, and they are either rotatable or nearly rotatable. It is a spherical design, with all points lying on a sphere of radius $\sqrt{2}$. Also, it does not contain any points at the vertices of the cubic region created by the upper and lower limits of each variable. This could be advantageous when the points on the corners of the cube represent factor-level combinations that are prohibitively expensive or impossible to test because of physical process constraints (**Montgomery, 2004 and Box *et al.*, 1978**).

1.3 Motivation

Various publications have discussed about the stability and formation of w/o nano-emulsions using non-ionic surfactants. The effect of temperature and salt addition had been studied by **Shinoda and Saito (1969,1971)** on hydrophile–lipophile balance (HLB) and phase diagram of water-cyclohexane system stabilized using a non-ionic surfactant, i.e, polyoxy-ethylene-nonylphenylether. **Uson *et al.* (2004)** investigated the phase behavior of w/o system with non-ionic surfactant. **Porrasa *et al.* (2004)** investigated the formation of w/o nano-emulsion using mixed non-ionic surfactants and also the breakdown mechanisms of emulsions prepared. **Liu *et al.* (2006)** studied the stability and formation of o/w nano-emulsion stabilized using non-ionic surfactant (Span 80/Tween 80). **Mei *et al.* (2011)** studied the stability of paraffin o/w nano-emulsions using non-ionic surfactants (Span 80/Tween80) and influence of different types of inorganic salts on the PIT. Studies on the addition of salts on emulsions shows that salting out salts in water can reduce PIT (phase inversion temperature) of the systems to an optimum temperature such that it exhibits ease in the formation of nano-emulsions. **Santos *et al.* (2011)** studied the stability, rheology and droplet size of heavy o/w emulsions stabilized with mixture of normal alcohols and ethoxylated surfactants. **Xin *et al.* (2013)** investigated the properties of nano-emulsion as a function of emulsifier content and the addition of ionic surfactants including CTAB and SDS. **Jiang *et al.* (2013)** investigated the stability and effect of inorganic salts such as

$NaCl$, $CaCl_2$ and Na_2SO_4 on the formation of w/o emulsion. Information about the stability of w/o emulsion stabilized with non-ionic surfactant taking several factors at a time is very limited. In this context we have investigated the stability of oil in water emulsion using a non-ionic surfactant with turbidity at different wavelengths as a parameter taken after emulsion preparation.

1.4 Objectives of the present work

The main objective of the present work is to determine the stability of water–in–diesel emulsion using non–ionic surfactants and to develop a mathematical model relating the stability of the emulsion. The specified objectives are as follows:

- State of art literature review of oil in water and water in oil emulsions.
- Determine the stability of water in diesel emulsions using non-ionic surfactants with turbidity at different ultraviolet light wavelengths as a parameter taken after emulsion preparation.
- Develop a mathematical model relating the turbidity of water in diesel emulsions to the water concentration, surfactant concentration, amplitude of ultrasonication and time using Box-Behnken Design.
- Optimizing parameters (oil concentration, surfactant concentration, amplitude and time) using steepest ascent method.

1.5 Scope

As it may be seen that there is a need to reduce the pollution and save the fuel. Entire universe has given much attention and many research works are going on based on the alternate fuel to the IC engines. This research on the stability of water in oil may be helpful in meeting our desire for a cleaner environment and saving the fuel. Water in diesel emulsion is helpful in decreasing the NO_x emissions from the diesel engine and improving the combustion. The stability of water-in-diesel emulsion using non-ionic surfactant may be of significant importance to get better results for IC engines.

1.6 Report organization

Chapter 1 is divided into two sections. An introduction and overview is provided in section 1 while section 2 presents a discussion on emulsions and design and analysis of experiments. Chapter 2 presents a brief literature review. Materials and methods are provided in Chapter 3. Chapter 4 gives the results, modeling and optimization and discussion. Chapter 5 provides the conclusions and recommendations. The final section gives the references consulted.

CHAPTER 2

LITERATURE REVIEW

This section presents the overview of the researches that had been done in the field of formation and stability of oil in water or water in oil emulsions by using different types of surfactants; effect of electrolytes on the emulsion; effect of temperature, etc.

Oren and Mackay (1976) studied the effect of electrolyte and pH on stability of water-in-Guanipa crude emulsions. In it, the electrolyte concentration and pH of monovalent and polyvalent metal chlorides in initial aqueous phase was taken into consideration. Stability of emulsion was discovered to be highly dependent on pH of the initial aqueous phase and emulsion breakdown occurred at $10 < pH < 13.5$. Within the stability gap boundaries, base addition either before or after formation of emulsion had considerable effect on the degree of emulsion collapse. The concentration of elctrolyte at the isoelectric point of the sytem was related with threshold concentration of electrolyte for emulsion collapse. The results showed that the parameters taken affect the stability of water-in-Guanipa crude appreciably.

Masson and Jost (1986) investigated oil in water emulsions stabilized using whey proteins. Emulsion preparation was done mixing grape-seed oil with water and stabilizing agent used was whey protein concentrate. And different pH emulsions were prepared. Particle size and droplet size distribution were measured with reference to light scattered and surface charge density was evaluated using electrophoretic mobility. The emulsifying properties of stabilizing agent were derived in terms of particle size, droplet size distribution and surface charge density. At pH = 4.4, the prepared emulsion had shown poor stability and isoelectric point of the stabilizing agent concentrate was also at this pH.

Binks *et al.* (2000) studied the stability of o/w emulsions in a low interfacial tension arrangement. In this study, emulsions were prepared using pre-equilibrated phases with the help of Winsor I systems and the stability of o/w emulsions with respect to creaming and coalescence was derived in terms of concentration of salt in oil-in-water emulsions stabilized by AOT. The creaming rate of emulsion was found to be decreasing for increasing NaCl concentration upto 0.035M while for salt concentration above 0.035 M upto 0.055M (which is phase inversion salt concentration) the creaming rate was found to be increasing with increasing salt concentration and the coalescence rate became considerable. The creaming rate at low NaCl concentrations was found to be active mainly because of buoyancy motion of single drops. A simple model was developed for the timely evolution of resolved water was developed which satisfactorily explains the behavior. On analyzing the droplet size changes, Ostwald ripening was found to be the reason behind it. Ostwald ripening rate was seen to be decreasing with salt concentration. With the help of experimentally determined values of drop radius, intyerfacial tension and zeta potential, the energy of inter-drop interaction was being derived allowing for droplet deformation. Because of low interfacial tension, the droplets started deforming at high salt concentration and droplet to droplet attraction became significant which in turn resulted in flocculation which lead to coalescence instability.

Ikeda *et al.* (2004) thermodynamically studied the single emulsion film stabilized with tetradecyltrimethylammonium bromide (C14TAB) in dodecane phase. In this work, the relation of thermodynamic quantities of thin films with different experimental parameters such as temperature, concentration of solutes and pressure was studied. Taking in consideration the influence of adding inorganic salt (KBr) on the emulsion film, the film tension and film surface tension was studied thermodynamically by using the equations derived in report. The effect of dodecane phase on the film properties was also studied by comparing the results for foam and emulsion films.

Pichot *et al.* (2010) investigated the stability of o/w emulsions using both surfactants and colloidal particles against coalescence. The effect of the type of surfactant and their concentration on oil-in-water emulsion was studied. Selection of two types of surfactants was on the basis of their ability to stabilize the type of emulsion (water-in-oil or oil-in-water). One (Tween 60 and Sodium Caseinate) is selected such that it helps in forming o/w emulsion and other (lecithin) such that it helps in forming w/o emulsion. Three oil-in-water emulsions were prepared using both particles and one of the three surfactants. Emulsions formed were stable against coalescence but for different surfactant, system behavior was different and depends on the surfactant concentration. At low concentration of Tween 60 or Sodium Caseinate, droplet size of emulsions was smaller than those when emulsion is prepared using either surfactant or colloidal particle. The droplet sizes of emulsions increased for intermediate surfactant concentration while for higher concentrations, the influence of colloidal particles is completely overwhelmed by surfactants and system behaves as a surfactant-only stabilized emulsion. On the other hand emulsion prepared using lecithin as a surfactant; no change in the emulsion behavior was being noticed for change in surfactant concentration.

Kundu *et al.* (2013) studied the stability of oil in water macroemulsion using an anionic surfactant and analyzing the effect of electrolyte and temperature on the stability of emulsion. The emulsion was prepared by using diesel oil, NaOH, distilled water, NaCl and anionic surfactant (SDBS) and was stirred at 2000 rpm for 10 minutes. The concentration of NaCl was varied in the range of 0.1–5.0 (M) and the surfactant to oil ratio(s/o) (w/w) was varied in the range of 0.1–0.7. A fixed oil concentration of 30% was kept for the experiments. Phase inversion temperature (PIT) of emulsion was determined by conductivity measurement in terms of different s/o ratios’ temperature. Taking in consideration different kinds of inorganic salts, by making measurements of zeta potential, conductivity and turbidity of the emulsion, their influence on the PIT, long term stability and electrophoretic properties of the o/w emulsion were studied. The destabilizing mechanisms of the o/w emulsion were explained by studying the development of droplet size of emulsion, and turbidity of emulsion with time. It was discovered that Ostwald ripening and coalescence could be the main destabilizing mechanisms of prepared emulsion.

Xin *et al.* (2013) studied the effect of CTAB and SDS on oil-in-water nano-emulsion using Span 20/ Tween 20 and paraffin. Emulsion was prepared using EIP method (emulsion inversion phase) at 25^0C taking paraffin as an oil phase and a mixture of Span 20 and Tween 20 as emulsifiers. Effect of adding ionic surfactants and emulsifier content added on the emulsion properties was analyzed. It was observed that the emulsion droplet size decreases with increasing emulsifier concentration. Similarly it decreased with ionic surfactants addition. On analysis of zeta potential it was found that it was negative when there is no addition of ionic surfactants but on addition of SDS, it decreased even further resulting in long term stability. However, on addition of CTAB zeta potential increased though it remained negative resulting in lowering down of emulsion stability. These results deduced that the main factor for the determination of emulsion stability was electrostatic interaction. Interfacial rheological measurements had shown that the single adsorption layer of Tween 20 at oil/water interface was higher than the maximum values taken for both Tween 20/SDS and Tween 20/CTAB dilational moduli.

Ushikubo and Cunha (2014) investigated the stability of liquid water-in-oil emulsions in using two different oils. Several emulsions were prepared using three different emulsifiers and two different oils at different water to oil ratios. Emulsifiers used were Span 80, PGPR and lecithin. Oils used were hexadecane and soybean oil. Emulsion prepared with water and soybean oil stabilized using PGPR and water and hexadecane using Span 80 had higher kinetic stability and had shown a low interfacial tension interface and constant complex viscoelastic modulus with time. Thus resulting in smaller droplets formation and a stable elastic interface helped resisting coalescence. Better chemical affinity of the hydrophobic moieties of the emulsifier and the oil led to more stable interface. At higher water volume fraction content, steric stability was obtained and also in more viscous systems. The water‑soybean oil emulsions using Span 80 or lecithin as emulsifiers formed a gelled structure not a macroemulsion. This study investigated many factors that could affect the emulsion stability and its formation.

CHAPTER 3

MATERIALS AND METHODS

This chapter deals with the materials used and the methods used for emulsion preparation. This also focuses on the methods used for stability and model determination, and optimization of parameters.

