The Effect of Additives and Temperature on the Rheological Behavior of Invert (W/O) Emulsions

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Abstract

The main aim of this research is to study the effect of temperature on the rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions by using different additives to obtain the best rheological properties.

Twenty seven emulsion samples were prepared; all emulsions in this investigation are direct emulsions when water droplets are dispersed in diesel oil, the resulting emulsion is called water-in-oil emulsion (W/O) invert emulsions.

These emulsions including three different volume percentages of barite with three different volume percentages of emulsifier and three different concentrations of asphaltic material under temperatures (77, 122 and 167) °F.

The rheological properties of these emulsions were investigated using a couett coaxial cylinder rotational viscometer (Fann-VG model 35 A), by measuring shear stress versus shear rate.

By using the Solver Add in Microsoft Excel®, the Bingham plastic model was found to be the best fits the experimental results.

It was found that when the temperature increased, it causes a decrease in the rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions which due to the change in the viscosity of continuous phase of emulsion which is diesel oil.

Also it was found that the effect of additives on rheological properties of emulsions as follow: the increase in the concentration of asphaltic material tends to increase the rheological properties of emulsions, the increase in the volume percentage of barite tends to increase the rheological properties of emulsions and the increase in the volume percentage of emulsifier has a little effect on the value of rheological properties, but it increased the stability of emulsions with temperature because it surrounded water droplets.

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Nomenclature

Symbol	Meaning	Unit
A, B, C	Parameters in Equation (3.6)	-
A', B', C'	Parameters in Equation (3.7)	-
K	Consistency index of a power law fluid	-
K'	Generalized consistency index	-
n	Flow behavior index of a power law fluid	-
n'	Generalized flow behavior index	m/s

Abbreviations

W/O	Water-in-Oil (Invert emulsion)
O/W	Oil-in-Water (Direct emulsion)
µm	Micro meter
HLB	Hydrophilic-Lipophilic Balance
PPG	Pound per Gallon

Greek Letters

Symbol	Meaning	Unit
α	Constant	-
$\dot{\gamma}$	Shear rate	rpm
η	Viscosity	cp
η_{∞}	Newtonian limiting viscosity	cp
θ	Dial reading	deg
τ	Shear rate	lb/100 ft^2
τ_m	Shear stress at mean viscosity	lb/100 ft^2
$\tau_{\circ}$	Yield stress	lb/100 ft^2
Y_p	Yield point in Equation (3.11)	lb/100 ft^2
η_p	Bingham plastic viscosity	cp
η_a	Apparent viscosity	cp

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Chapter One

Introduction

Rheology is the study of the deformation and flow of a matter under the influence of an applied stress, for example a shear stress or extensional stress. The experimental characterization of a material's rheological behavior is known as rheometry, although the term rheology is frequently used synonymously with rheometry, particularly by experimentalists. Theoretical aspects of rheology are the relation of the flow/deformation behavior of material and it's internal structure, and the flow/deformation behavior of materials that cannot be described by classical fluid mechanics or elasticity. This is also often called Non-Newtonian fluids [1,2].

Rheology has important applications in engineering, geophysics and physiology. In particular, hemorheology, the study of blood flow, has an enormous medical significance [3].

Rheology modifiers are also a key element in the development of paints and achieving paints that will level but not sag on vertical surfaces [4].

Rheology of emulsion has two aspects in order to determine the rheological properties of emulsions. The first concerned with their effects on emulsion stability while the other involves the effects of deterioration of the emulsion on it's rheological properties.

The principle factors, which influence the flow properties of emulsions, are related to the dispersed phase, continuous phase and the emulsifying agent.

A change in one or more of these factors will affect the rheological properties of an emulsion. Factors which related to the dispersed phase are concentration (i.e. phase volume ratio), viscosity and the size of the dispersed droplet [5,6].

A direct relation ship between the viscosity of emulsion and the viscosity of the dispersion medium always exists. Sherman (1964) describes the viscosity of the dispersion medium as not only the viscosity of the pure dispersion fluid but it's viscosity when all the ingredients in the formula have been dissolved in it , e.g. Emulsifying agent [7].

Different emulsifying agents give rise to different flow properties. The chemical nature of emulsifing agent is also important which may lead to the flocculation of the dispersed droplet, that will tend to produce plastic flow [8,9].

An additional factor, which may affect the viscosity of the emulsions which is the electro viscous effect. Highly charged dispersed droplet require an additional shear in order to destroy the configuration of the electrical double layer around each droplet so such emulsions exhibit a higher viscosity [9].

Applications of emulsion in oil engineering as a drilling fluid. The more important or interesting uses of emulsions in chemical engineering are listed below [9, 10]:

- Cosmetic emulsions.
- Polishes.
- Emulsion paints.
- Agriculture sprays.
- Food emulsions.

- Medical emulsions.
- Asphalt emulsions.

Among the miscellaneous emulsions are : dry-cleaning emulsions; emulsions for metal cleaning or for corrosion prevention; emulsion adhesives; roofing and flooring compounds; radiographic emulsions, and emulsified battery electrolytes .

Aim of work :

1. Study the effect of temperature on rheological properties of (W/O) invert emulsions.
2. Study the effect of additives (asphaltic material, barite, and emulsifier) on the rheological properties of (W/O) invert emulsions.

Chapter Two

Literature Survey

In this chapter we will focus on the recent works that studied the rheology of emulsions.

Hildebrand (1941) [11], has pointed out that the rupture of a film separating two droplets can be resisted by the larger rise in the interfacial tension at the threatened point, which results if the reserve emulsifying agent is dissolved in the liquid forming of film, in the external phase, owing to the lower rate of adsorption in the case considered. This is, of course, a more sophisticated justification for Bancroft's rule, relating the solubility of the emulsifying agent with nature of the external phase.

King (1941) [12], has pointed out that there are three main types of emulsions:

1. Oil hydrosols. There are unstabilized emulsions, mostly O/W, and contain less than one percent internal phase.

2. Emulsions stabilized by electrolytes. Low concentrations of them are capable of stabilizing W/O emulsions.

3. Emulsions stabilized by emulsifying agent. This class includes what is commonly thought of as being an emulsion, the emulsifying agents being either colloidal materials (including surface - active agents) or finely divided solids.

He supplied an interesting sidelight on the last two types by pointing out that sodium oleate at a concentration of one percent normally gives an oil-in-water emulsion; at much lower concentrations, however, a water-in-oil emulsion may result, i.e., the sodium oleate is behaving as a normal electrolyte rather than as colloidal electrolyte.

Kremnev (1948) [13], has recently studied the stabilization of concentrated emulsion by using mixed emulsifier. It was found that the highly stable concentrated emulsion of benzene in water could be obtained by the use of thixotropic mixtures of aliphatic alcohols and sodium oleate, owing to their capacity of rapid restoration of the thixotropic structure, perturbed in the process of emulsification. With alcohol introduced either in the benzene or in the one percent sodium olate solution, the stability of emulsion increase with the chain length of the alcohol and with the concentration of alcohol.

Sherman (1953) [14], has studied the properties of the interfacial films of sorbitan sesquioleate, a nonionic emulsifier, in water-in-oil emulsions. The film formed at the mineral oil-water interface was viscous and solid appearance.

Blakck and Lawrence (1954) [15], have noted that the high interfacial viscosities do not occur in a great many stable systems. High viscosities were, indeed, found in systems involving metal carboxylates, where, however, the interfacial layer is probably thicker than animalcular. Interestingly enough, these investigators did found some sort of correlation between emulsion stability and presence of a surface plasticity. In general, they concluded that interfacial viscosity plays no part in the stabilization of oil-in-water emulsions, but many play a role for water-in-oil systems.

Simpson et.al (1961) [16], discussed a new look in emulsion technology. They referred to the materials used in preparing the emulsion, which are bodying agent for oil, primary emulsifier of water in oil, suspension agent, wetting agent and filtration control agent. Both suspension and filtration control agent. Also they stated that the properties of emulsion can be varied over wide range, and the emulsions can be converted from type to another by adjusting the oil/water ratio.

Watkins (1962) [17], formulated an emulsion with new emulsifier. This emulsifier was a modified mixed salt of fatty acids, which was formed by mixing the anionic emulsifier with calcium and sodium salts in oil phase. As the water mixed, some of the emulsifier was converted into the sodium salt initially and then to the less water-soluble calcium salt at the interface, which provide the necessary film strength. He concluded from circulation tests carried on this emulsion using various amounts of emulsifier, at different temperature up to 350 °F, that the viscometric properties were satisfactory. He indicated that the emulsion could prepared with a weight as low as 7.5 PPG to weights as high as 18 PPG with satisfactory viscometric properties.

Carins et. al. (1976) [18], investigated the influence of changes in pH and salt content of water on the rheology of the crude oil-water interface and how this affects water/crude oil emulsion stability. They found that, the favorable conditions to form stable W/O emulsion are: a high oil-water viscosity ratio, a rapid initial adsorption of natural surfactant (rapid fall in interfacial tension) and at the pH at which the interfacial viscosity greatest. They also found that, the asphaltene content of a crude oil does not indicate the existence of a high interfacial viscosity.

Jones et. al. (1978) [19], have investigated the stability of water in crude oil emulsions and attempted to correlate it with interfacial tension, interfacial shear viscosity and interfacial film compressibility measurements. They concluded that the interfacial elasticity plays important role in affecting coalescence behavior (i.e. stability).

Gelot et al. (1984) [20], found that an increase in particle concentrations decreased emulsion droplet sizes and increased emulsion volumes, providing more area for interfacial adsorption.

Lakatos et. al. (1985) [21], investigated crude oil-water emulsions in presence of non-ionic surfactants. Their investigations were focused on the determination of the stability and rheological properties of emulsions prepared from natural oil and it's fractions, using ion-free water and aqueous tensed solutions. The effect of temperature on the stability and rheological properties of emulsions were also investigated. They concluded that, with increasing temperature the originally plastic emulsion first assumes pseudoplastic properties, and later Newtonian flow behavior. They attributed this, to the paraffin crystals present at low temperature in the crude oil, which also stabilize the emulsion structure. They also show that, asphaltenes not only stabilize the tensed-free emulsions, but play a decisive role in shaping the rheological properties as well.

John Wiley and Sons (1986) [22], investigated the effect of temperature on the systems containing nonionic surfactants has been studied extensively because the solution properties of the system change drastically and the emulsion type inverts from oil/water (O/W) to water/oil (W/O) with temperature elevation.

Nonionic surfactant is hydrophilic at lower temperature and lipophilic at higher temperature. A temperature rise in nonionic surfactant solution corresponds to a shortening of the hydrophilic chain length of the surfactants. Hence, the effect of hydrophilic chain length of nonionic surfactants on various properties can be learned from the studies of one surfactant as a function of temperature.

Menon and Wasan (1988) [23], reviewed the recent developments and highlighted the factors affecting the formation and stabilization of emulsions containing finely divided solids. They discussed the various factors affecting the formation and stability of these emulsions, such as: contact angle, demulsifies concentration, temperature, interfacial rheology and soild-liquid interactions.

Johansen et. al. (1988,1989) [24], studied the formation, characterization and stability correlations of water-in-oil emulsions based on north sea crude oils (Norwegian continental shelf). They took crude oil s (from 32 different wells) by means of density, viscosity, surface and interfacial tension measurements. They also found that the ability to form stable emulsions varies very much, depending on the crude oil itself. Their study showed that the correlation between observed and calculated stability can be adequately described by an equation containing three crude oil parameters.

Yan and Masliyah (1994) [25], determined the maximum emulsion stability at clay contact angles of 90° for experiments performed with constant concentrations of solids. At this contact angle, the concentration of solids at the interface was the highest. For experiments in which the particle concentration at the interface was constant, emulsion stability decreased with increasing contact angle, as particles were more immersed in the oil phase, providing a smaller barrier to coalescence.

Aamir Sattay (1998) [26], described an experimental work for classing the water-in-curde oil emulsion in three different types of Iraqi crude oils. It was found out that the mixture of phenol and sulfonic acid was the best chemical additive used to sparate water from three different types of crude oils normely; blend of Basrah, blend of Kirkuk and East Baghdad crude oils. The separation of water from Basrah and Kirkuk crude oils was higher than separation of water from East Baghdad crude oil. Factors such as temperature, pH, salinity, original water content and diluation with kerosene were investigated using bottle test. Theoretical studies using mathematical correlations to evaluate the Hydrophile-Lipophile Balance (HLB) and their effects on the separation of water from crude oil were also accomplished.

A.A. Mohammad (2000) [27], study the effect of using water/ gas oil emulsions as fuel for diesel engines. The engine used was a single cylinder diesel engine type Ricardo (E6/US). In general, it was found that using emulsions cause significant decrease of Smoke for all ranges of load and speed. Experimental tests indicated that further addition of water to gas oil (more than 30 percent) was limited by engine knock.

K. M. B. Jansen, et.al. (2001) [28], found a new scaling parameter for the viscosity of surfactant stabilized emulsions was proposed. It was suggest that the attractive force between emulsion droplets is caused by the small surfactant micelles in the continuous phase of an emulsion.

$$Fl_d = \frac{4\pi\eta_s \dot{\gamma} a^2 a_m}{KT \phi_m} \qquad \ldots(1.1)$$

The new scaling parameter will be referred to as the depletion flow number, , and is defined as the ratio between the viscous energy needed to separate the droplets and the depletion energy which opposes this separation. Here η_s, a, a_m and ϕ_m are the solvent viscosity, dispersed phase droplet radius, micelle radius and micelle volume fraction, respectively. Fl_d is of order unity at the onset of shear thinning and is capable of explaining all previously observed effects of drop size, solvent viscosity and surfactant concentration. With the master curves which are obtained by using Fl_d as the running parameter, a relatively simple empirical model is constructed which could reproduce the viscosity curves of many previously reported publications.

M. J. Thompson, et.al. (2001) [29], present experimental findings and matching modeling concerning the effect of water droplets on the rheology of a high viscosity alkyd resin. In the flow regime where significant droplet deformation occurs, the shear viscosity of the fluid containing highly extended filaments was found to be lower than that of the alkyd resin on its own. A theoretical mechanism for this high shear rate viscosity reduction is proposed, and reasonable agreement established with experimental observation. At intermediate shear rates a crossover between viscosity enhancement and viscosity reduction correlates with a capillary number close to one. At low shear rates classic viscosity enhancement was observed.