3.1 Materials

The materials used for emulsion preparation are as follows: diesel oil (density, ρ= 810 kg/m^3, viscosity, μ= 2.0-4.5 cSt) (Bharat Petroleum Corporation Ltd., India), Span 80 (Himedia, Mumbai), Tween 80 (Himedia, Mumbai),NaOH (RCFL, New Delhi), NaCl (SRL, Mumbai), double distilled water. All the reagents were used as procured.

3.2 Methods

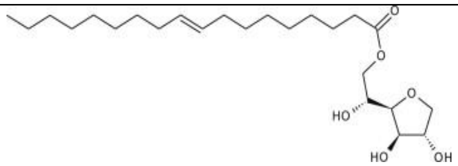
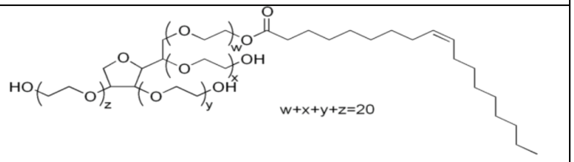
Following are the methods used for emulsion preparation, stability and model determination, and parameter optimization.

3.2.1 Preparation of w/o emulsion

Premix water with NaCl, NaOH and Tween 80. Span 80 is dissolved in Diesel. Non-stable pre-emulsion is prepared by means of magnetic stirrer (600 rpm, for 5 minutes) and then stable emulsion is prepared by ultrasonication at fixed cycle time 0.5 and varying amplitude range (40-100%) and time (10-20 minutes). Then emulsion's turbidity is measured at different wavelengths using UV Spectrophotometer.

Span 80 and Tween 80 are used as surfactants and its HLB is maintained at 5.5.Their physical properties are shown in Table 3.1. Double distilled water was used for the preparation of all w/o emulsions

Table 3.1 Physico-chemical properties of Span 80 and Tween 80.

Characteristics	**Span 80**	**Tween 80**
Type	Non-ionic surfactant	Non-ionic surfactant
Molecular formula	$C_{24}H_{44}O_6$	$C_{64}H_{124}O_{26}$
Molecular weight	428.60	1310
Structural formula		
Appearance	Amber colour viscous liquid	Amber colour viscous liquid
Density (g/ml)	0.986	1.095
Solubility in water	Insoluble	Very Soluble

Compositions of emulsion constituents used for experimentation are shown in Tables 3.2 and 3.3.

Table 3.2 Composition of NaOH and NaCl for 1 dm^3 of emulsion preparation.

NaOH	**NaCl**
4 g	0.5844 g

Table 3.3 Composition of surfactants Span 80 and Tween 80 for different surfactant concentration for 1dm^3 of emulsion preparation.

Surf. Conc. (%)	**Water (%)(v/v)**					
	5		**17.5**		**30**	
	Span 80 (g)	**Tween 80 (g)**	**Span 80 (g)**	**Tween 80 (g)**	**Span 80 (g)**	**Tween 80 (g)**
3	22.504	2.838	23.149	2.92	23.795	3.001
6.5	50.584	6.38	52.034	6.563	53.485	6.746
10	80.847	10.197	83.167	10.489	85.485	10.782

3.2.2 Determination of Stability

The stability of emulsion was characterized by the turbidity of the emulsion at different ultraviolet light wavelengths, defined as the ratio of the product of Absorption and Dilution factor to the Length of the cuvette. The higher the ratio, the greater is the emulsion stability.

$$\tau = \frac{AD}{l}$$

where τ is Turbidity, A is Absorption, D is Dilution factor and l is length of cuvette.

3.2.3 Determination of model equations

A mathematical model was developed relating the turbidity of water in oil emulsion at different light wavelengths to the water concentration, surfactant concentration, ultrasonication amplitude and time using Box Behnken design using statistical software Design Expert V9.

3.2.4 Optimizing parameters

The four parameters, i.e., water concentration, surfactant concentration, ultrasonication amplitude, and time were optimized using steepest ascent method to maximize the stability of emulsions by maximizing the turbidity of emulsion. This was done using the statistical software, Design Expert V9.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter provides the results obtained by experimental and statistical analysis. Further, a brief discussion is also done on the results obtained.

4.1 Turbidity analysis for water–in–oil emulsions

Turbidity of emulsions was recorded for prepared emulsion taking different parameters (water concentration, surfactant concentration, amplitude and time) at different ultraviolet light wavelengths using UV spectrophotometer as shown in Table 4.1 where Turbidity 200, Turbidity 400, Turbidity 600 and Turbidity 800 are the turbidity of w/o emulsion at 200, 400, 600 and 800 nm wavelengths, respectively.

Table 4.1 Experimental values for turbidity of water in diesel emulsions for different wavelengths for different levels of BBD.

Run No.	**Water conc. (v/v%)**	**Surf. Conc. (w/w%)**	**Amplitude (%)**	**Time (min)**	**Turbidity 200**	**Turbidity 400**	**Turbidity 600**	**Turbidity 800**
1	5	3	70	15	1104	290	269	259
2	30	3	70	15	1780	204	180	167
3	5	10	70	15	3039	660	289	651
4	30	10	70	15	2978	1340	1103	922
5	17.5	6.5	40	10	968	550	470	427
6	17.5	6.5	100	10	3970	2352	1713	1030
7	17.5	6.5	40	20	3799	2385	1756	1059
8	17.5	6.5	100	20	3802	2010	1135	612
9	5	6.5	70	10	1765	475	467	452

10	30	6.5	70	10	2000	838	733	646
11	5	6.5	70	20	2982	688	575	243
12	30	6.5	70	20	3518	1871	878	463
13	17.5	3	40	15	3250	695	538	495
14	17.5	10	40	15	2355	545	513	499
15	17.5	3	100	15	2829	932	803	734
16	17.5	10	100	15	4021	1809	1362	1010
17	5	6.5	40	15	2471	317	300	295
18	30	6.5	40	15	3449	1144	803	492
19	5	6.5	100	15	3148	386	310	282
20	30	6.5	100	15	3926	2126	1449	865
21	17.5	3	70	10	2135	431	339	294
22	17.5	10	70	10	2845	1221	972	771
23	17.5	3	70	20	3391	1667	1151	771
24	17.5	10	70	20	3671	1749	1532	1221
25	17.5	6.5	70	15	3699	2256	1888	1360
26	17.5	6.5	70	15	3800	2300	1956	1413
27	17.5	6.5	70	15	3550	2165	1806	1302
28	17.5	6.5	70	15	3622	2198	1848	1318
29	17.5	6.5	70	15	3702	2268	1895	1358

4.2 Selection of model

Selection of model was done on the basis of sequential model sum of squares calculations and lack of fit tests which depends on F value. The greater the F value the lesser the Prob > F value and better the model fits. And, the model summary statistics is also analysed to see which model best fits the experimental results obtained in Table 4.1 The results obtained for selecting appropriate model is shown in Table 4.2 and 4.3, where L is Linear, M is Mean, Q is Quadratic and C is Cubic.

Table 4.2 Selection of adequate model

Sour-ce	Turbidity 200		Turbidity 400		Turbidity 600		Turbidity 800		Remarks
	F Value	**Prob> F**	**F Value**	**Prob> F**	**F Value**	**Prob> F**	**F Value**	**Prob> F**	
Sequential Model Sum of Squares									
L vs M	4.62	0.0066	3.32	0.0266	1.96	0.1331	1.25	0.3166	
2FI vs L	1.39	0.2730	0.65	0.6903	0.60	0.7320	0.34	0.9072	
Q vs 2FI	15.2	<0.0001	27.85	<0.0001	39.4	<0.0001	24.16	<0.0001	Suggested
C vs Q	1.94	0.2180	4.45	0.0427	7.37	0.0127	7.52	0.0121	Aliased
Lack of Fit Tests									
L	22.77	0.0040	272.82	<0.0001	194.73	<0.0001	76.11	0.0004	
2FI	22.16	0.0043	320.35	<0.0001	232.08	<0.0001	97.66	0.0002	
Q	5.47	0.0579	49.72	0.0009	26.14	0.0033	16.95	0.0075	Suggested
C	6.20	0.0595	34.16	0.0031	10.26	0.0266	5.87	0.0646	Aliased

Table 4.3 Model summary statistics

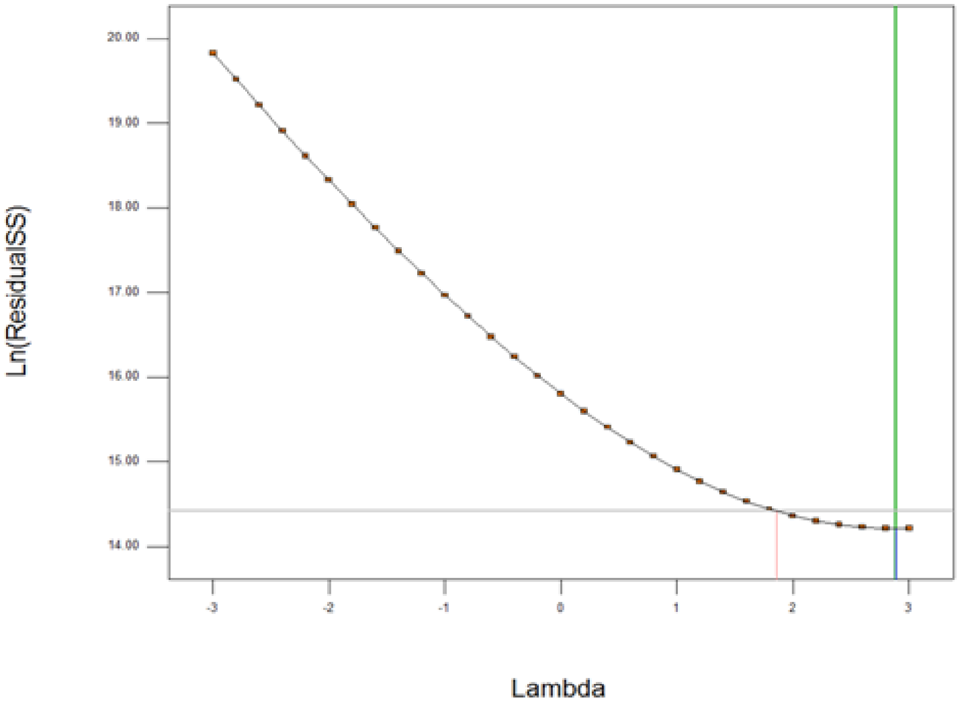
Source	R-Squared	Adjusted R-Squared	Predicted R-Squared	Remarks
Turbidity 200				
L	0.4352	0.3410	0.1750	
2FI	0.6137	0.3991	-0.0093	
Q	0.9278	0.8556	0.6047	Suggested
C	0.9798	0.9059	-1.2022	Aliased
Turbidity 400				
L	0.3565	0.2492	0.1091	
2FI	0.4710	0.1771	-0.2218	
Q	0.9409	0.8819	0.6617	Suggested
C	0.9915	0.9602	-0.1603	Aliased
Turbidity 600				
L	0.2462	0.1206	-0.0136	
2FI	0.3710	0.0216	-0.3263	
Q	0.9487	0.8974	0.7077	Suggested
C	0.9953	0.9779	0.4274	Aliased
Turbidity 800				
L	0.1725	0.0345	-0.0673	
2FI	0.2564	-0.1566	-0.4254	
Q	0.9059	0.8118	0.4672	Suggested
C	0.9915	0.9602	0.0797	Aliased

4.3 Box-Cox plot for power transform for all responses

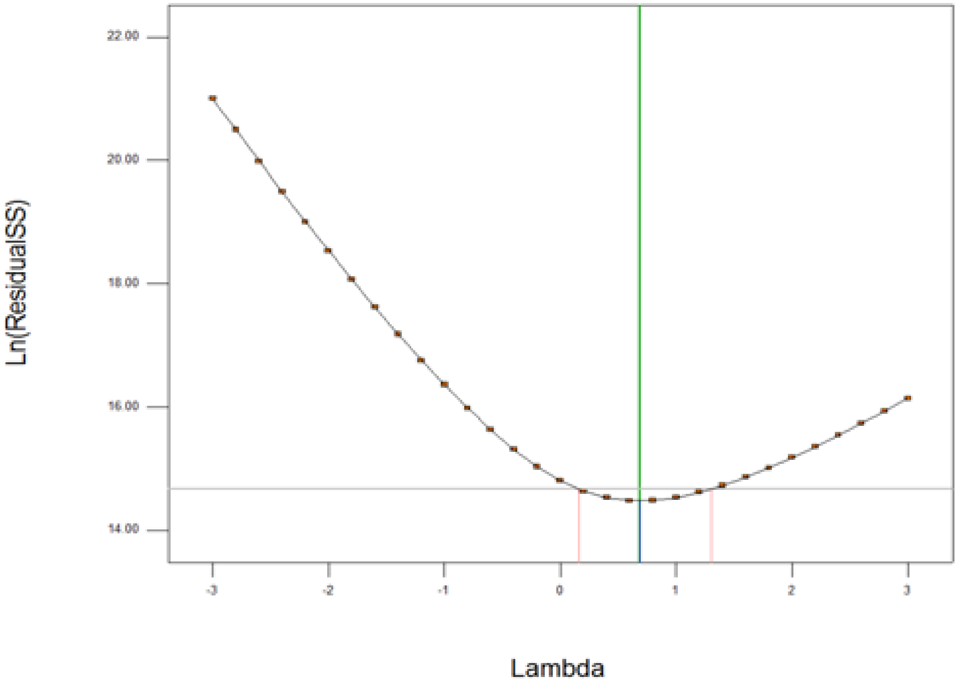
Box-Cox plot is helpful when defining a measure of the normality of the resulting transformation. It helps in choosing power transform which should be taken in consideration for the desired model. Figure 4.1 shows Box-Cox Plot for power transforms for the predicted model for turbidity at different wavelengths.

With the help of Tables 4.2 and 4.3 and Figures 4.1A and 4.1B, following conclusions could be made:

- The model equation for turbidity at 200 nm wavelength best fits a quadratic model with power law transform with lambda = 2.89. The quadratic model was selected because it has least lack of fit and least standard deviation among the models available for modeling. The power law transform was needed because the model thus predicted has least sum of squares of error among all the power transforms as evident from the Box-Cox plot (Figure 4.1A i).
- The model equation for turbidity at 400 nm wavelength best fits a quadratic model with power law transform with lambda = 0.69.The quadratic model was selected because it has least lack of fit and least standard deviation among the models available for modeling. The power law transform was needed because the model thus predicted has least sum of squares of error among all the power transforms as evident from the Box-Cox plot (Figure 4.1A ii).
- The model equation for turbidity at 600 nm wavelength best fits a quadratic model with power law transform with lambda = 0.66.The quadratic model was selected because it has least lack of fit and least standard deviation among the models available for modeling. The power law transform was needed because the model thus predicted has least sum of squares of error among all the power transforms as evident from the Box-Cox plot (Figure 4.1B i).
- The model equation for turbidity at 800 nm wavelength best fits a quadratic model with power law transform with lambda = 1.19.The quadratic model was selected because it has least lack of fit and least standard deviation among the models available for modeling. The power law transform was needed because the model thus predicted has least sum of squares of error among all the power transforms as evident from the Box-Cox plot (Figure 4.1B ii).

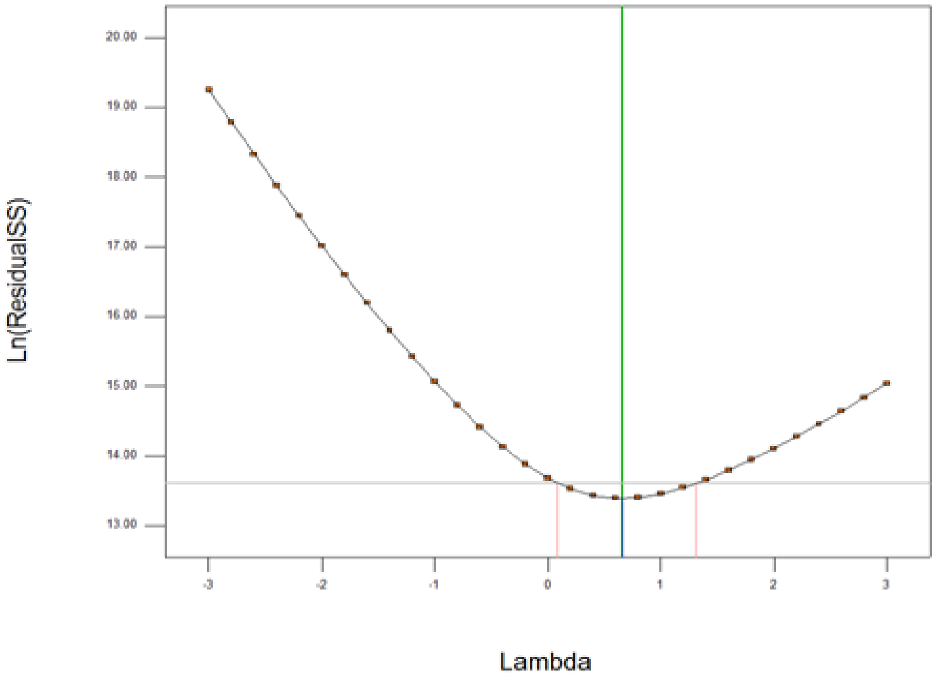


i) Turbidity 200

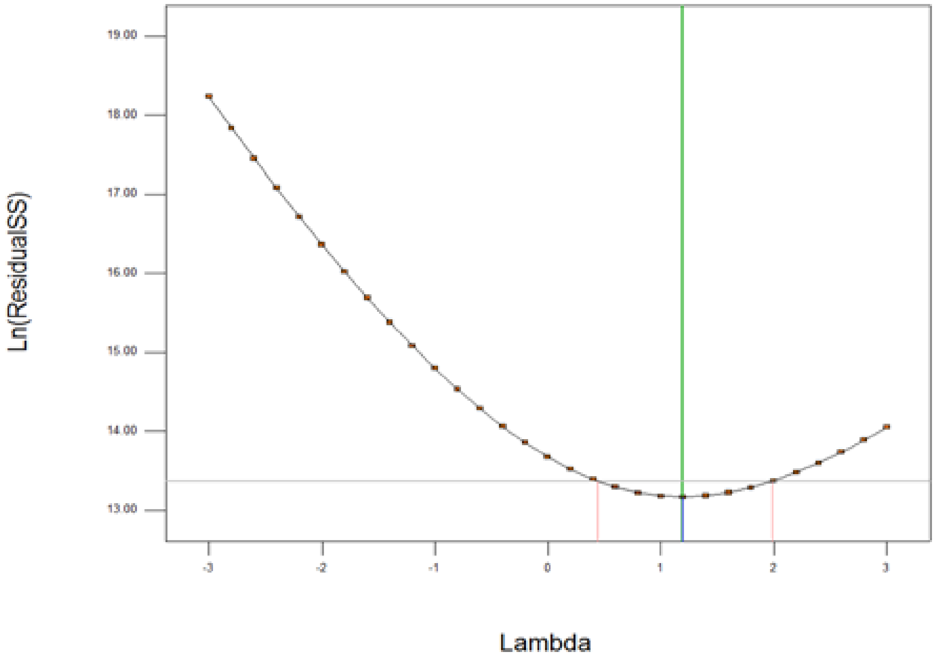


ii) Turbidity 400

Figure 4.1A Box-Cox Plot for power transformation of the predicted model for turbidity (at different wavelengths) of water in diesel emulsions using BBD.



i) Turbidity 600



ii) Turbidity 800

Figure 4.1B Box-Cox Plot for power transformation of the predicted model for turbidity (at different wavelengths) of water in diesel emulsions using BBD.

4.4 Model Equation

Model equations obtained after doing Box-Cox transformation for the predicted model for turbidity at different wavelengths are as follows:

$(\text{Turbidity } 200)^{2.89}$ =

-9.63827E+010

+1.87568E+009 * Water Conc.

+3.26713E+009 * Surf. Conc.

+3.78932E+008 * Amplitude

+7.83742E+009 * Time

+5.99810E+007 * Surf. Conc. * Amplitude

-4.11195E+007 * Amplitude * Time

-4.77194E+007 * Water Conc.^{2}

-5.06343E+008 * Surf. Conc.^{2}

-1.29843E+008 * Time^2

$(\text{Turbidity } 400)^{0.69}$ =

-761.32597

+18.16252 * Water Conc.

+65.64179 * Surf. Conc.

+8.18177 * Amplitude

+24.29250 * Time

-0.26338 * Amplitude * Time

-0.44630 * Water Conc.^{2}

-4.55795 * Surf. Conc.^{2}

-0.024131 * Amplitude^2

(Turbidity 600)$^{0.66}$ =

-622.67325

+10.75305 * Water Conc.

+38.46573 * Surf. Conc.

+6.55182 * Amplitude

+34.43480 * Time

+0.39510 * Water Conc. * Surf. Conc.

-0.18811 * Amplitude * Time

-0.34076 * Water Conc.^{2}

-3.17158 * Surf. Conc.^{2}

-0.023495 * Amplitude^2

-0.62154 * Time^2

(Turbidity 800)$^{1.19}$ =

-34499.69069

+572.98516 * Water Conc.

+1660.84293 * Surf. Conc.

+337.92496 * Amplitude

+2082.33500 * Time

-7.34190 * Amplitude * Time

-15.33618 * Water Conc.^{2}

-110.41980 * Surf. Conc.^{2}

-1.52447 * Amplitude^2

-50.49106 * Time^2

4.5 ANOVA and Regression analysis

ANOVA stands for Analysis of variance. It is an assembly of statistical models which is used to differentiate between the factors desired and factors undesired. Basically it compares the mean of variables/parameters or groups for statistical significance. On the other hand, doing regression analysis, i.e, by calculating R-squared, adjusted R-squared and Predicted R-squared; we come to know how best the predicted model fits the experimental results. Table 4.4 shows ANOVA analysis and Table 4.5 shows regression analysis.