S. Kokal and S. Aramco (2002) [30], they stated that the formation of emulsions during oil production is a costly problem, both in terms of chemicals used and due to production losses. They discussed production and operational problems related to crude oil emulsions, and present a review that will be very useful for practicing engineers.

Crude oil emulsions are stabilized by rigid interfacial films that form a “skin” on water droplets and prevent the droplets from coalescing. The stability of these interfacial films, and hence the stability of the emulsions, depends on a number of factors including the heavy polar material in the crude oil (asphaltenes, resins, waxes, etc), solids (clays, scales, corrosion products, etc), temperature, drop size and drop size distribution, pH, oil and brine composition. These effects on emulsion stability were reviewed.

The focus is on the destabilization of emulsions and the de-emulsification process. Emulsions were destabilized by increasing temperature and residence time, removal of solids, and controlling emulsifiers. The mechanisms involved in de-emulsification (flocculation, aggregation, sedimentation, creaming, and coalescence) were discussed in terms of the stability of the interfacial films. The methods involved in de-emulsification including thermal, mechanical, electrical, and chemical were also presented. Experience and economics determine which methods and to what degree each method is used for emulsion treatment.

Chapter Three

Theory

3.1 Definition Of Emulsion

An emulsion is a system containing two liquid phases, one of which is dispersed as droplets in the other. The liquid which is broken up into droplets is termed the dispersed phase, whilst the liquid surrounding the droplets is known as the continuous phase or dispersing medium. The two liquids, which must be immiscible or nearly so, are frequently referred to as the internal and external phases, respectively.

An emulsion is a heterogeneous system, consisting of at least one immiscible liquid intimately dispersed in another in the form of droplets, whose diameter, in general, exceeds 0.1 µm . Such systems possess a minimal stability, may be accentuated by such additives as surface-active agents, finely divided solid, etc [32].

3.2 Terminology of Emulsions

In discussing emulsions, it is necessary to be able to distinguish clearly each of the two phases present. The phase which is present in the form of finely divided droplets is called the disperse or internal phase while the phase which forms the matrix in which these droplets are suspended is called the continuous or external phase. The disperse phase may also be referred to as the discontinuous or internal phase.

Surface-active or other agents which added to an emulsion to increase its stability by interfacial action are known as emulsifiers or emulsifying agents. Stability may be increased by the different methods, such as, the addition of simple stirrers, homogenizers, or colloid mills. These three types of equipment are often generically called "emulsifiers." This, of course, may lead to confusion with chemical emulsifiers emulsifying agents. Therefore, it might be helpful to adopt the term emulator or emulsion to describe any mechanical aid to emulsification [9].

3.3 Types of Emulsions

There are many types of emulsions, depending on which one is the dispersed (internal) phase or dispersing (external) phase. It is common practice to describe an emulsion as being either oil-in-water (O/W) or water-in-oil (W/O). Where the first phase mentioned represents the dispersed phase and the second is the continuous phase.

The third type of emulsions is called multiple emulsions. A multiple is one, which grater of two types of emulsions simultaneously. An oil droplet may be suspended in an aqueous phase, which is turn encloses a water droplet. Thus giving what might be describe as W/O/W multiple emulsion or O/W/O multiple emulsion, which have the reverse composition.

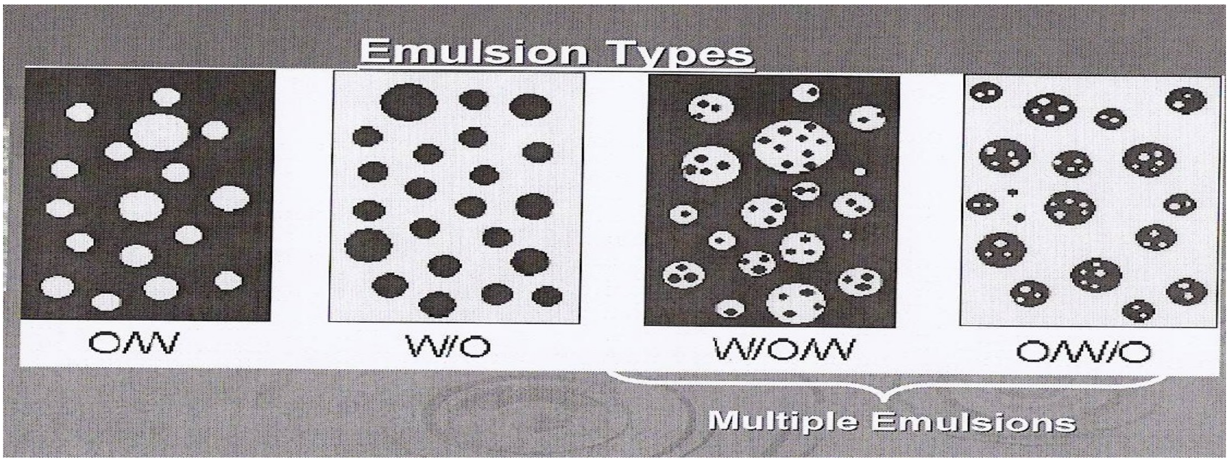


Figure (3.1) Different Types of Emulsions [34].

3.4 Physical properties of Emulsions

The physical properties of emulsion give indication for the specific emulsion and stability.

3.4.1 Particle Size and size Distribution

The internal phase of an emulsion was dispersed in droplets of a diameter greater than 0.1 µm. Very few emulsion droplets are smaller than 0.25 µm diameter, and the largest droplets size found are a bout a hundred time greater than 0.25 µm [9].

The semi-qualitative effect of particle size on the appearance of emulsions has been referred to in table (3.1) [34].

Table (3.1) Emulsion Appearance Due to particle Size [34].

Particle size	Appearance
Macro globules	**Two phases may be distinguished**
Greater than 1 µm	**Milky white emulsion**
1 to approximately 0.1µm	**Blue-white emulsion**
0.1 to approximately 0.05 µm	**Gray semitransparent (dries bright)**
0.05 µm to smaller	**Transparent**

3.4.2 Concentration (Phase Volume Ratio)

As the volume dispersed phase in the emulsion increase, the interfacial film expands further and further to surround the droplets of dispersed material, and the basic instability of the system increases. As the volume of dispersed phase increases beyond that of continuous phase, the type of emulsion (O/W or W/O) becomes basically more and more unstable relative to the other type of emulsion [6, 9, 35].

Interfacial area that is now enclosing the dispersed phase is larger than that which would be needed to enclosing the continuous phase. It often happens therefore that the emulsion reaches the inversion point [6, 35, 36].

The concentration of emulsion may be stated by weight percent, morality (for pure substance). The convenient measure of concentration is the volume fraction of the dispersed phase (internal phase) [9].

3.4.3 Viscosity

The rheological properties of emulsions (especially viscosity) had been dealt and studied extensively [37].

Six factors [14], which may affect the rheological properties of emulsion, as follow:

- Viscosity of external (continuous) phase.
- Volume concentration of the dispersed phase.
- Viscosity of the internal (dispersed) phase.
- Nature of the emulsifying agent and interfacial film formed at the interface.
- Electro viscous effect.
- Droplet size distribution in continuous phase.

3.5 Stability of Emulsions

Schwartz and Perry [38], have indicated that the a proper theory of emulsions should be capable of explaining the following important behavior characteristics:

- Formation
- Stability
- Breaking and inversion
- The role of emulsifying agents and other chemical factors such as pH and non-surface-active ions.
- The influence of physical factors on emulsion.

It was stated that the existence of interfacial film requires the presence of the two interfacial tensions (i.e. one of each side of the interfacial film).

The film will curve toward the higher interfacial tension, thus the dispersed phase will be on the side of the film [9].

Figure (3.2) shows various possible mechanisms of emulsion stabilizers [34].

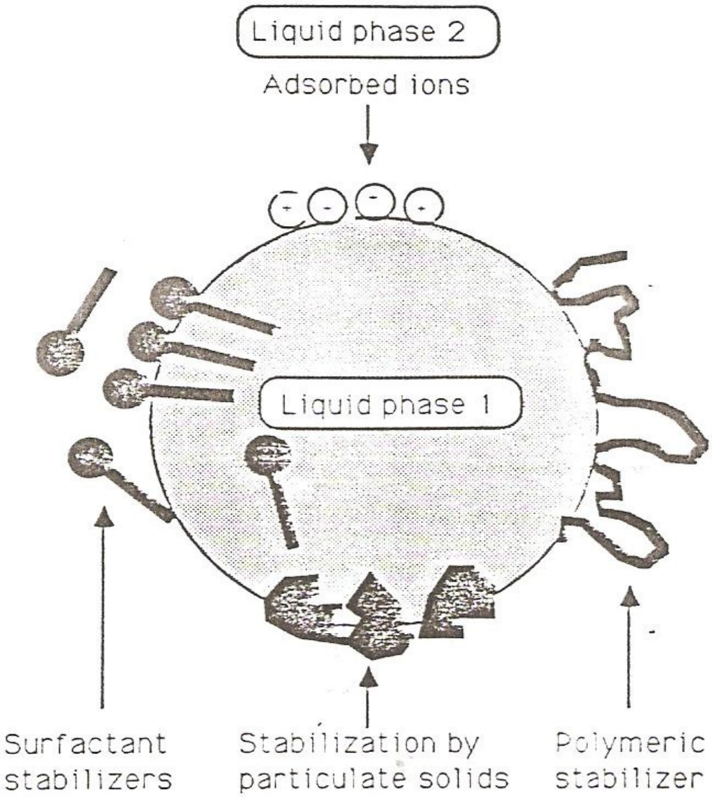


Figure (3.2) Various Possible Mechanisms of Emulsion Stabilizers [34]**.**

It was found out that the highest surface pressure, the greater was the stability of the emulsion. The adsorbed molecules can reduce the potential energy of the dispersed system by the lowering in the interfacial tension. It can also erect a rigid or higher viscous barriers at the interface capable of preventing the coalescence of droplets that collide as a result of random Brownian motions, thermal convection, or mechanical agitation [9, 6, 36].

Similarly in some cases it was found that the adsorbed molecules carry an electric charge, resulting in the formation of an electrical double layer that lessens the frequency and effectiveness of close droplet approach and contact leading to droplet growth. The effects of the interfacial tension are less important to over all long-term emulsion stability than are the effects of the nature of film. So, attentions will now be turned more specifically to the role of surfactants in the stabilization and preparation of emulsion [33].

3.5.1 General Considerations of Emulsion Stability

Four terms usually encountered in emulsion science and technology, related to stability, these are "Breaking", "Coalescence", "Creaming" and "Flocculation" [33].

Coalescence refers to the joining of two (or more) drop of greater volumes, but smaller interfacial area, figure (3.3).

The coalescence will result in significant microscopic changes in the conditions of the dispersed phase (i.e. changes in average particle size and distribution). But it is not necessary to result a macroscopically apparent alteration of the system. The breaking of an emulsion refers to a process in which a gross separation of the two phases occurs. Obviously the identity of individual droplets lost a long with physical and chemical properties of the emulsion [6, 33].

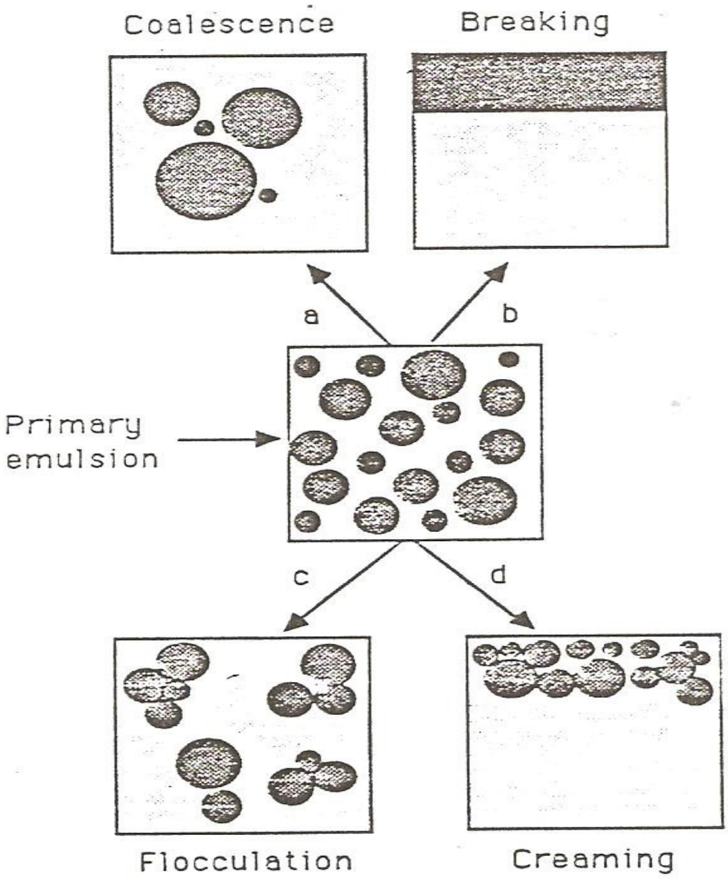


Figure (3.3) Types of Instability in Emulsion [33].

Flocculation refers to the mutual attachment of individual droplets to form flocs of particles in which the identity of each maintained. Flocculation can be, in many cases, a reversible process which was overcome by the input of much less energy than was required in the original emulsification process [6, 33, 36].

Creaming receives its name from the most common instance: the separation of the cream of unhomogenized milk. The emulsion is separated into two emulsions, one of which is richer in the disperse phase, the other poorer, than the original emulsion. The emulsion which is more concentrated is the "cream" [33].

It is obvious that both in creaming and in flocculation the droplets can "touch" each other without combination between them to make single droplet, whereas when there is no active agent group in the dispersion, coalescence is the rule [6].