Table 4.4 ANOVA

Source	**Turbidity 200**		**Turbidity 400**		**Turbidity 600**		**Turbidity 800**	
	F Value	Prob> F	F Value	Prob> F	F Value	Prob> F	F Value	Prob> F
Model	24.18	< 0.0001	17.79	< 0.0001	23.27	< 0.0001	16.44	< 0.0001
A	10.41	0.0044	19.34	0.0003	21.78	0.0002	5.44	0.0309
B	15.09	0.0010	9.57	0.0057	15.11	0.0011	16.51	0.0007
C	32.82	< 0.0001	12.53	0.0021	12.53	0.0023	4.93	0.0387
D	44.65	< 0.0001	16.42	0.0006	12.31	0.0025	1.91	0.1829
CD	20.87	0.0002	9.96	0.0050	7.14	0.0156	10.73	0.0040
A^2	20.01	0.0003	52.21	< 0.0001	19.02	0.0004	82.34	< 0.0001
B^2	49.19	< 0.0001	33.47	< 0.0001	109.81	< 0.0001	26.24	< 0.0001
C^2	34.04	< 0.0001	5.06	0.0358	58.47	< 0.0001	26.99	< 0.0001
D^2	9.32	0.0065	17.79	< 0.0001	17.32	0.0006	22.85	0.0001
Lack of Fit	4.09	0.0916	65.10	0.0005	26.24	0.0031	13.73	0.0107

Table 4.5 Regression Analysis

	Turbidity 200	**Turbidity 400**	**Turbidity 600**	**Turbidity 800**
R-Squared	0.9197	0.8768	0.9282	0.8862
Adj R-Squared	0.8817	0.8275	0.8883	0.8323
Pred R-Squared	0.8081	0.7409	0.8236	0.7266
Adeq Precision	16.716	14.428	14.090	12.636

ANOVA for the model (Table 4.4) shows that the contribution of water concentration, surfactant concentration, amplitude % and time of ultrasonication are significant. The amplitude % and time interaction is far more significant than any other interaction for all turbidity responses except for turbidity at 200 nm wavelength in which surfactant concentration and amplitude interaction is also significant and for turbidity at 600 nm wavelength in which water concentration and surfactant concentration interaction is also significant.

Regression analysis (Table 4.5) shows R-squared, adjusted R-squared and predicted R-squared value are 0.92, 0.88 and 0.81, respectively for turbidity at 200 nm wavelengths; 0.88, 0.83 and 0.74, respectively for turbidity at 400 nm wavelengths; 0.93, 0.89 and 0.82, respectively for turbidity at 600 nm wavelengths; and 0.89, 0.83 and 0.73, respectively for turbidity at 800 nm wavelengths. Therefore it can be concluded that the experimental values fit into the predicted model with a high fitness value. High value of R-squared is not a good indicator for fitness as it increases with the number of input parameters involves, even if the new parameter does not influence the physical factors affecting the model. Adjusted R-squared of more than 0.8 indicates a good fitness and shows that the model can reasonably predict turbidity for a combination of input parameters other than the ones used for model prediction.

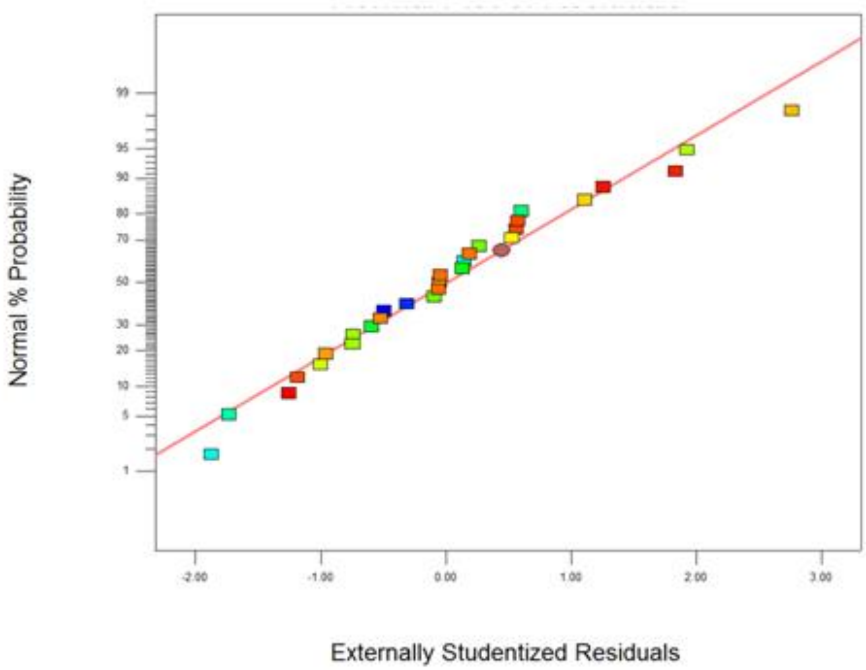
4.6 Determination of outliers

Outliers for the experiments were determined by analysing the residuals, studentized residuals and Cook's distance, as shown in Table 4.6. The graph between Normal %probability and studentized residuals should be a straight line as shown in Figure 4.2A and B. The deviation shows human errors. Figure 4.3A and B shows graph between residuals and predicted values. A continuous increase in the magnitude of studentized residuals (i.e. residual/ root/ mean square error) with increase in the predicted value shows that background noise or error is playing a role in the predicted value and human error or instrumentation error is involved. Increase and decrease of studentized residuals against the predicted values for the model predicted for the above physical phenomenon shows that the model is accurate.

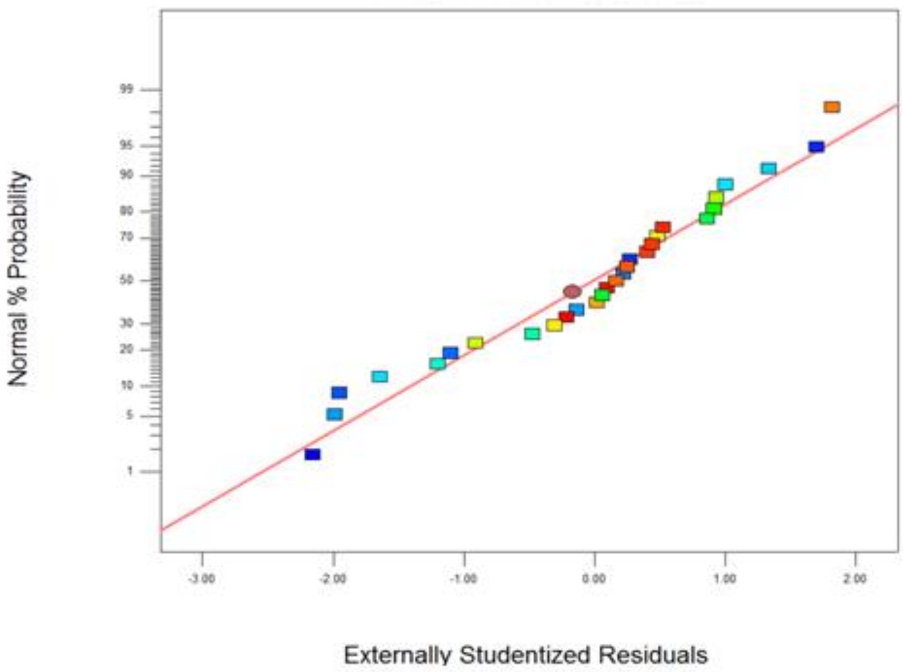
Table 4.6 Determination of outliers

Run No.	**Turbidity 200**				**Turbidity 400**		
	Residuals	**Studentized Residuals**	**Cook's Distance**		**Residuals**	**Studentized Residual**	**Cook's Distance**
1	-0.316	-0.308	0.005		1.623	1.698	0.139
2	-1.762	-1.875	0.148		-1.983	-2.156	0.208
3	1.803	1.928	0.155		1.307	1.332	0.090
4	-0.751	-0.742	0.027		0.920	0.916	0.045
5	-0.502	-0.491	0.029		-0.141	-0.137	0.003
6	1.241	1.260	0.180		0.096	0.093	0.001
7	-1.172	-1.184	0.160		-0.218	-0.213	0.006
8	0.571	0.561	0.038		0.018	0.018	0.000
9	0.153	0.149	0.001		0.229	0.223	0.002
10	-1.647	-1.731	0.129		-1.185	-1.197	0.063
11	-0.752	-0.743	0.027		-1.575	-1.640	0.112
12	-0.049	-0.047	0.000		-0.310	-0.303	0.004
13	0.535	0.525	0.033		1.002	1.002	0.053
14	-0.603	-0.592	0.042		-1.853	-1.985	0.181
15	-0.097	-0.094	0.001		-0.486	-0.476	0.012
16	-1.234	-1.253	0.178		0.496	0.486	0.013
17	0.136	0.132	0.001		0.278	0.272	0.004
18	2.380	2.765	0.229		0.870	0.864	0.040
19	-1.002	-1.003	0.041		-1.829	-1.953	0.177
20	1.728	1.832	0.121		1.725	1.822	0.157
21	0.611	0.601	0.018		-1.091	-1.097	0.054
22	0.272	0.265	0.004		0.064	0.062	0.000
23	1.105	1.112	0.058		0.939	0.936	0.040
24	0.192	0.187	0.002		-0.912	-0.908	0.037
25	-0.062	-0.060	0.000		0.417	0.409	0.003
26	0.586	0.575	0.005		0.536	0.526	0.005
27	-0.957	-0.955	0.014		0.170	0.165	0.000
28	-0.533	-0.523	0.004		0.260	0.254	0.001
29	-0.043	-0.042	0.000		0.450	0.441	0.004

Run No.	**Turbidity 600**				**Turbidity 800**		
	Residuals	**Studentized Residuals**	**Cook’s Distance**		**Residuals**	**Studentized Residual**	**Cook’s Distance**
1	0.256	0.249	0.008		0.771	0.763	0.030
2	-0.899	-0.894	0.103		-1.429	-1.472	0.102
3	1.150	1.161	0.168		0.602	0.592	0.018
4	-0.005	-0.005	0.000		1.036	1.038	0.054
5	0.536	0.525	0.037		1.090	1.096	0.166
6	-0.023	-0.023	0.000		-0.214	-0.208	0.006
7	0.274	0.267	0.010		0.834	0.827	0.097
8	-0.285	-0.277	0.010		-0.470	-0.460	0.031
9	1.166	1.179	0.062		0.933	0.930	0.044
10	-0.239	-0.233	0.003		0.677	0.667	0.023
11	-0.510	-0.499	0.012		-1.418	-1.459	0.100
12	-1.788	-1.916	0.145		-1.617	-1.695	0.131
13	0.606	0.595	0.017		0.441	0.432	0.010
14	-2.329	-2.708	0.247		-2.404	-2.805	0.289
15	-0.081	-0.079	0.000		0.624	0.613	0.019
16	0.433	0.423	0.009		-0.086	-0.084	0.000
17	0.323	0.315	0.005		0.382	0.373	0.007
18	0.760	0.751	0.026		0.060	0.058	0.000
19	-2.091	-2.335	0.199		-1.271	-1.293	0.081
20	1.982	2.178	0.179		1.274	1.296	0.081
21	-1.514	-1.575	0.104		-1.409	-1.449	0.099
22	0.182	0.177	0.002		-0.893	-0.888	0.040
23	1.497	1.555	0.102		1.002	1.002	0.050
24	0.808	0.800	0.030		1.745	1.853	0.152
25	0.042	0.041	0.000		0.075	0.073	0.000
26	0.339	0.330	0.003		0.490	0.480	0.006
27	-0.320	-0.312	0.002		-0.375	-0.366	0.004
28	-0.134	-0.130	0.000		-0.251	-0.245	0.002
29	0.073	0.071	0.000		0.060	0.058	0.000

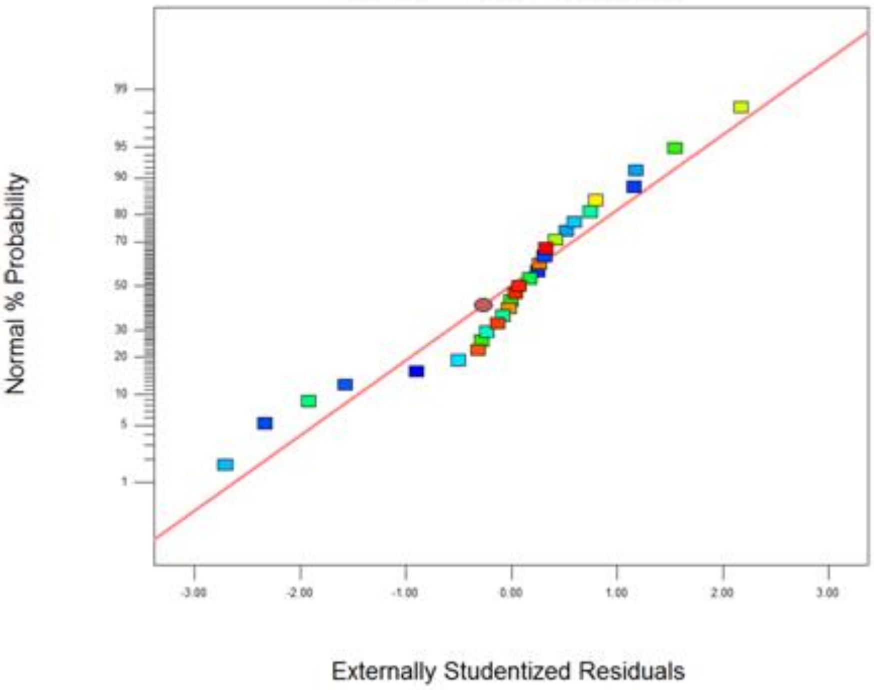


i) Turbidity 200

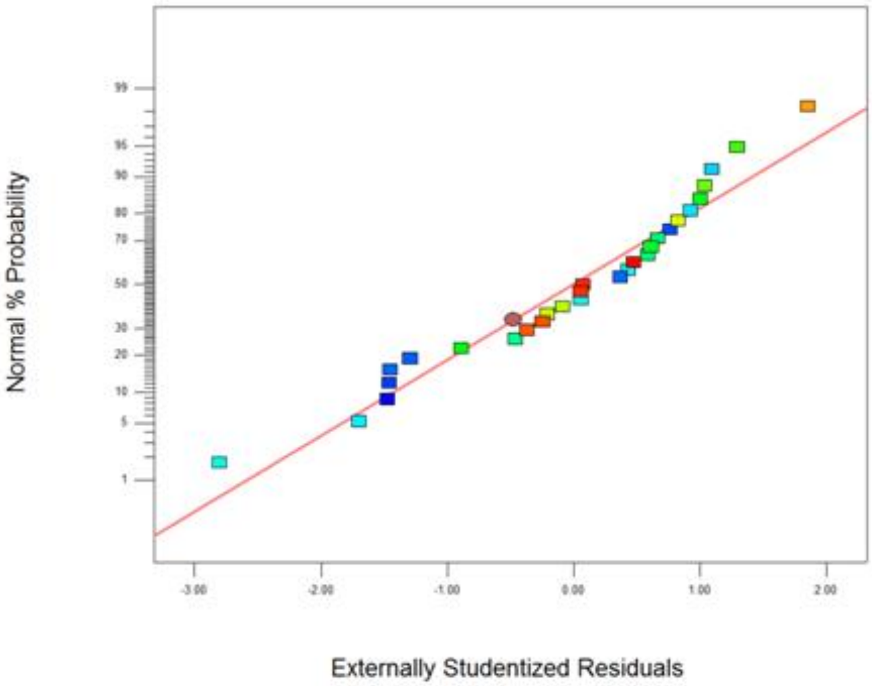


ii) Turbidity 400

Figure 4.2A Normal plot of the residuals of the predicted model for w/o emulsion.

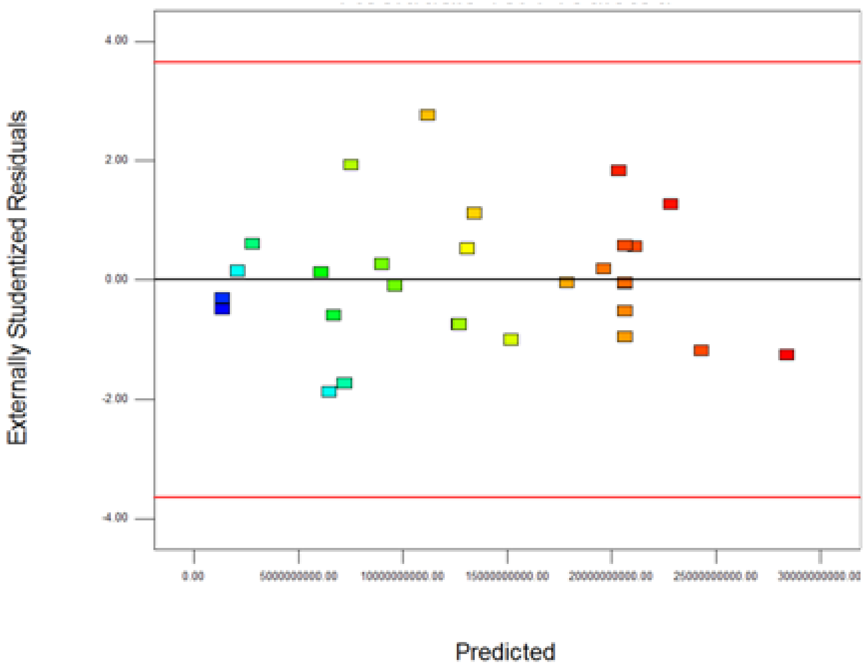


i) Turbidity 600

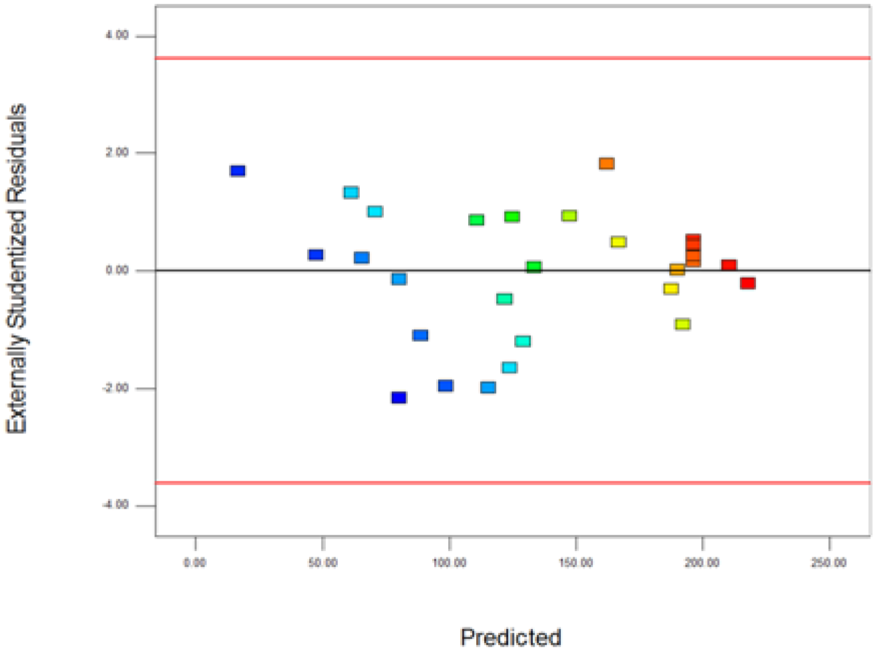


ii) Turbidity 800

Figure 4.2B Normal plot of the residuals of the predicted model for w/o emulsion.

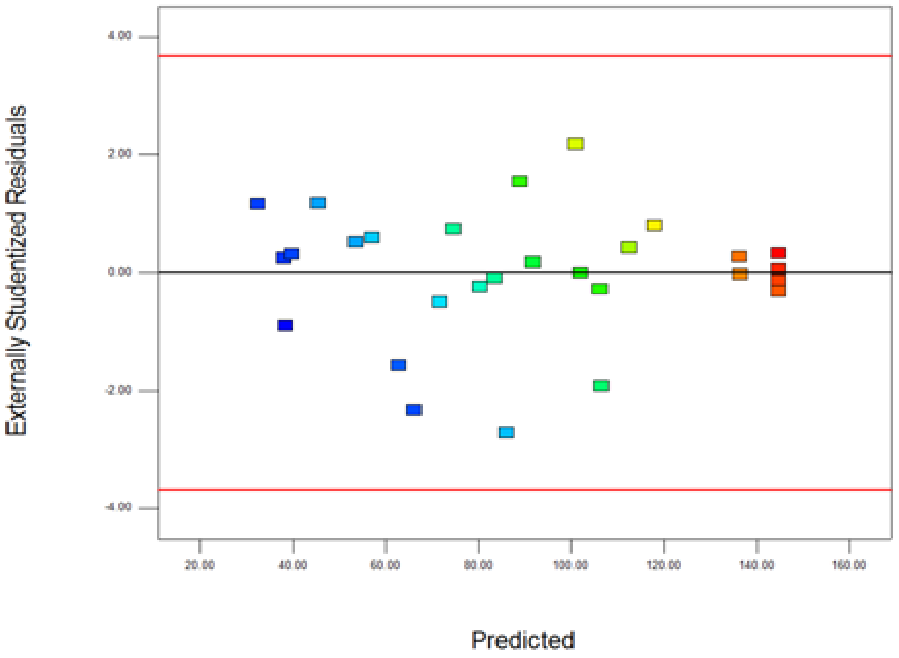


i) Turbidity 200

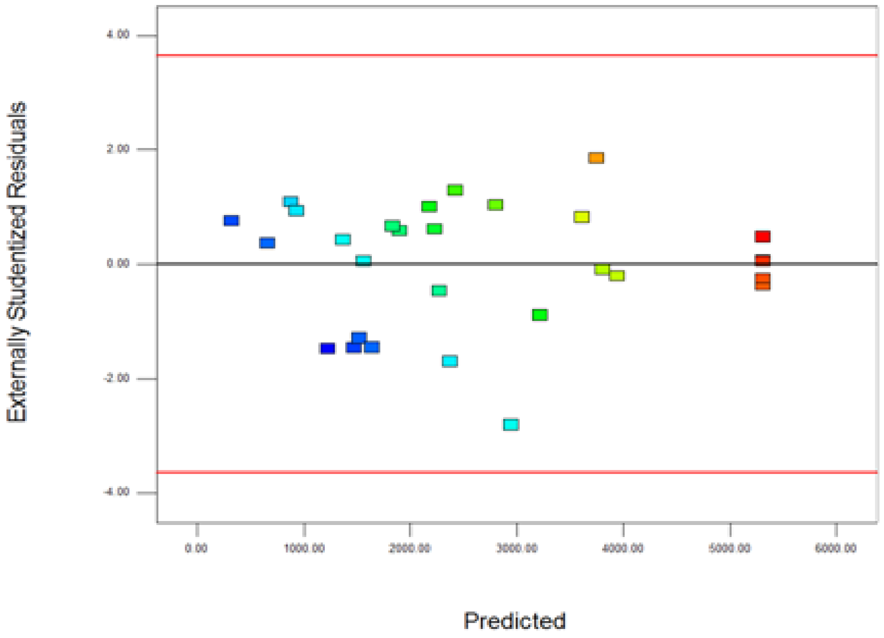


ii) Turbidity 400

Figure 4.3A Residuals vs Predicted values for the predicted model for turbidity of w/o emulsions.