3.5.2 Thermal Stability of Emulsion

The stability of emulsions to extremes of temperature is of greater particle importance, since commercial emulsion may have to be stored for varying periods of time in warehouses where they may be exposed to extremely high as well as extremely low temperatures. In view of this, it is extraordinary how little attention has been devoted to this point from a fundamental point of view.

In view of the approximations in evolved, it is perhaps futile to consider the effect of temperature on the double layer, but the increase in Brownian motion on raising the temperature will of course have a tendency to increase the rate of flocculation. Similar, it is known that the interfacial viscosity may be temperatures-dependent, falling rapidly to vary low values at temperatures which are not excessively high. This would contribute to the increased coalescence rate, through an increased probability of film rupture [9].

3.6 Emulsifier

An emulsifier is a substance which stabilizes an emulsion, frequently a surfactant. Examples of food emulsifiers are egg yolk (where the main emulsifying chemical is lecithin). Detergents are another class of surfactant, and will chemically interact with both oil and water, thus stabilizing the interface between oil or water droplets in suspension. This principle is exploited in soap to remove grease for the purpose of cleaning.

A wide variety of emulsifiers are used in pharmacy to prepare emulsions such as creams and lotions [39].

Whether an emulsion turns into a water-in-oil emulsion or an oil-in-water emulsion depends on the volume fraction of both phases and on the type of emulsifier. Generally, the Bancroft rule applies: emulsifiers and emulsifying particles tend to promote dispersion of the phase in which they do not dissolve very well; for example, proteins dissolve better in water than in oil and so tend to form oil-in-water emulsions (that is they promote the dispersion of oil droplets throughout a continuous phase of water) [39].

Emulsifying agents can be classified according to: 1) chemical structure; or 2) mechanism of action. Classes according to chemical structure are synthetic, natural, finely dispersed solids, and auxiliary agents. Classes according to mechanism of action are monomolecular, multimolecular, and solid particle films. Regardless of their classification, all emulsifying agents must be chemically stable in the system, inert and chemically non-reactive with other emulsion components, and nontoxic and nonirritant. They should also be reasonably odorless and not cost prohibitive.

The usual method for choosing an emulsifier is known as the Hydrophilic-Lipophilic Balance (HLB) system which uses a scale of 0 to 20 based on their affinity for oil and water. Emulsifiers with low HLB-values are more lipophilic, while higher HLB compounds are hydrophilic In general, emulsifiers with HLB values of 3 – 8 give W/O-emulsions, whereas those with values of above 9 are more water-soluble and result in O/W-emulsions [40].

Table (3.2) Emulsifier Function of HLB-Values [40].

HLB 1 - 3	**Antifoaming Properties**
HLB 3 - 8	**W/O-Emulsification**
HLB 7 - 9	**Wetting Properties**
HLB 9 - 18	**O/W-Emulsification**
HLB 15 - 20	**Solubilizing Properties**

Sometimes several emulsifiers are mixed together before using them in formulas. Such emulsifying blends are commonly called emulsifying waxes [40].

3.6.1 HLB System

System first developed by Griffin to quantitatively correlate surfactant structures with their effectiveness as emulsifiers. HLB numbers are experimentally determined for the different emulsifiers. If an emulsifier has a low HLB number, there is a low number of hydrophilic groups on the molecule and it will have more of a lipophilic character. For example, the Spans generally have low HLB numbers and they are also oil soluble. Because of their oil soluble character, Spans will cause the oil phase to predominate and form an W/O emulsion [40].

The higher HLB number would indicate that the emulsifier has a large number of hydrophilic groups on the molecule and therefore should be more hydrophilic in character. The Tweens have higher HLB numbers and they are also water soluble. Because of their water soluble character, Tweens will cause the water phase to predominate and form an O/W emulsion [40].

Combinations of emulsifiers can produce more stable emulsions than using a single emulsifier with the same HLB number.

3.6.2 Classification of Emulsifying Agents

For purposes of discussion, it is useful to have some method of classifying emulsifying agents. Although such classifications are rather arbitrary and may even tend to obscure certain relationships [29].

A simple classification into three major classes of emulsifying agents may be made [33]:

- Surface-active materials.
- Naturally-occurring materials.
- Finely-divided solids.

3.6.2.1 Classification of Synthetic Surface-Active Agents

The surface-active emulsifying agents, in the sense indicated above, probably represent the principal type used in industry [38].

The agents are classified according to the hydrophilic group in the molecule [9].

I. Anionic

A. Carboxylic Acids

  1. Carboxyl joined directly to hydrophobic group.
  2. Carboxyl joined through an intermediate linkage.

B. Sulfuric Esters (Sulfates*)*

  1. Sulfate joined directly to hydrophobic group.
  2. Sulfate group joined through intermediate linkage.

C. Alkane Sulfonic Acids

1. Sulfonic group directly linked to hydrophobic group.
2. Sulfonic group joined through intermediate linkage.

D. Alkyl Aromatic Sulfonic Acids

1. Hydrophobic group joined directly to sulfonated aromatic nucleus.
2. Hydrophobic group joined to sulfonated aromatic nucleus through Intermediate linkage.

E. Miscellaneous anionic Hydrophilic Groups

1. Phosphates and phosphoric acids.
2. Persulfates, thiosulfates, etc.
3. Sulfonamides.
4. Sulfamic acids, etc.

II. Cationic

A. A mine Salts {Primary, Secondary, and Tertiary)

1. Amino group joined directly to hydrophobic group.
2. Amino group joined through intermediate link.

B. Quaternary Ammonium Compounds.

1. Nitrogen joined directly to hydrophilic group.
2. Nitrogen joined through an intermediate group.

C. Other Nitrogenous Bases.

1. Nonquaternary bases (e.g., guanidine, thiuronium salts, etc.).
2. Quaternary bases.

D. Nonnitrogenous Bases.

1. Phosphonium compounds.
2. Sulfonium compounds, etc.

III. Nonionic

- **A.** Ether Linkage to Solubilizing Groups.
- **B.** Ester Linkage.
- **C**. Amide Linkage.
- **D.** Miscellaneous Linkages.
- **E.** Multiple Linkages.

IV. Ampholytic

- **A.** Amino and Carboxy.
  - **1.** Nonquaternary.
  - **2.** Quaternary.

- **B.** Amino and Sulfuric Ester
  - **1.** Nonquaternary.
  - **2.** Quaternary.

- **C.** Amino and Alkane Sulfonic Acid.

- **D.** Amino and Aromatic Sulfonic Acid.

- **E.** Miscellaneous.

  Combinations of Basic and acidic Groups.

V. Water-Insoluble Emulsifying Agents

- **A.** Ionic Hydrophilic Group.
- **B.** Nonionic Hydrophilic Group.

3.6.2.2 Natural Emulsifying Agents

A varieties of emulsifiers are natural products derived from plant or animal tissue. Most of the emulsifiers form hydrated lymphatic colloids (called hydrocolloids) that form multimolecular layers around emulsion droplets. Hydrocolloid type emulsifiers have little or no effect on interfacial tension, but exert a protective colloid effect, reducing the potential for coalescence, by:

- providing a protective sheath around the droplets.
- imparting a charge to the dispersed droplets.
- swelling to increase the viscosity of the system.

Hydrocolloid emulsifiers may be classified as:

- vegetable derivatives, e.g., acacia, tragacanth, agar, pectin, carrageen an, lecithin.
- animal derivatives, e.g., gelatin, lanolin, cholesterol.
- Semi-synthetic agents, e.g., methylcellulose, carboxymethylcellulose Synthetic agents, e.g., Carbopols.

Naturally occurring plant hydrocolloids have the advantages of being inexpensive, easy to handle and nontoxic. Their disadvantages required relatively large quantities to be effective as emulsifiers, and they are subject to microbial growth, thus their formulations require a preservative. Vegetable derivatives are generally limited to use as O/W emulsifiers [39].

Semi-synthetic agents are stronger emulsifiers, nontoxic, and less subject to microbial growth. Synthetic hydrocolloids are the strongest emulsifiers, nontoxic, and do not support microbial growth.

However, their cost may be prohibitive. These synthetic agents are generally limited to use as O/W emulsifiers [39].

3.6.2.3 Finely Divided Solid

These agents form a particulate layer around dispersed particles. Most them will swell in the dispersion medium to increase viscosity and reduce the interaction between dispersed droplets. Most commonly they support the formation of O/W emulsions, but some of them may support W/O emulsions. These agents include bentonite, veegum, hectorite, magnesium hydroxide, aluminum hydroxide and magnesium trisilicate [39].

3.7 Techniques of Emulsification

The mod e of addition, effect of mixing technique, mixing time, and also equipments available will be reviewed [6,9].

3.7.1 Mode Addition

Modes of addition had been stated as follows [9]:

1. **Agent-in-water method**.

In this method, the emulsifying agent is dissolved directly in the water, and the oil is then added, with considerable agitation. This procedure makes O/W emulsions directly; should a W/O emulsion be desired, the oil addition is continued until inversion takes place.

2. Agent-in-oil method.

The emulsifying agent is dissolved in the oil phase. The emulsion may then be formed in two ways:

A. Adding the mixture directly to the water. In this case, an O/W emulsion forms spontaneously

B. Adding water directly to the mixture. In this case, a W/O emulsion is necessary method, it is necessary to invert the emulsion by the addition of further water.

3. Nascent soap (in situ) method.

This method is suitable for those emulsions which are stabilized by soaps, and may be used to prepare either O/W or W/O types. The fatty acid part of the emulsifying agent is dissolved in the oil, and the alkaline part in the water. The formation of the soap (at the interface), as the two phases are brought together, results in stable emulsions.

3.7.2 Time of Mixing

The effect of the time on particle sizes in emulsion is great. The prolonging agitation beyond an optimum time interval does little to improve the quality of emulsions. Under normal conditions of emulsification, the mean size of the particles decreases very rapidly in the first few seconds and then gradually decreases till attains the limiting value in (1–5) minutes [6].

3.7.3 Intensity of Mixing

Intensity of mixing an important factor in producing emulsion. More efficient agitation gives stable emulsions. The interfacial area increases with the increase of the rotational speed and the diameter of the stirrer, and with the decrease of the diameter of the container [6].

3.7.4 Temperature

Since both viscosity and interfacial tension decrease with the rise of temperature, any increase in temperature usually makes emulsification easier.

There is also some evidence that a large increase or decrease of temperature tends to coagulate droplets, there by causing a deterioration of emulsion.

3.8 De-emulsification

De-emulsification is not exactly the reverse of emulsification. It involves settling. Flocculation and coalescence and it require disrupting the stabilized layers of the interface.

De-emulsification has been used for a wide range of application (e.g. butter manufacture and crude oil dehydration, which is the present research we regard) [41].

3.9 Types of fluids

A plot of shear stress versus shear rate Is called a (flow curve) or (rheogram). Generally, fluid may be classified according to the observed flow curve or rheogram into:

3.9.1 Newtonian fluids

A Newtonian fluid is a fluid in which shear stress is proportional to the velocity gradient. The constant of proportionality is known as the viscosity. The constant of proportionality, η (or the ratio of the shear stress to the rate of shear) which is called Newtonian viscosity is, by definition, independent of shear rate $\dot{\gamma}$ or shear stress τ and depend only on the material and it's temperature and pressure. The plot of shear stress against shear rate for Newtonian fluid is a straight line of slop η , and passing through the origin. Figure (3.4) explain the situation.

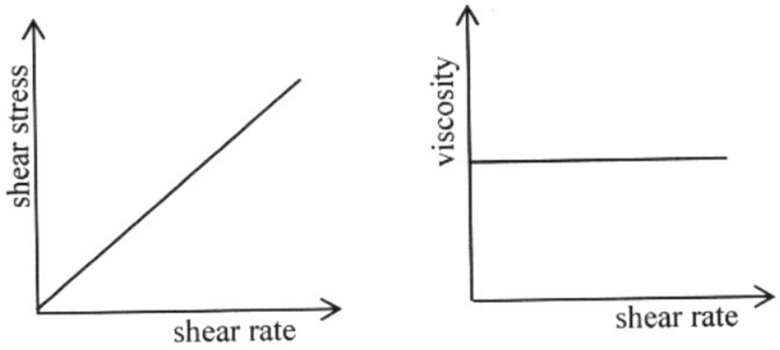


Figure (3.4) Flow curve of Newtonian fluid and viscosity

Examples of Newtonian fluids include water, benzene, hexane and most solution of simple molecules. At a given temperature a viscosity of Newtonian fluid remains constant.

3.9.2 Non-Newtonian fluids

In these fluids, the shear rate – shear stress ratio is not constant or the shear stress - shear rate relationship is non-linear. Non-Newtonian fluids may not have a well-defined viscosity; it changes as the shear rate is varied. The measured viscosity is the **apparent viscosity**.

In the category of non-Newtonian fluids one can include most dispersion. The complexity of the microstructure of the system is influencing the viscosity measurement. If shear forces are applied, the structure of material may change therefore the viscosity is changing [42, 43].

Example of non-Newtonian fluids in clued drilling muds, cement slurries, apple sauce, polymers, paints, blood, and coal slurries.

3.10 Classification Of Non-Newtonian fluids

3.10.1 Time-Independent Fluids

Fluid of the first type whose properties are independent of time (the shear stress of these fluids at constant temperature is solely dependent on the rate of shear at this temperature).

These fluids may be conveniently subdivided into three distinct types, which are:

3.10.1.1 Pseudo plastic

This type of fluid will display a decreasing viscosity with an increasing shear rate, as shown in the figure (3.5). Pseudo plastics include paints, emulsions, dispersions of many types, shampoo, slurries, printer ink and paper pull. This type of flow behavior is called shear-thinning [44].

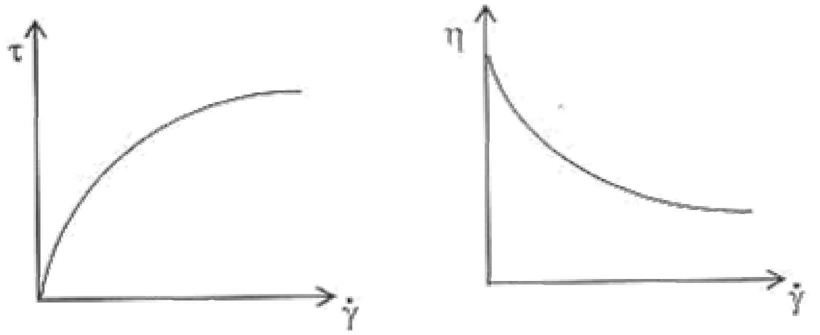


Figure (3.5) Shear thinning behavior [44].