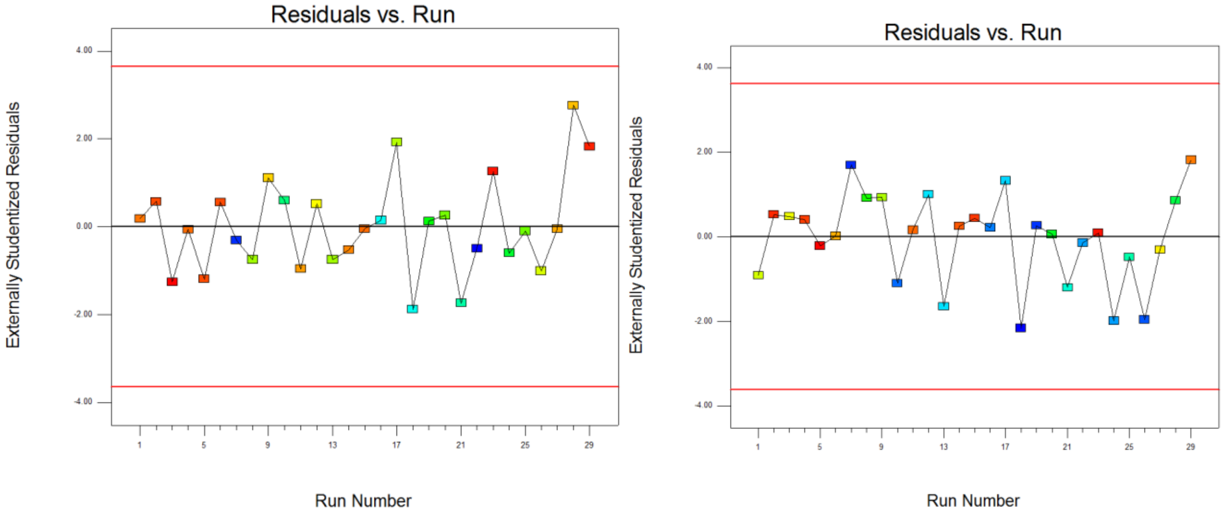
i) Turbidity 600



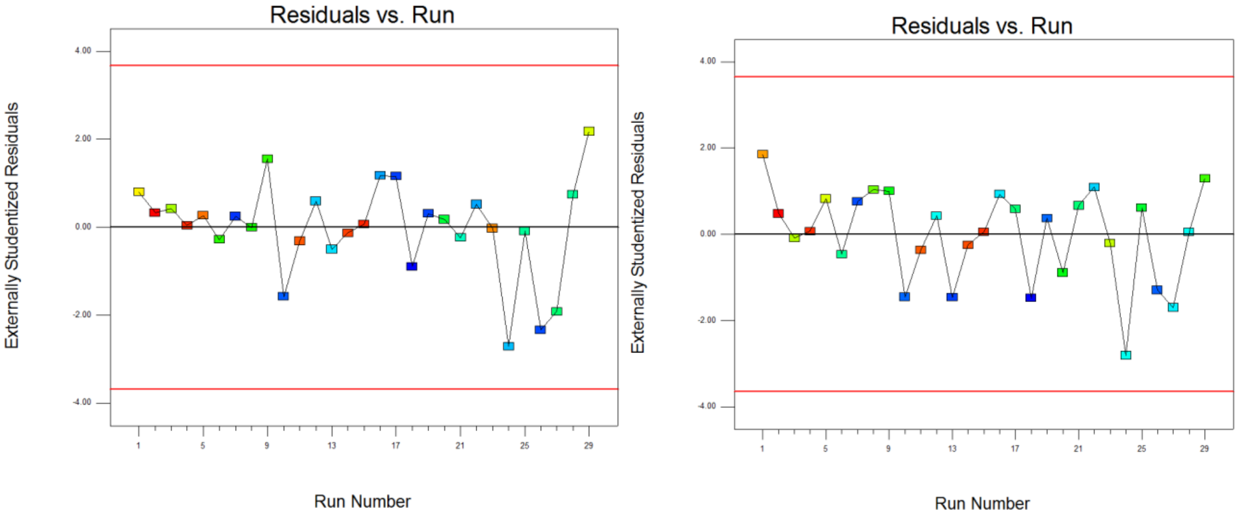
ii) Turbidity 800

Figure 4.3B Residuals vs Predicted values for the predicted model for turbidity of w/o emulsions.

Figure 4.4 shows graph between residuals and run number of experiments. Analysis of plot of student residuals against the run number or experiment number shows that there are runs of positive and negative values. It does not show any signs of continuous negative values or continuous positive values with the experiment number. Thus the accuracy of model is well established. Figure 4.5A and B shows graph between predicted vs actual values.

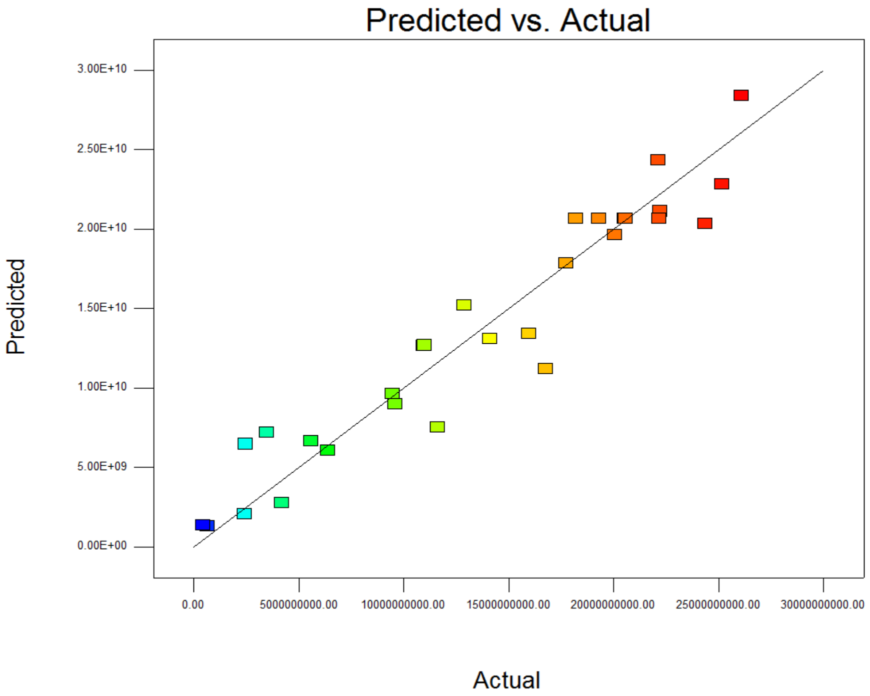


a) Turbidity 200 **b) Turbidity 400**

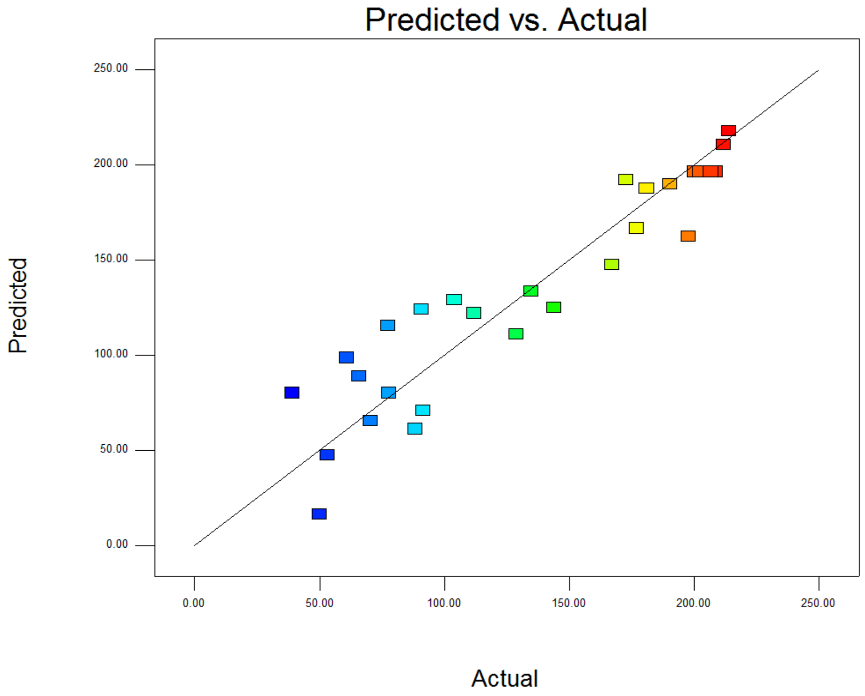


c) Turbidity 600 **d) Turbidity 800**

Figure 4.4 Residuals vs run number for the predicted model for turbidity of w/o emulsions.



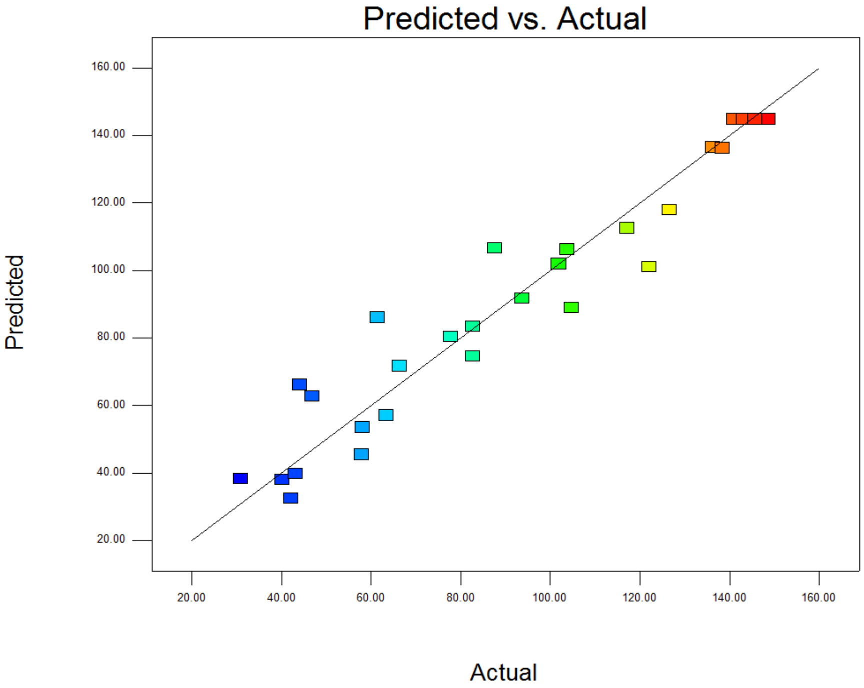
i) Turbidity 200



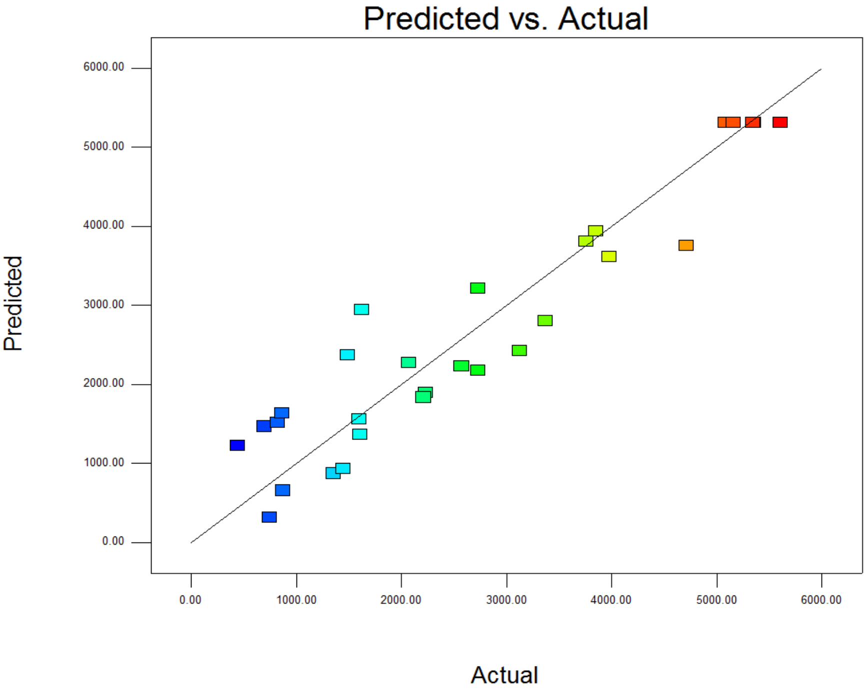
ii) Turbidity 400

Figure 4.5A Values predicted by model for w/o emulsions vs actual values (experimental values).