3.10.1.2 Dilatant (shear-thicking behavior)

Increasing viscosity with an increase in shear rate characterizes the dilatants fluid; as shown in the figure (3.6). Although rarer than pseudo plasticity, dilatancy is frequently observed in fluids containing high level of deflocculated solids such as clay slurries, candy compounds, corn starch in water, and sand/water mixtures [44].

Dilatancy is also referred to as shear-thickening flow behavior. In these suspensions shear-thicking occurs due to rearrangements in the microstructure evoked by shear.

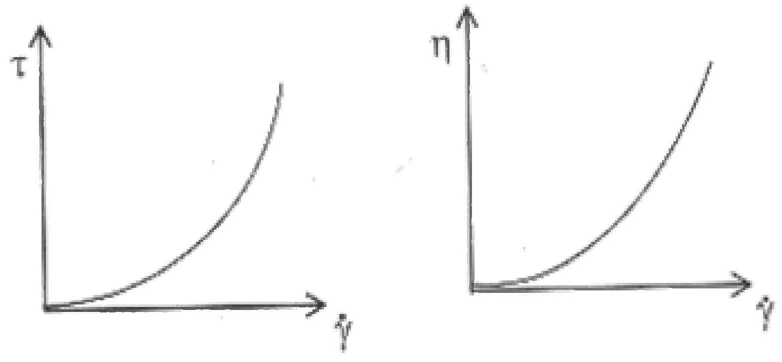


Figure (3.6) Shear-thicking behavior [44].

Examples of dilatants fluids: Wet sand, concentrated starch suspensions, Starch in water, Clay slurries, Candy compounds, Peanut butter.

3.10.1.3 Bingham Plastic Fluids

This type of fluid will behave as a solid under static conditions. A certain amount of force must be applied to the fluid before any flow is induced; this force is called the "yield value". Once the yield value is exceeded and flow begins, plastic fluids may display Newtonian, pseudo plastic, or dilatant flow characteristics [44].

Examples of plastic fluids include: Ketchup, Tooth paste, Hand cream, Chewing Gum and Thermoplastic polymer solutions.

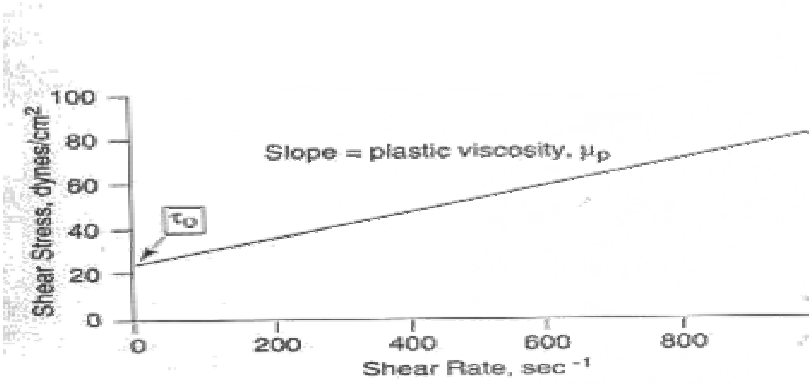


Figure (3.7) Idealized Bingham Plastic Fluid [44].

3.10.2 Time-Dependent Fluids

The shear stress of these fluids at constant temperature is a function of both magnitude and duration of the shear rate . The equivalent viscosity of these fluids depends not only on the rate of shear but also on the time of shear has been applied.

- Time - dependent fluids can be classified in to two types :

Thixotropy and Rheopexy

3.10.2.1 Thixotropic fluids

As shown in the figure (3.8), a thixotropic fluid undergoes decrease in viscosity with time, while it is subjected to constant shearing.

Such behavior, where systems that look rather solid like but upon stirring become liquid like, with decreasing viscosity, is called thixotropy. At rest the viscosity increases again. A special structure which is building up again causes the viscosity to increase again [44].

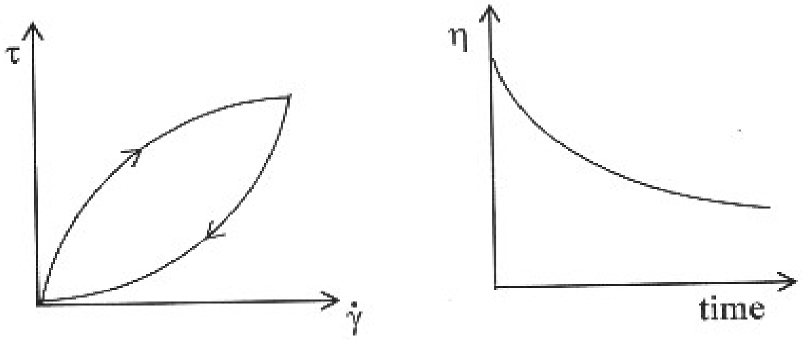


Figure (3.8) Viscosity dependence on time for thixotropic fluids [42].

Examples of thixotropic fluids whose viscosity decreases with time include: Paint, Yogurt; milk, Mayonnaise, Carboxymethyl cellulose, Asphaitic Grease, Heavy printing inks, Glues, Starch and Fruit juice concentrates.

3.10.2.2 Rheopectic fluids

This is essentially the opposite of thixotropic behavior, in that the fluid's viscosity increases with time as it is sheared at a constant rate. As shown in figure (3.9).

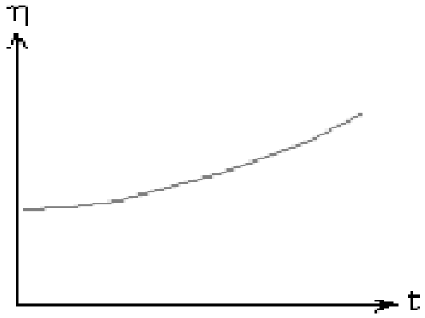


Figure (3.9) Viscosity dependence on time for Rheopectic fluids [42].

3.11 Rheological properties of Bingham Plastic Fluids

The following rheological properties determined are:

3.11.1 Plastic viscosity

The plastic viscosity is the shearing stress in excess of yield point that the will induce rate of shear. It is a part of fluid resistance to flow caused by mechanical friction that occurs:

- Between the solids presented in the emulsion.
- Between the solids and the liquid that surrounds them.
- With the shearing of the liquid that itself.

For practical purposes, plastic viscosity depends upon:

- The concentration of the solids in the emulsion.
- The size and shape of the solid particles.

An increase in the concentration of the solid particles in the emulsion or decreasing the diameter of solid particles will result in an increase in the plastic viscosity.

The addition of water increases the plastic viscosity, while the addition of oil tends to decrease it. Plastic viscosity of emulsions is largely affected by the temperature [8].

3.11.2 Yield point

The yield point is the second part of fluid resistance to flow, which is a measurement of the electrochemical forces, or attractive forces between the solid particles that encountered in the emulsion under flow conditions. These forces are a result of negative and positive charges located on or near the surface of the solid particles [42].

The yield point depends upon:

- The surface properties of the emulsion's solids.
- Concentration of the emulsion′ s solids.
- The electrical environment of the solid particles.

Generally, the introduction of more solids in the emulsion will increase the yield point.

Also, the yield of the emulsion can be increase by the addition of emulsified water or gelling agent, and some times it can be decrease by addition of oil [8].

Both plastic viscosity and yield point can be obtained by using different instruments, i.e., Baroid rheometer, Multi speed rotational viscometers such as Fann V.G meter, and Fann viscometer model – 35 A.

Plastic viscosity and yield point are absolute flow properties of emulsions and reflect the surface – active behavior of solids in emulsion.

The plastic viscosity and yield point show much better indication of the condition of the emulsion under high temperature.

3.12 Factors Affects on the Rheological Properties

3.12.1 Temperature

One of the most obvious factors that can have an effect on the rheological behavior of a material is temperature. Some materials are quite sensitive to temperature, and a relatively small variation will result in a significant change in viscosity. Others are relatively insensitive. Consideration of the effect of temperature on viscosity is essential in the evaluation of materials that will be subjected to temperature variations in use or processing, such as motor oils, greases, and hot-melt adhesives [43].

3.12.2 Shear Rate

When a material is to be subjected to a variety of shear rates in processing or use, it is essential to know it's viscosity at the projected shear rates. If these are not known, an estimate should be made. Viscosity measurements should then be made at shear rates as close as possible to the estimated values [43].

It is frequently impossible to approximate projected shear rate values during measurement due to these values falling outside the shear rate range of the viscometer. In this case, it is necessary to make measurements at several shear rates and extrapolate the data to the projected values. This is not the most accurate method for acquiring this information, but it is often the only alternative available, especially when the projected shear rates are very high.

In fact, it is always advisable to make viscosity measurements at several shear rates to detect rheological behavior that may have an effect on processing or use. Where shear rate values are unknown or not important.

Examples of materials that are subjected to, and are affected by, wide variations in shear rate during processing and use are: paints, cosmetics, liquid latex, coatings, certain food products, and blood in the human circulatory system.

3.13 Flow Models

Many flow models have been proposed, which are useful for the treatment of experimental data or for describing flow behavior. However, it is likely no given model fits the rheological behavior of material over an extended shear rate range. Nevertheless, these models are useful for summarizing rheological data and are frequently encountered in the literature.

Table (3.3) Flow equations for flow models [46,47].

Flow model	Flow equation	Equ.no.
Newtonian	$\tau = \eta\,\dot{\gamma}$	…(3.1)
Bingham plastic	$\tau - \tau_{\circ} = \eta_{p}\dot{\gamma}$	…(3.2)
Power law	$\tau = k\dot{\gamma}^{n}$	…(3.3)
Modified power law	$\tau - \tau_{\circ} = k\dot{\gamma}^{n}$	…(3.4)
Casson fluid	$\tau^{1/2} - \tau_{\circ}^{1/2} = \eta_{\infty}^{1/2}\,\dot{\gamma}^{1/2}$	…(3.5)
Robertson-Stiff	$\tau = A\ (\ \dot{\gamma} + C)^{B}$	…(3.6)
Modified Robertson-Stiff	$\tau - \tau_{\circ} = A'(\dot{\gamma} + C')^{B'}$	…(3.7)
Williamson	$\eta = \eta_{\infty +}\dfrac{(\eta_{\circ} - \eta_{\infty})}{1 + \dfrac{\lvert\tau\rvert}{\tau_{m}}}$	…(3.8)
Cross	$\eta = \eta_{\infty} + \dfrac{(\eta_{\circ} - \eta_{\infty})}{1 + \propto \dot{\gamma}^{n}}$	…(3.9)

Of the model listed in table (3.3), the Newtonian is the simplest. The other model can be applied to non-Newtonian materials where time dependant effects are absent.

This situation encompasses many technical important materials from polymer solution to lattices, pigment slurries, and polymer melts.

At high shear rates most of these materials tend to Newtonian viscosity limit. At low shear rates they tend either to a yield point or to a low shear Newtonian viscosity. At intermediate shear rates, the power law or Casson model is useful [45].

The Bingham plastic model, $\tau - \tau_{\circ} = \eta \quad \dot{\gamma}$, is the two parameter model which has been widely used as a model for non-Newtonian fluids such as drilling fluid and emulsion. Fluids that exhibit Bingham Plastic behavior are characterized by a yield point (τ_o) and a plastic viscosity (η) that is independent of the shear rate as shown in figure (3.7). The presence of a yield stress means that a certain critical shear stress must be exceeded before flow can begin. If the fluid exhibits Newtonian flow after the yield value is exceeded, it is called a Bingham Plastic fluid.

In Fann VG- viscometer 35A plastic viscosity in (cp), the yield point in (lb/100 ft^2) and apparent viscosity in (cp) can be determined from:

$$\eta_p = \theta_{600} - \theta_{300} \qquad \dots (3.10)$$

$$Y_p = \eta_p - \theta_{300} \qquad \dots (3.11)$$

$$\eta_a = \frac{\theta_{600}}{2} \qquad \dots (3.12)$$

Where

θ_{600} = Dial reading at 600 rpm

θ_{300} = Dial reading at 300 rpm

Another model is the power law, $\tau = k\dot{\gamma}^{n}$, is widely used for non-Newtonian fluids. It holds many solutions and can describe Newtonian, shear-thinning, and shear-thickening behavior, depending on the power factor, *n*, also called the flow behavior index.

For Newtonian fluid, *n*=1 and the equation reduces to Newtonian model. If *n* is less than 1, the fluid is shear thinning; if it is greater than 1, the fluid is shear thickening. A test of whether the power law applies and a means to determine *n* is to plot the log shear stress vs. the log shear rate. If the plot is linear the power law applies. The value of *n*, which is the slope of the line, can be used as a measure of the degree of shear thinning or shear thickening.

The power law can be extended by including the yield value $\tau - \tau_{\circ} = k \quad \dot{\gamma}^{n}$, or by adding the Newtonian limiting viscosity, η_{∞}. The later is done in the Sisko model, $\eta_{\infty} + \kappa \quad \dot{\gamma}^{n-1}$. These two models, along with the Newtonian, Bingham, and Casson models, is often included in data-fitting software supplied for the newer computer-driven viscometer [45].

The Casson model is useful in establishing the flow characteristics of inks, paint, and other dispersions. An early from this expression equation (3.13) was modified to give equation (3.14) [46].

$$\tau^{1/2} = k_{\circ} + k_{1} \quad \dot{\gamma}^{1/2} \qquad \dots (3.13)$$

$$\eta^{1/2} = \eta_{\infty}{}^{1/2} + \tau_{\circ}{}^{1/2} \quad \dot{\gamma}^{-1/2} \qquad \dots (3.14)$$

The square root of viscosity is plotted against the reciprocal of the square root of shear rate. The square of the slope is $\tau_{\circ}$, the yield stress; the square of the intercept is η_{∞} the viscosity at infinite shear rate. No material actually experiences an infinite shear rate, but η_{∞} is a good representation of the condition where all rheological structure has been broken down. The Casson stress $\tau_{\circ}$ is some what different from the yield stress discussed earlier in that there may or may not be an intercept on the shear stress-shear rate curve for the material.