Figure 4.5B Values predicted by model for w/o emulsions vs actual values (experimental values).

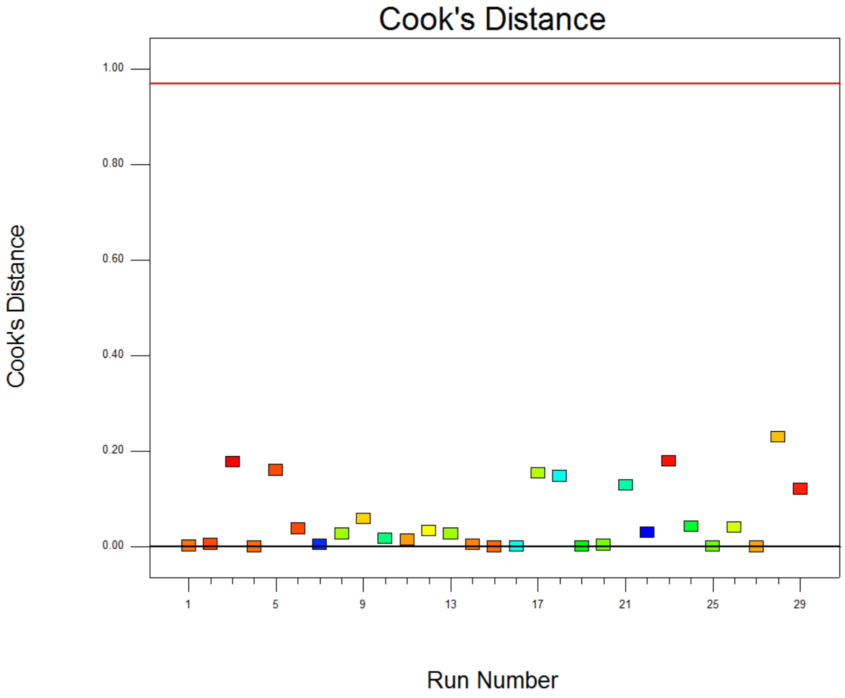


c) Turbidity 600

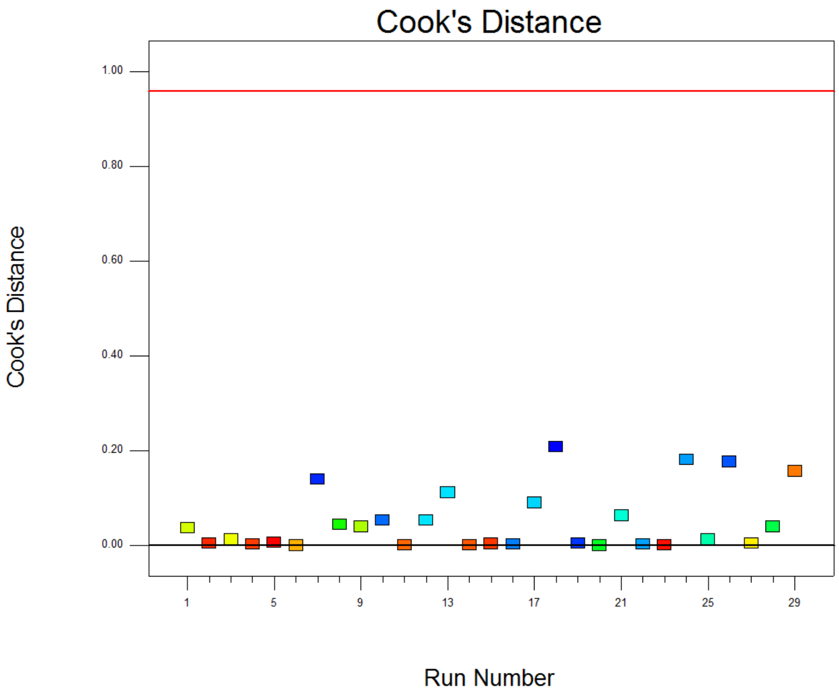


d) Turbidity 800

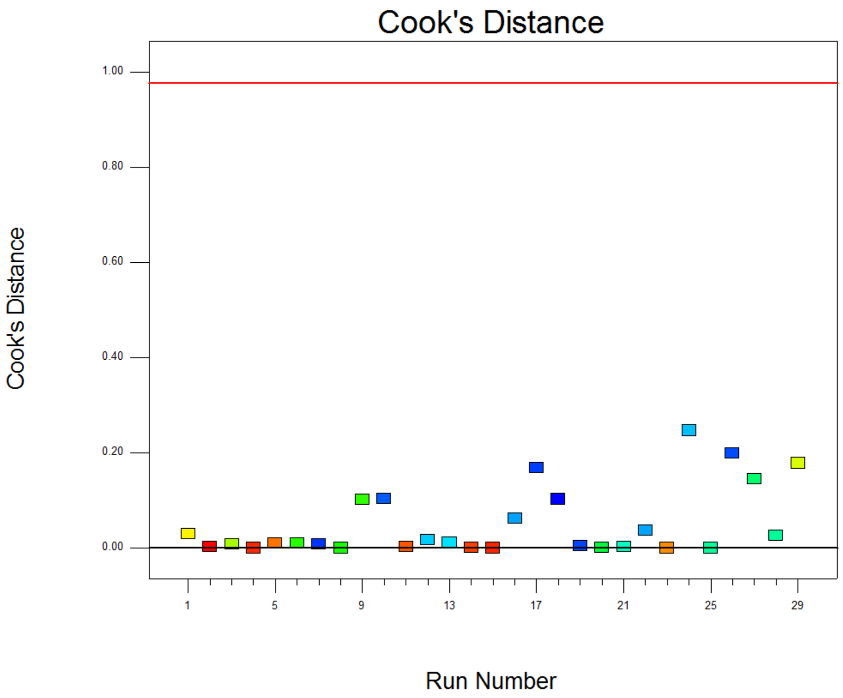
Figure 4.6 shows cook's distance with respect to run number which helps us find out the outliers. Cook’s distance is a good indication of possible outliers i.e. predicted values which have large residuals and can introduce significant errors in the model predicted. A simple operational guideline of cook’s distance should be less than 1 is suggested by many. Some suggest that it should be less than 4/n (n = number of observations). An analysis of cook’s distance against the run number for the model predicted above shows that at least 95% of the experimental runs have cook’s distance below 4/n (i.e. 0.15) and for the remaining experimental runs it is below 0.2, except one or two for different responses(Figure 4.6).



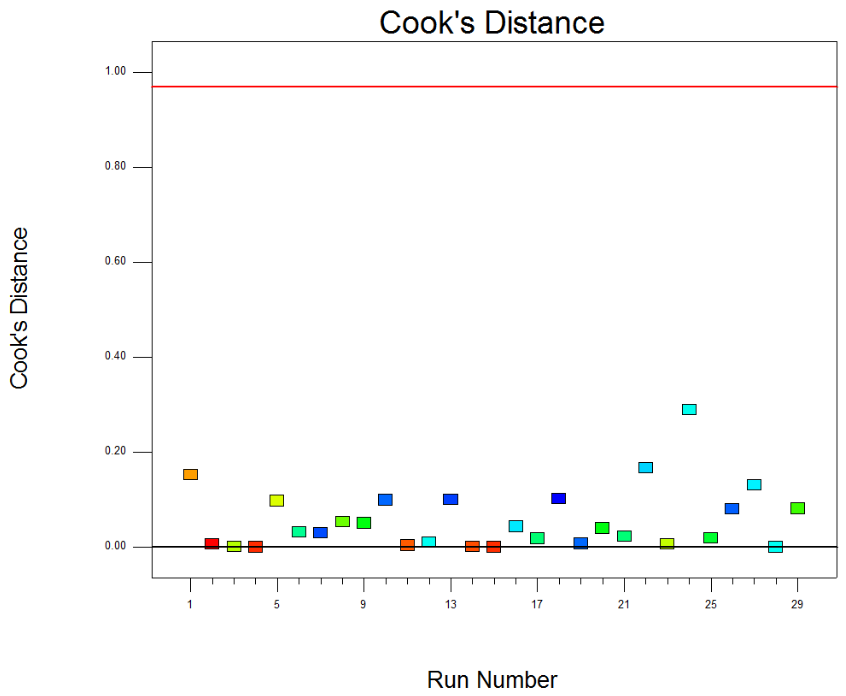
a) Turbidity 200



b) Turbidity 400



c) Turbidity 600

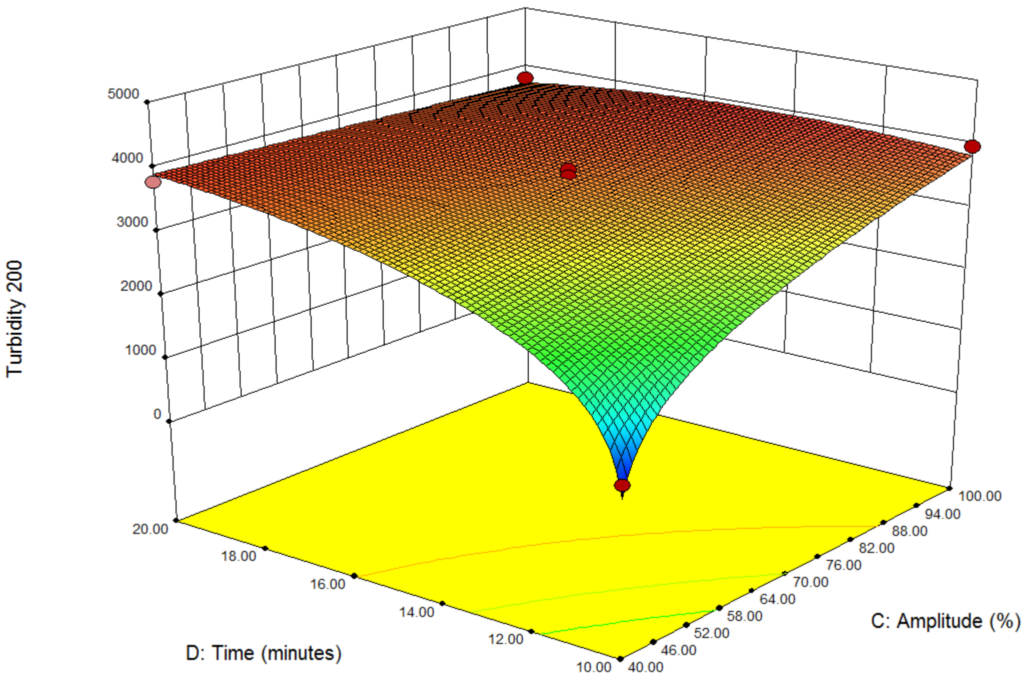


d) Turbidity 800

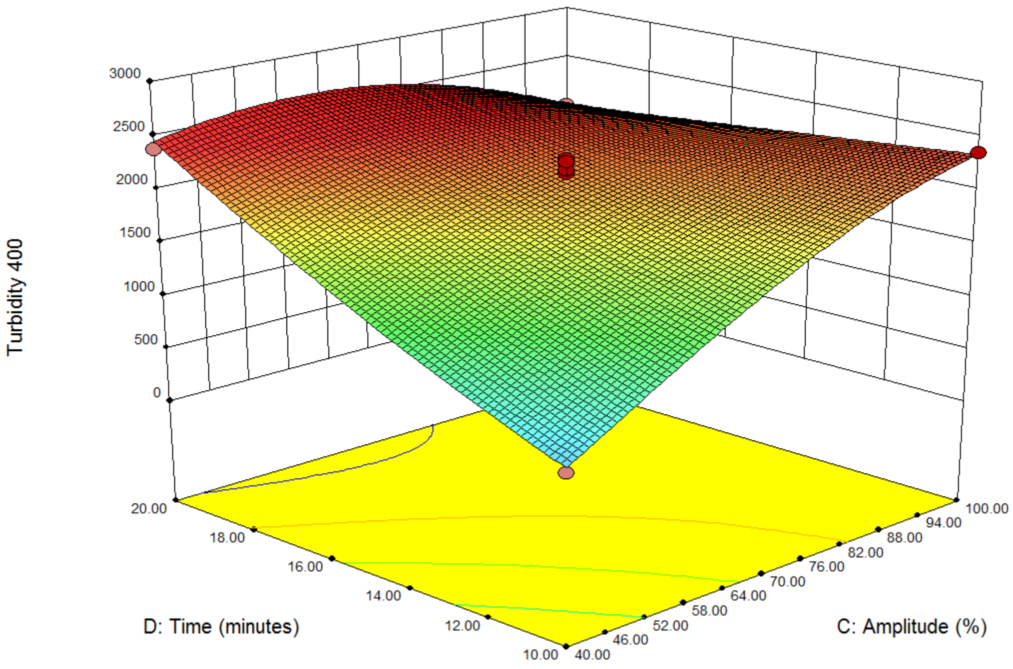
Figure 4.6 Cook’s distance for experimental points for model prediction of turbidity for w/o emulsions using BBD.

4.7 Model Graphs

The relation between the effective parameters and the response or output is shown in Model graphs. These model graphs are plotted between turbidity, amplitude (%) and time fixing water concentration = 17.5 v/v% and surfactant concentration = 6.5 w/w%. Figure 4.7A (i) shows that for turbidity at 200 nm wavelength increases as amplitude % for short ultrasonication time while this trends reverses as we move towards long ultrasonication time and turbidity also increases with increase in ultrasonication time for low amplitude % but this trend also reverses for high amplitude %. Figure 4.7A (ii) and 4.7B (i) shows that for turbidity at 400 nm and 600 nm wavelength increases continuously with increase in amplitude % for short ultrasonication time but it first increases then decreases with increase in amplitude % for long ultrasonication time. Figure 4.7B (ii) shows that for turbidity at 800 nm wavelength first increases then decreases with increase in amplitude % for all ultrasonication time.

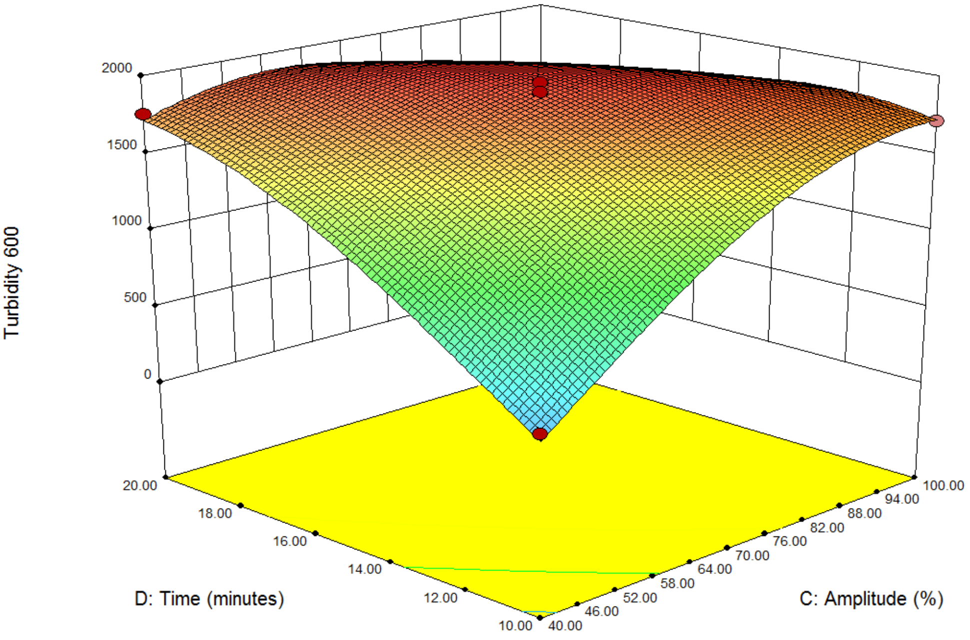


i) Turbidty 200

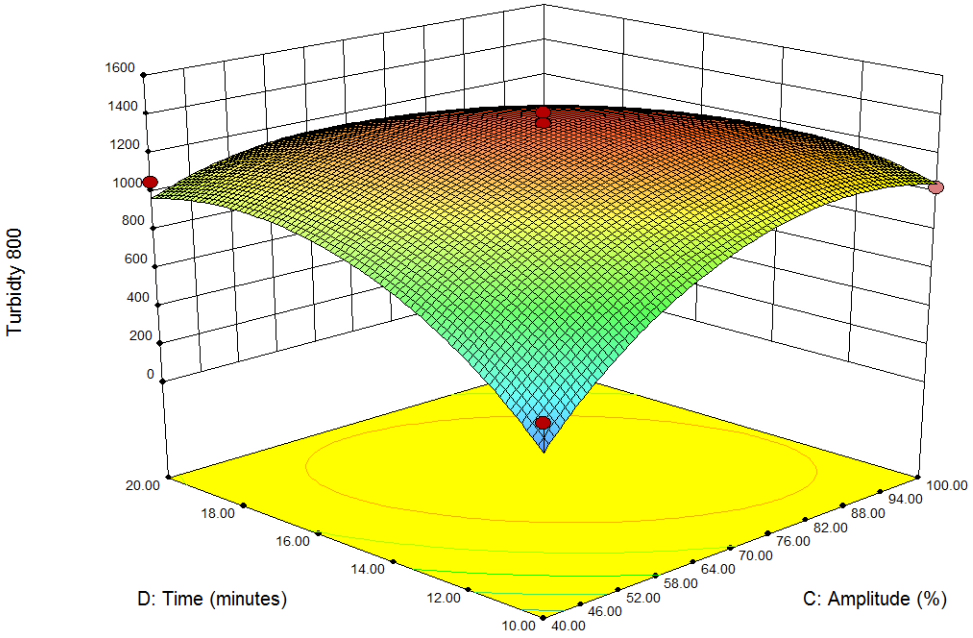


ii) Turbidity 400

Figure 4.7A Model graph for turbidity vs ultasonication time and amplitude (water concentration = 17.5 v/v% and surfactant concentration = 6.5 w/w%).



i) Turbidity 600



ii) Turbidity 800

Figure 4.7B Model graph for turbidity vs ultasonication time and amplitude (water concentration = 17.5 v/v% and surfactant concentration = 6.5 w/w%).

4.8 Optimization using steepest ascent method

The model predicted for turbidity was optimised using steepest ascent optimization and we get 7 possible solutions for better desirability of stable emulsion as shown in Table 4.7.

Table 4.7 Determination of optimum solutions.

S. No	Water Conc. (v/v%)	Surf. Conc. (w/w%)	Amplitude (%)	Time (min)	T200	T400	T 600	T800	Desirability
1	19.50	7.41	76.22	16.75	3875.92	2384.99	1998.37	1351.69	0.976
2	19.51	7.42	76.54	16.75	3878.45	2384.89	1997.16	1350.66	0.976
3	19.48	7.39	76.46	16.75	3877.00	2385.00	1997.87	1351.18	0.976
4	19.55	7.39	75.76	16.75	3871.96	2384.99	2000.67	1353.17	0.975
5	19.48	7.38	77.08	16.73	3881.45	2384.99	1995.58	1349.07	0.975
6	19.67	7.39	76.98	16.71	3880.57	2384.96	1997.58	1349.39	0.975
7	19.34	7.40	76.97	16.77	3881.62	2384.97	1993.79	1348.85	0.975

T200 – Turbidity200; T400 – Turbidity400; T600 – Turbidity600; T800 – Turbidity800

CHAPTER 5

CONCLUSIONS AND RECCOMENDATIONS

In the present work optimization of the stability of water-in-oil emulsion using non-ionic surfactants was studied. Experiments were conducted by varying different parameters: water and oil concentration, surfactant concentration, ultrasonication amplitude and time). The optimization of different operating parameters was made on the basis of Box-Behnken Design (BBD) method of Response Surface Methodology (RSM). The water–in–oil emulsion stability was determined on the basis of turbidity measurements at different wavelengths, using a UV Spectrophotometer. The results shows that the quadratic model best fits with power law transform with lambda = 2.89, 0.69, 0.66 and 1.19 for Turbidity 200, 400, 600 and 800 responses, respectively.

ANOVA for the predicted model shows that the contribution of water concentration, surfactant concentration, amplitude % and time of ultrasonication are significant. The amplitude % and time interaction is far more significant than any other interaction for all turbidity responses except for turbidity at 200 nm wavelength in which surfactant concentration and amplitude interaction is also significant and for turbidity at 600 nm wavelength in which water concentration and surfactant concentration interaction is also significant.

From the regression analysis it can be concluded that the experimental values fit into the predicted model with a high fitness value. Cook's distance was below 0.2 except 2 experimental runs. Therefore, there might not be any outliers present. Thus the empirical model developed best fits the experimental results and it can predict the optimized values for different operating parameters considered in the present work.

The parameters were optimised using steepest ascent method (SAM)and the values for optimum parameters is 20% (v/v) water concentration, 7.4 % (w/w) surfactant concentration, amplitude 77% and time 61.75 minutes approximately.

Based on the optimized conditions obtained in the present work, it is proposed to study the effect of ionic surfactant on the interfacial tension, zeta potential, droplet size, droplet size distribution. Further it is proposed to study the effect of ionic (cationic and anionic) surfactant on the emulsion obtained using optimised conditions.

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