If there is an intercept, but the material is shear thinning, a Casson plot gives a value for $\tau_\circ$ that is indicative of the degree of shear thinning [46].

The Robertson-Stiff equation, $\tau = A \ (\ \dot{\gamma} + C)^B$, describe the shear stress-shear rate relationship for most fluids and cement slurries.

It can be shown from the above Equation that when the values of B=1, C= 0 it will describe the flow behavior of Newtonian fluid. The parameter C is considered as a correction for the shear rate and term $(\dot{\gamma} + C)$ can be considered as an "effective shear rate" while A and B are similarly to the parameters of the power law model (n and k) [47].

A log-log plot of τ versus $(\dot{\gamma} + C)$ gives as straight line of slope *B*, and intercept of A at $(\dot{\gamma} + C) = 1$. The parameter C can be evaluated from plotting τ versus $\dot{\gamma}$ and from the geometric mean of shear stress τ_m [47].

$$\tau_m = (\tau_{\min} \times \tau_{\max})^{1/2} \qquad \ldots (3.15)$$

Therefore (C) can be calculated from:

$$C = \frac{\dot{\gamma}_{\min}\dot{\gamma}_{\max} - \dot{\gamma}_m^{\ 2}}{2\dot{\gamma}_m - \dot{\gamma}_{\min} - \dot{\gamma}_{\max}} \qquad \ldots (3.16)$$

The Williamson equation is useful for modeling shear-thinning fluids over a wide range of shear rates. It makes provision for limiting low and high shear Newtonian viscosity behavior, where τ is the absolute value of shear stress and τ_m is the shear stress at which viscosity is the mean of the viscosity limits η_o and η , i.e., at $\eta = (\eta_\circ + \eta_\infty)/2$.

The Cross equation assumes that the shear thinning fluid has high and low limiting viscosity, where α and *n* are constants. The value for n is often given as 2/3. The constant α is associated with rupture of the linkages in the structure of the fluid [48].

Chapter four

Experimental Work

A general description of the experimental work, which is included materials that have been used to complete the laboratory tests , as well as procedure of testing , will be explained in this chapter.

4.1 Emulsions Used

All emulsions prepared in this investigation are invert emulsions when water droplets are dispersed in oil the resulting emulsion is called water- in - oil emulsion (W/O). Generally, W/O-emulsions are preferred when a large amount of oil is desired. This system has a greasier feel and leaves larger-lasting residues.

4.2 Materials and Additives

A detailed description of the materials and additives with their advantages as follows:-

4.2.1 Diesel Oil

It is used as the external phase of all samples being tested. Diesel oil has a flash point of 160 °F and aniline point of 145 °F that meets API specifications.

4.2.2 Water

Distilled water is used as the dispersed phase of emulsion samples prepared. Powdered sodium chloride is used to provide the salinity of the water phase. Concentration of sodium chloride depends upon the percent of water phase and salinity requirements. 7 gm of Nacl was added to all samples.

4.2.3 Barite

It is Barium sulfate ($BaSO_4$), it is a heavy spar, a white, yellow, blue, red, or colorless mineral. In all tests a yellow powder is used, which has the following properties [51]:-

1. High specific gravity (4.3).
2. Thermal resistance, low solubility and chemical inertness, excellent corrosion rest non-toxic, friction resistance, increase density.
3. Dispersing particles.
4. It is used as a weight material.

Barite contains high purely Barium Sulfate, which can be used to produce barium salt such as $BaCl_2$,$BaSO_4$, $BaCO_3$,BaO, $Ba(NO_3)_2$, Barium Titanium carbonate, and so on.

4.2.4 Quick Lime

Calcium oxide (CaO) commonly known as burnt lime or quick lime, is widely used as chemical compound. It is a white, caustic and alkaline crystalline solid. As a commercial product, lime often also contains magnesium oxide, silicon oxide and smaller amounts of aluminum oxide and iron oxide lime.

It had the disadvantage of decomposing rapidly on exposure to air and moisture, and the burnt had to be fresh and unslaked [52].

Table (4.1) Properties of Quick Lime [52].

Properties	
Molecular Formula	**CaO**
Molar Mass	**56.077 g/mol**
Appearance	**White solid**
Density	**3350 Kg/m^3, solid**
Melting point	**2575 °C (2845 K)**
Boiling point	**2850 °C (3121 K)**
Solubility in water	**reacts**

4.2.5 Emulsifier soluble oil additive (Lubrizol Becroson)

A soluble oil additive is used to act as emulsifying agent. It is fast acting and compatible with all other emulsion products. The soluble oil additive has a dark tan color and should be added in a sufficient quantity to prepare a stable emulsion.

4.2.6 Organophilic clay

It is used to suspend the weight material presented in the emulsions. It has benefits of providing viscosity, gel strength. Treatment levels for organophilic clay are highly dependent upon oil/water ratio and solid content or emulsion weight.

4.2.7 Asphaltic material

It is special asphaltic type materials provide emulsion stability at high temperature, even in excess of 450 °F, and gel strength with out appreciable increase in the viscosity.

4.3 Equipments Used

The main equipments used in this study are:

1- Fann VG-Viscometer, Model 35A [Figure (4.1)].
2- Hamilton Beach mixer and cup [Figure (4.2)].
3- Electronic balance.
4- Drying oven.
5- Hot plate heater.
6- Thermometer (0 – 100 °C).
7- Stop watch.

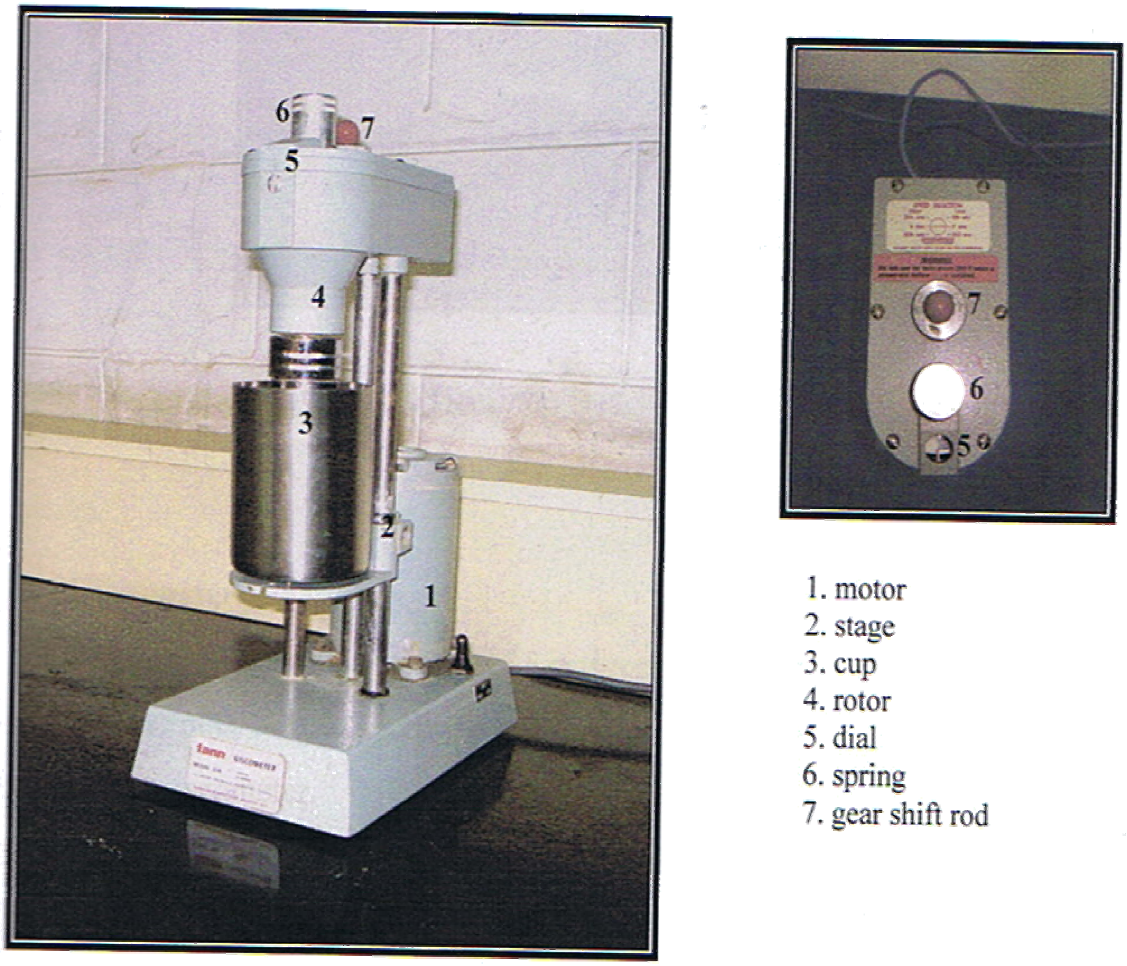


Figure (4.1) Fann VG-Viscometer, Model 35A.

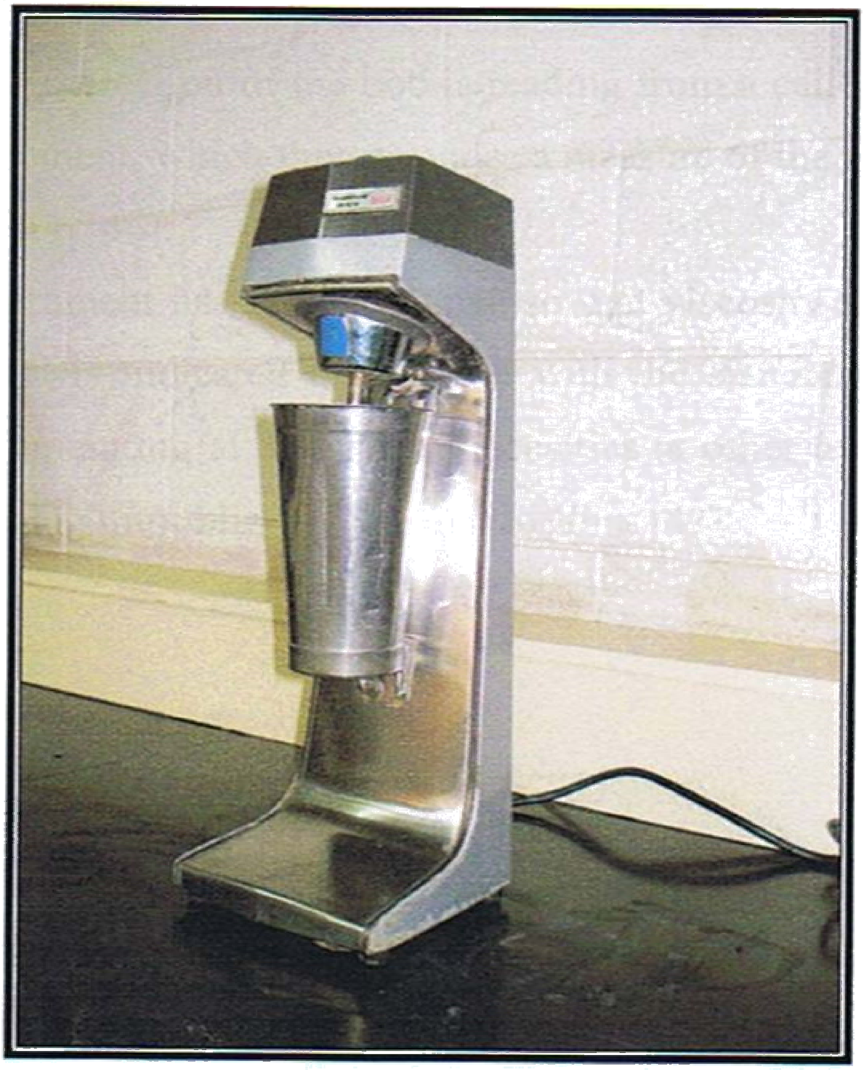


Figure (4.2) Hamilton Beach mixer and cup.

4.4 Viscometer

The Fann viscometer model 35 A, is direct reading instrument which has six speeds : 600, 300, 200, 100, 6 and 3 rpm. It is a Couette coaxial cylinder rotational viscometer. This instrument is a form of concentric cylinder viscometer that enables the variation of shearing stress with shear rate to be observed. The essential elements are shown in figure (4.3).

A bob suspended from a spring hangs concentrically in an outer cylinder. The assembly is lowered to a prescribed mark in a cup of solution, and the other cylinder rotated at a constant speed.

The viscosity drag of the solution turned the bob until balance by the torque in the spring. The deflection of the bob is reading from a librated dial on the top of the instrument, thus provides a measure of the shear stress at the surface of the bob [53].

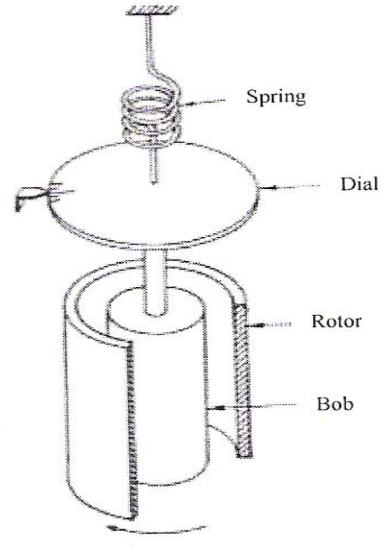


Figure (4.3) The Essential Elements of Rotational Viscometer.

4.4.1 Calibration of Viscometer

This procedure used for calibration by using only a Newtonian certified calibration fluids. Fann calibration fluids are available in nominal 20, 50, 100, 200 and 500 cp.

1. The instrument must be clean before immersing the rotor and bob into the calibration fluid. If necessary to remove the rotor and thoroughly clean the bob shaft and rotor.

2. Fill the sample to the scribed line with the calibration fluid and place it on the instrument stage. Elevate the stage so that the rotor is immersed to the proper immersion depth.

3. Place a thermometer into the sample until the bob touches the bottom and then secure it to the side of viscometer to prevent breakage.

4. Operate the instrument at 300 rpm for three minutes. This equalizes the temperature of the bob, rotor and the fluid.

5. Read the dial at 300 rpm and 600 rpm. Record these numbers, and the temperature from the thermometer to nearest 0.1 C.

4.5 Experimental procedure

It was found that the following mixing procedure included sequence of additives and mixing periods gave a best results in preparing emulsions as shown below:-

1. 475 ml diesel oil was measured in a beaker and placed in the Hamilton Beach cup.

2. 25 ml of water was measured in beaker.

3. Add salt (Nacl) to beaker of water.

4. Add desired concentration of emulsifier (Lubrizol becrosan) concentrate drop by drop to the diesel oil in the Hamilton Beach cup while mixing, and mix for 60 minutes.

5. All powder material and additives was weighted by using electronic balance, some of these material are changed in tests and the others are constant as shown in table below:

Table (4.2) Constant material for all tests.

Material	Weight (gm)
Lime (CaO)	**23.7**
Organophilic clay	**2.37**
Nacl (salt)	**7**

6. Slowly add lime additive, and mix for 30 minute.

7. Slowly add the required volume of brine while mixing and mix for 45 minutes.

8. Slowly add asphaltic material additive, and mix for 30 minutes.

9. Slowly add organophilic clay additives, and mix for 30 minutes.

10. Slowly add the total amount of barite as slow as possible to obtain the required final percentage volume of barite. Then mix the final mixture for 30 minutes.

11. The prepared solution was kept at rest at room temperature for 24 hour prior to conducting the rheological measurements.

4.6 Fann Viscometer model 35 A testing procedure

Twenty seven emulsion samples were tested using the Fann viscometer model-35 A. These samples included three various volume percentage of barite, with three different volume percentage of emulsifier and three different concentrations of asphaltic material.

The emulsion samples were tested for rheological properties under three different temperatures of (77 °F, 122 °F and 167 °F), at each temperature the rheological properties were measured. The emulsions prepared must be sieved after finished mixing and before testing in order to remove the undissolved additives or materials which affect the accuracy of shear stress results.

Before any test, the viscometer must be calibrated for both shear rate and shear stress to be insure that it will give accurate results.

The general procedure to operate this viscometer can be summarized in the following steps:-

1. The instrument was cleaned using distilled water before immersing the rotor and bob into the emulsion solution. If necessary , the rotor was removed and the bob shaft and the rotor cleaned thoroughly.

2. The sample was prepared at 25 °C (77 °F) then put it in cup and filled the cup with emulsion solution to the scribed line, after that placed the cup on the instrument stage. The instrument stage was elevated so that the rotor was immersed to the proper immersion depth.

3. The instrument was operated at 300 rpm for three minutes to equalize the temperature of the bob, rotor and emulsion solution.

4. The instrument speed switched to 600 rpm and the dial reading was recorded.

5. Step 4 was repeated for 300, 200, 100, 6 and 3 rpm.

6. Raising the temperature of the same sample to 122 °F by using hot plate heater and cover the sample cup by using caver with hole to put the thermometer inside the hole to be sure that the temperature reached to122°F , then repeated the step (1, 2, 3, 4, 5).

7. Repeat step 6 to raise the temperature from 122 °F to 167 °F.

Chapter Five

Results and Discussion

In this chapter we first study the rheological properties of emulsions. Secondly, the effect of temperature on rheological properties of emulsions.

Thirdly the effect of additives such as (Asphaltic material, Emulsifier and Barite) on rheological properties of emulsions. Finally, find the best model that fits the experimental results.

5.1 Experimental Results

Fann viscometer, model 35, was used to measure the shear stress at each shear rate value, so that the shear rate measured in rpm and shear stress was taken from dial reading in lb/100 ft^2 unit. Twenty seven emulsion samples were prepared, these emulsion samples were prepared from materials and additives mentioned in chapter four. The concentrations of some materials and additives were kept constant for all samples prepared such as diesel oil, brine water, lime, and organophilic clay, while the other additives such as emulsifying agent (soluble oil additive), asphaltic material concentrations and barite were varied to show their effect on rheological properties of emulsions, and secondly their effecting on thermal stability of the emulsions samples prepared.

Three different concentrations of barite were used as volume percentage (0.46, 0.65 and 0.84).

Nine emulsion samples of 0.46 % vol. of barite were prepared including three different volume percentages of emulsifier (2.4, 3.2 and 4) % and three different concentration of asphaltic material which are (35.5,40.5 and 45.5) gm.

Nine emulsion samples of 0.65 % vol. of barite also prepared with the same different concentrations of both emulsifier and asphaltic material.

Finally, another nine emulsion samples of 0.84 % vol. of barite were prepared also with the same values of changeable additives (emulsifying agent and asphaltic material).

The wide difference in concentrations of both asphaltic material and emulsifier were considered in order to show their influence on the rheological properties (plastic viscosity, yield point and apparent viscosity) of the emulsions and in turn on the behavior of these samples with increasing temperature.

5.2 Effect of Temperature on Rheological properties of Emulsions

The results of over all tests are tabulated in tables (5.1) to (5.9).
These experimental results are presented in figures (5.1) to (5.9), which are plot of (yield point, plastic viscosity and apparent viscosity) versus temperature. From these figures, one can notice that the increase in temperature will decrease the rheological properties (yield point, plastic viscosity and apparent viscosity), due to the change in the viscosity of the continuous phase of emulsions which is diesel oil.

Temperature causes reduction in the viscosity of diesel oil and in the friction forces between the solid particles in the emulsions mixture, which will result in a noticeable decrease in plastic viscosity of emulsions samples, also the yield point decreased due to reduction in the attraction forces between the solid particles in the emulsions since the distance between these particles becomes larger. Apparent viscosity decreased due to these effects in the emulsion mixture.

In other meaning, it may be said that temperature causes an expansion of sample.

It was found that the concentration of asphaltic material which was 35.5 gm was effective for emulsions samples of 0.46 % vol. of barite and 2.4 % vol. of emulsifier to be stable at temperatures up to 167 °F, no flocculation was observed. Since the values of (plastic viscosity, yield point and apparent viscosity) decreases gradually as temperature increased.

The same effect of 35.5 gm of asphaltic material was obtained on emulsions samples of 0.65 % vol. of barite. The emulsions sample of 0.84 %. vol. barite follow the same behavior.

These samples which were prepared with emulsifier concentration of 2.4 % by volume, it was found that 2.4 % emulsifier sufficient to coat all the water droplets. Insufficient emulsifier concentration will result in a break down of emulsion with increasing temperature that will lead to a free water phase in the emulsion, which causes water-wetting of solid constituents in the emulsions, especially barite. Water-wetting of barite causes it to be settled, that will increase the rheological properties.

The samples prepared with emulsifier concentration of 2.4 % by volume had stable properties in all vols. % of barite used, where no flocculation occurred.

The concentrations of 35.5 gm of asphaltic material and 2.4 % emulsifier were the optimum to be selected in preparing emulsions samples with vols. % of barite (0.46,0.65 and 0.84), without thermal flocculation up to 167 °F.

The emulsifier is not only effective by forming a mechanical barrier that surrounded water droplets, but it also overcomes the problem of moisture of solid components of emulsions especially barite.

Although, the emulsions prepared were in satisfactory conditions at temperatures up 167 °F with 35.5 gm asphaltic material, it was decided to increase the concentration of asphaltic material to 40.5 and 45.5 gm, with three different vols. % of barite to demonstrate its effect on rheological properties of emulsion with temperature. Increasing the asphaltic material to 40.5 and 45.5 gm of samples of 0.46 % vol. of barite, resulted in better behavior of rheological properties with temperature. This is due to the low solubility factor of asphaltic material which is related to the temperature and will always be present in the fluid as a tacky undissolved solid and will work continuously as a plastering agent, thus it improves emulsion behavior, especially at high temperatures and reduces chances of flocculation. A similar effect of 40.5 and 45.5 gm of asphaltic material was obtained on samples of 0.65 % vol. of barite. For 0.84 % vol. of barite, also 40.5 and 45.5 gm tend to improve the behavior of rheological properties.

The emulsifier concentration was increased to 3.2 % and 4 % by volume to establish it's effect on rheological properties of emulsion under temperature. It was noticed that this increase has no appreciable effect on the values of plastic viscosity, yield point and apparent viscosity but it resulted in a stronger with better tolerance to temperature.

Table (5.1) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 2.4) Vol. %

1- Asphaltic material = 35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
1-	77	38.33	24.6	50.63
2-	122	30.11	21.68	40.95
3-	167	26.35	18.14	35.42

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
4-	77	44.86	25.37	57.55
5-	122	34.89	23.5	46.64
6-	167	28.27	19.83	38.19

3- Asphaltic material = 45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
7-	77	48.56	29.04	63.08
8-	122	38.42	25.35	51.1
9-	167	30.19	22.52	41.45

Table (5-2) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 3.2) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
10-	77	40.26	23.51	52.02
11-	122	31.04	20.74	41.41
12-	167	29.19	19.83	39.11

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
13-	77	45.79	25.36	58.47
14-	122	32.96	23.36	44.64
15-	167	30.11	20.76	40.49

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
16-	77	49.48	27.2	63.08
17-	122	39	25.19	51.6
18-	167	31.04	22.59	42.34

Table (5-3) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 4) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
19-	77	42.1	23.52	53.86
20-	122	32.88	22.6	44.18
21-	167	25.51	19.82	35.42

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
22-	77	46.71	24.44	58.93
23-	122	35.65	23.51	47.41
24-	167	26.43	21.67	37.27

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
25-	77	49.48	28.12	63.54
26-	122	40.26	24.43	52.48
27-	167	29.21	23.5	40.96

Table (5-4) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.65 , Emulsifier = 2.4) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
28-	77	55.93	29.97	70.92
29-	122	45.79	27.2	59.39
30-	167	33.8	23.52	45.56

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
31-	77	60.54	30.89	75.98
32-	122	50.4	28.13	64.47
33-	167	35.76	25.33	48.43

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
34-	77	63.3	34.59	80.6
35-	122	52.24	30.9	67.69
36-	167	37.49	29.05	52.02

Table (5-5) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.65 , Emulsifier = 3.2) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
37-	77	57.77	30.9	73.22
38-	122	46.67	28.21	60.78
39-	167	34.72	25.37	47.41

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
40-	77	60.54	33.66	77.37
41-	122	50.32	29.21	64.93
42-	167	35.65	26.28	48.79

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
43-	77	63.3	35.51	81.06
44-	122	54.09	30.89	69.54
45-	167	38.11	28.9	52.56

Table (5-6) Effect of Temperature on Rheological properties of Emulsioms with (Barite = 0.65 , Emulsifier = 4) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
46-	77	58.7	30.89	74.15
47-	122	48.55	27.21	62.16
48-	167	35.64	25.37	48.33

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
49-	77	62.39	32.73	78.76
50-	122	52.24	28.13	66.31
51-	167	36.57	27.2	50.17

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
52-	77	65.15	35.5	82.9
53-	122	54.09	30.89	69.54
54-	167	39.34	29.04	53.86

Table (5-7) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 2.4) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
55-	77	68.84	36.42	87.05
56-	122	57.77	30.9	73.22
57-	167	40.11	27.9	54.06

2- Asphaltic material = 40.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
58-	77	71.61	38.26	90.74
59-	122	60.53	31.83	76.45
60-	167	41.18	29.97	56.17

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
61-	77	73.45	40.11	93.51
62-	122	61.47	34.57	78.76
63-	167	43.94	30.9	59.39

Table (5.8) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 3.2) Vol. %

1- Asphaltic material =35.5 gm

Exp. No.	**Temp.°F**	η_p	Y_p	η_a
64-	77	70.68	35.51	88.44
65-	122	58.7	30.89	74.15
66-	167	41.17	28.14	55.24

2- Asphaltic material = 40.5 gm

Exp. No.	**Temp.°F**	η_p	Y_p	η_a
67-	77	72.53	37.34	91.2
68-	122	60.53	31.83	76.45
69-	167	43.18	30.05	58.21

3- Asphaltic material =45.5 gm

Exp. No.	**Temp.°F**	η_p	Y_p	η_a
70-	77	74.37	38.27	93.51
71-	122	61.47	34.57	78.76
72-	167	44.87	31.81	60.78

Table (5-9) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 4) Vol. %

1- Asphaltic material =35.5 gm

Exp. **No**	**Temp.°F**	η_p	Y_p	η_a
73-	77	70.86	36.25	88.99
74-	122	58.7	30.89	74.15
75-	167	43.02	28.13	57.09

2- Asphaltic material = 40.4 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
76-	77	73.45	37.34	92.12
77-	122	61.46	31.82	77.37
78-	167	45.79	29.05	60.32

3- Asphaltic material =45.5 gm

Exp. **No.**	**Temp.°F**	η_p	Y_p	η_a
79-	77	74.37	39.19	93.97
80-	122	62.39	33.65	79.22
81-	167	48.56	30.89	64.01

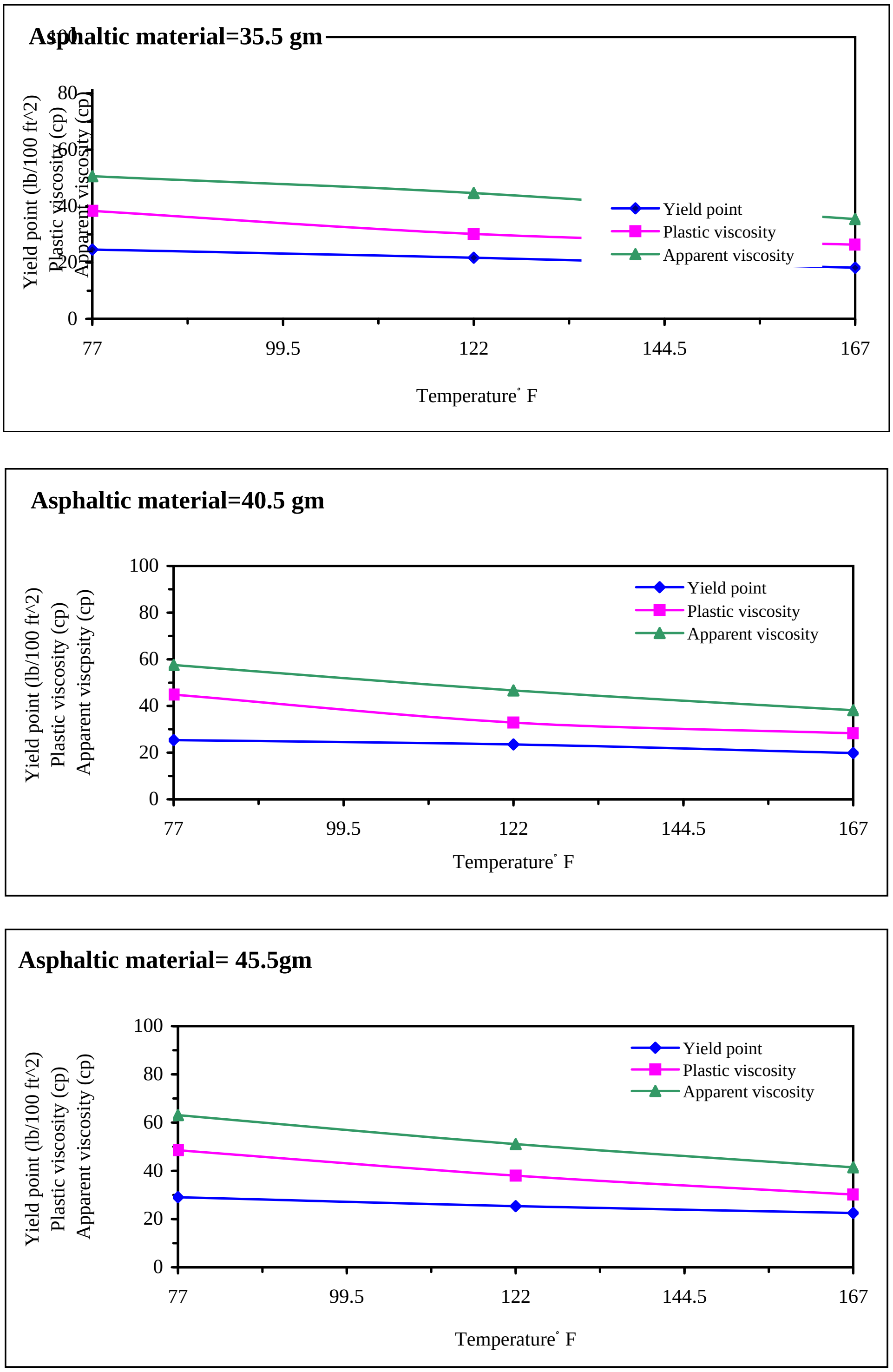
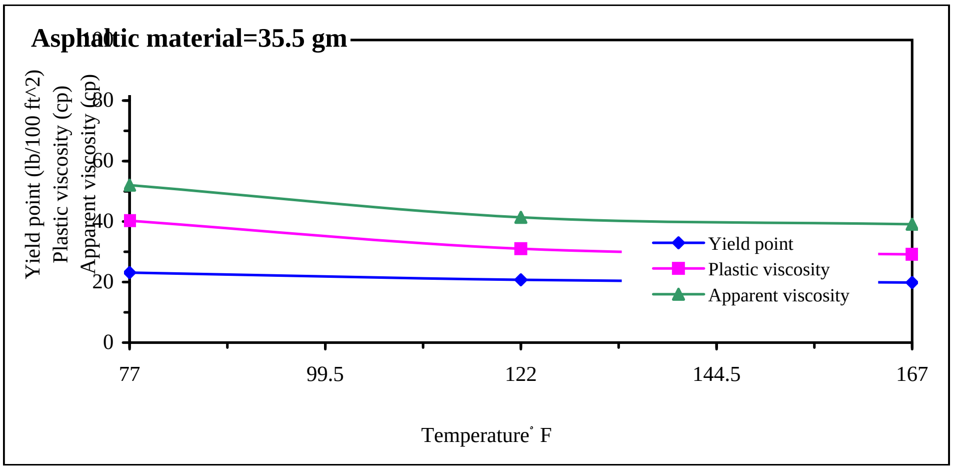
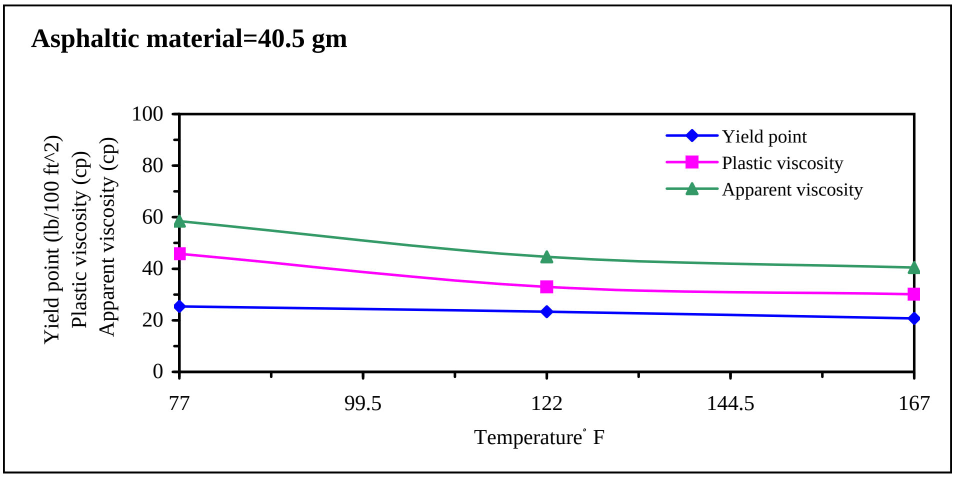


Figure (5.1) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 2.4) Vol. %





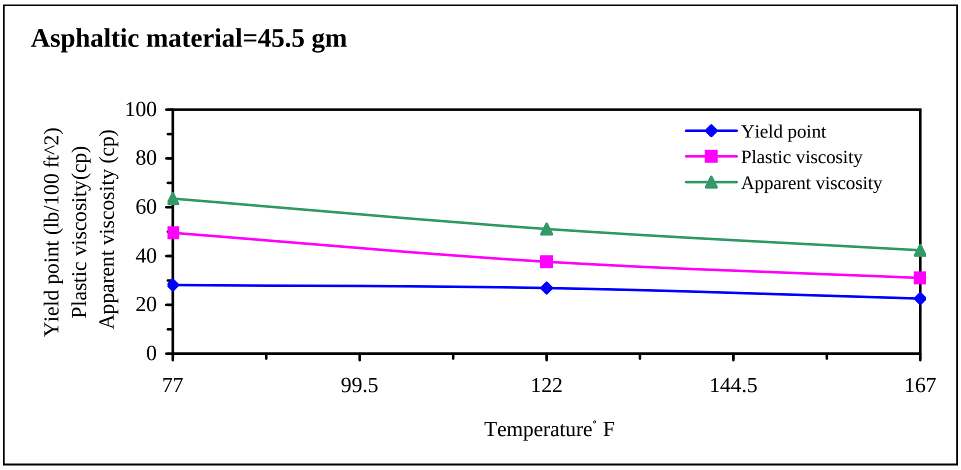


Figure (5.2) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 3.2) Vol. %

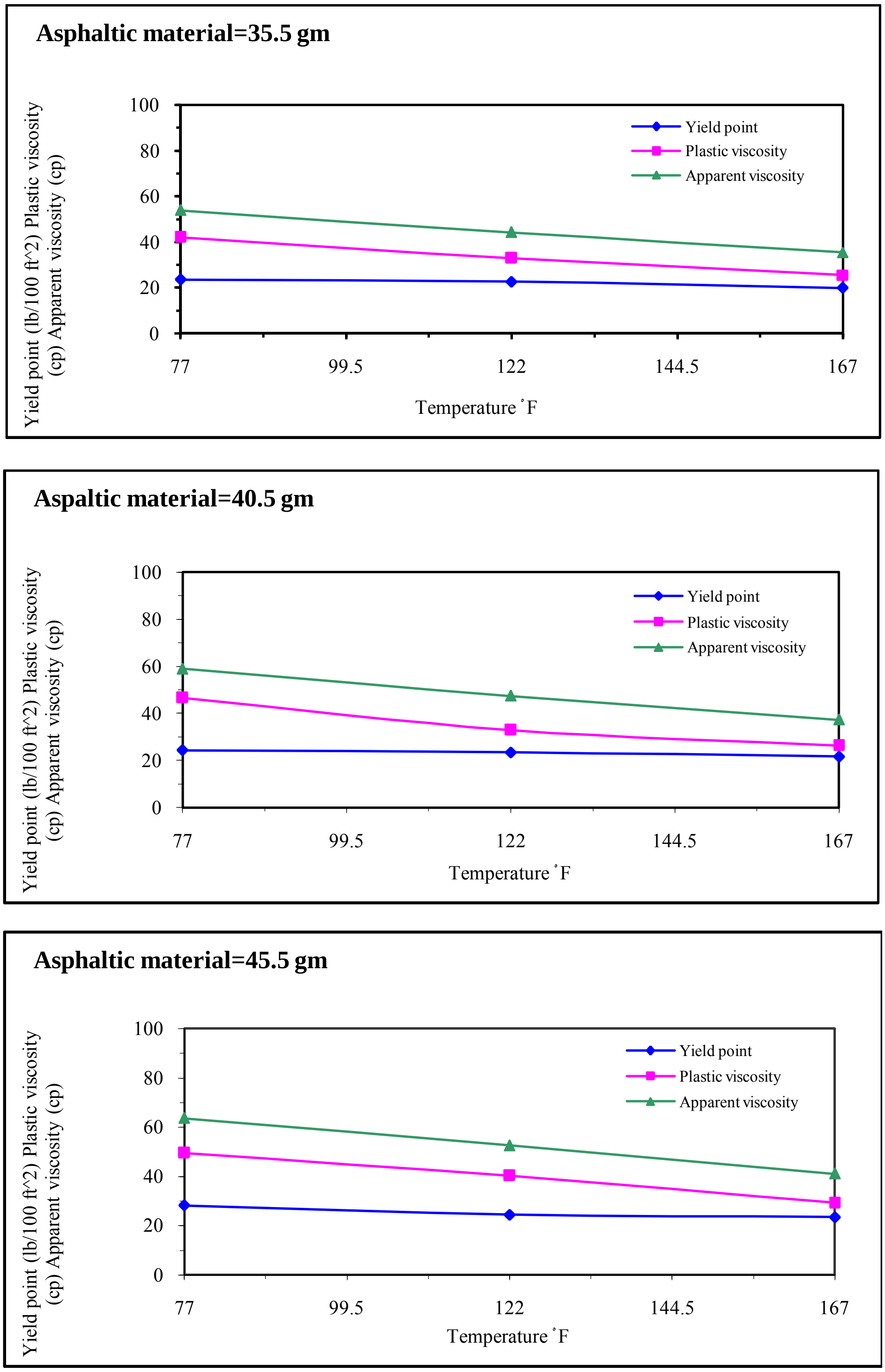


Figure (5.3) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.46 , Emulsifier = 4) Vol. %

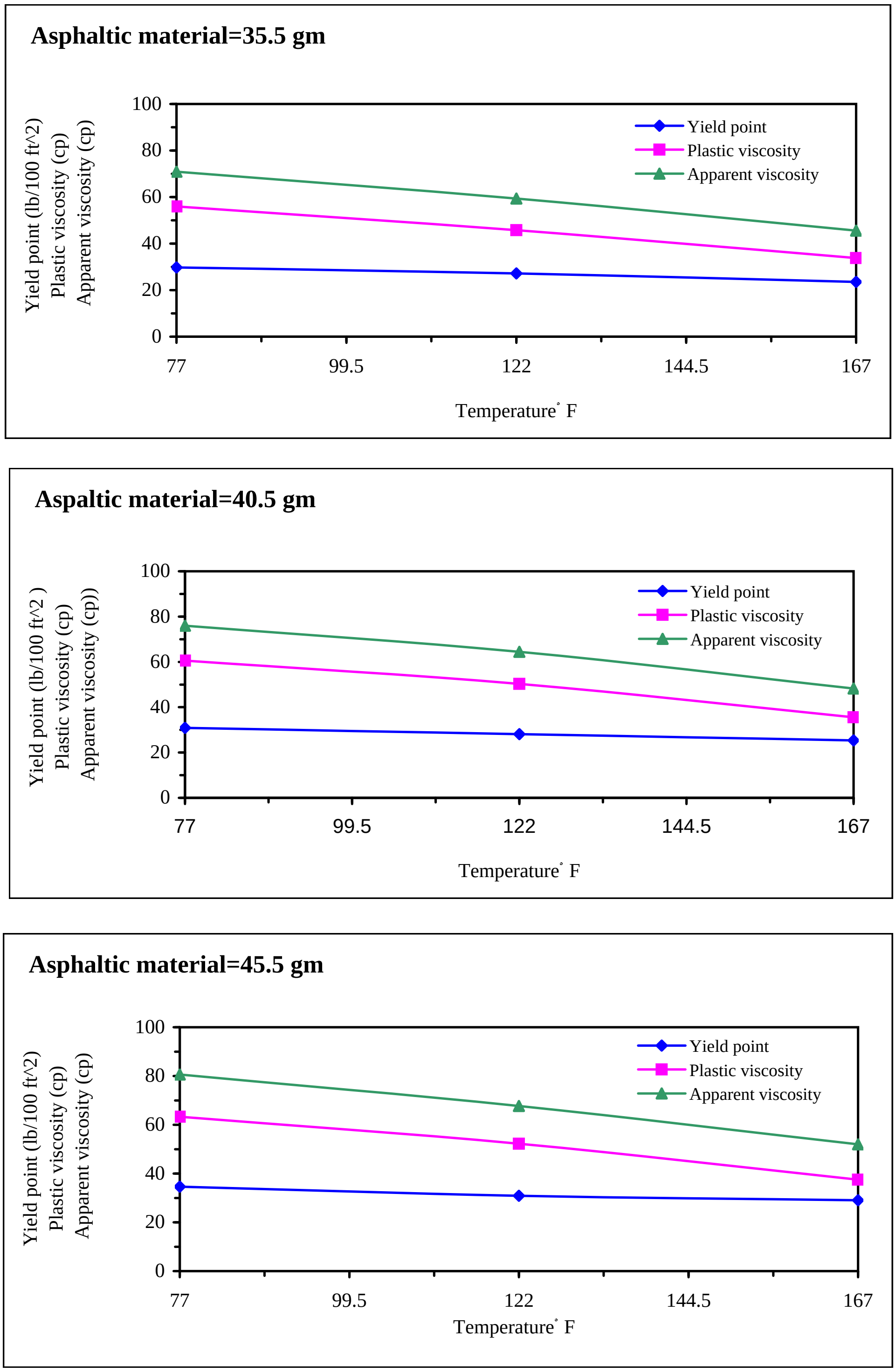
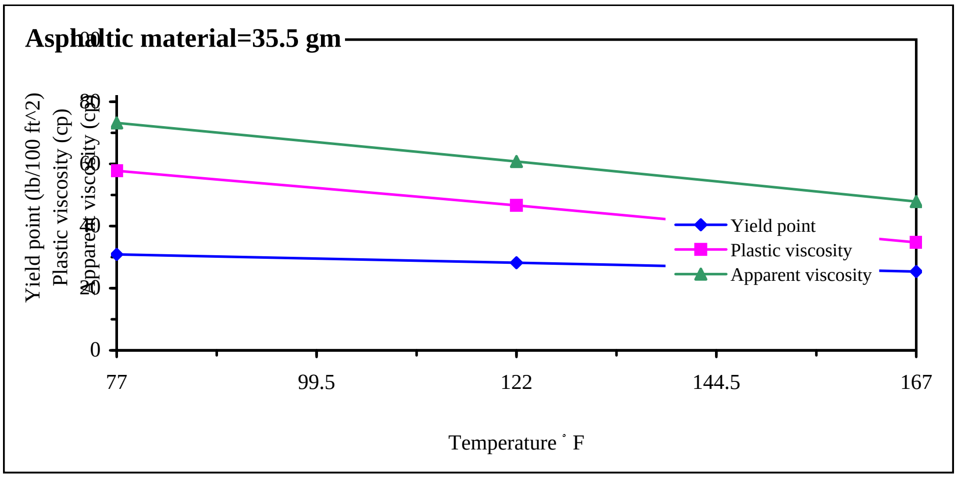
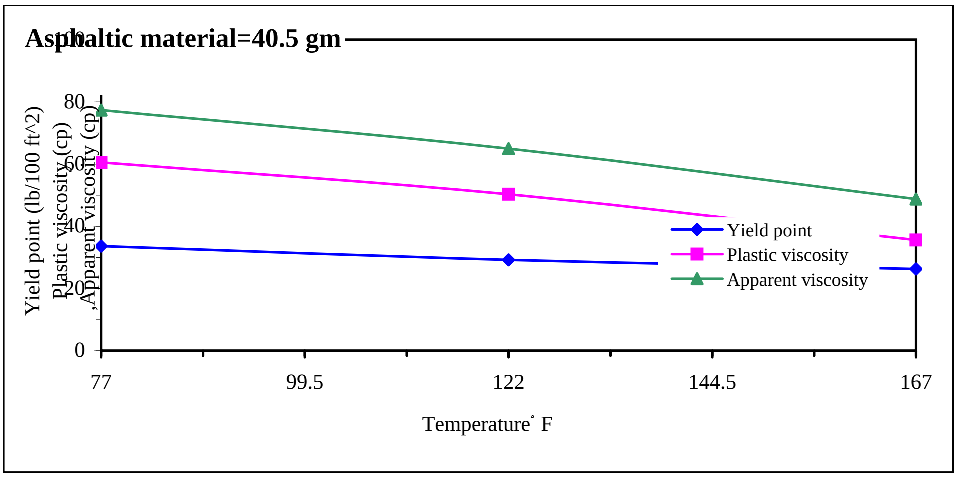


Figure (5.4) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.65 , Emulsifier = 2.4) Vol. %





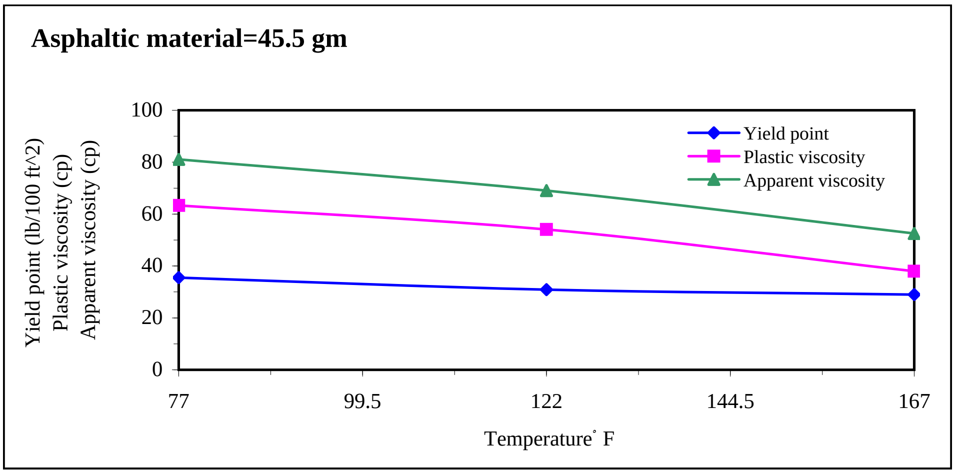


Figure (5.5) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.65 , Emulsifier = 3.2) Vol. %

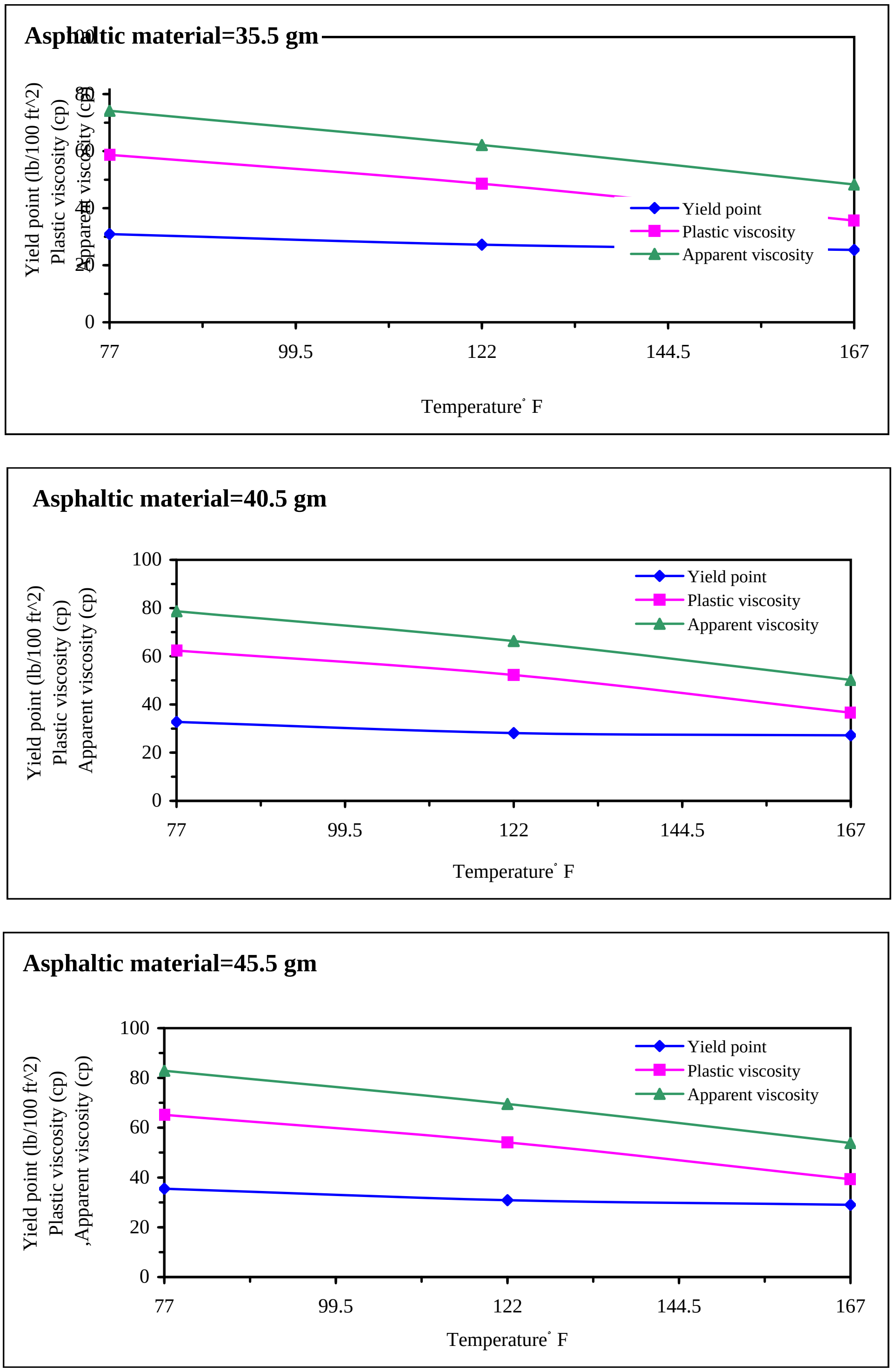
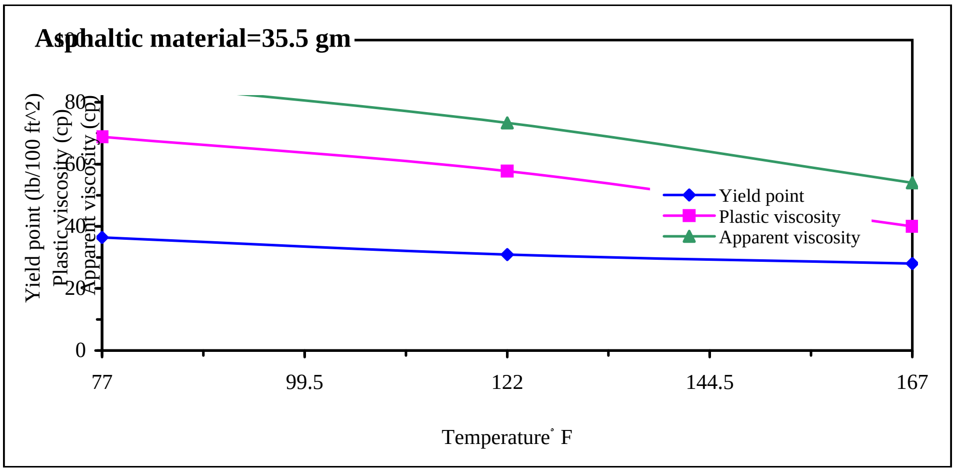
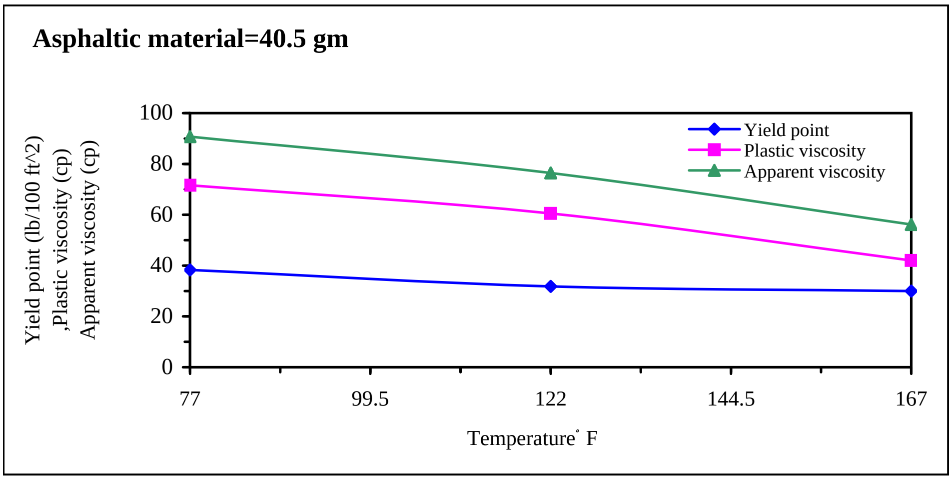


Figure (5.6) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.65 , Emulsifier = 4) Vol. %





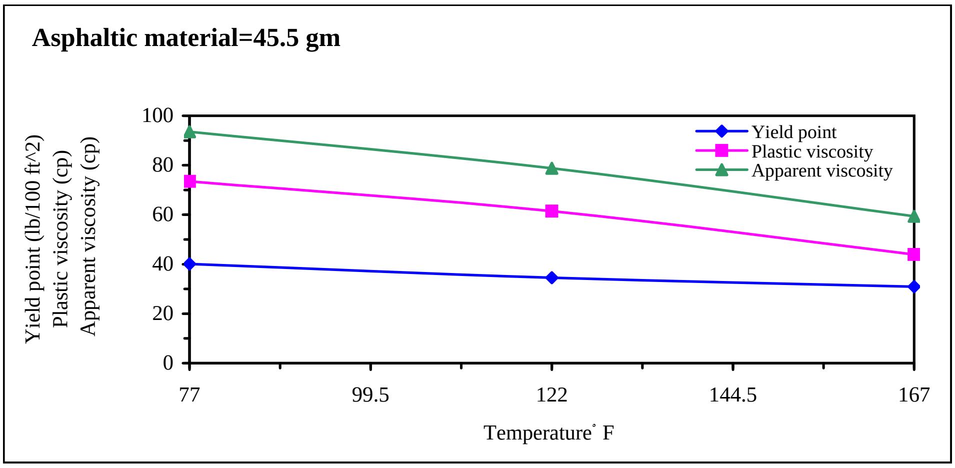
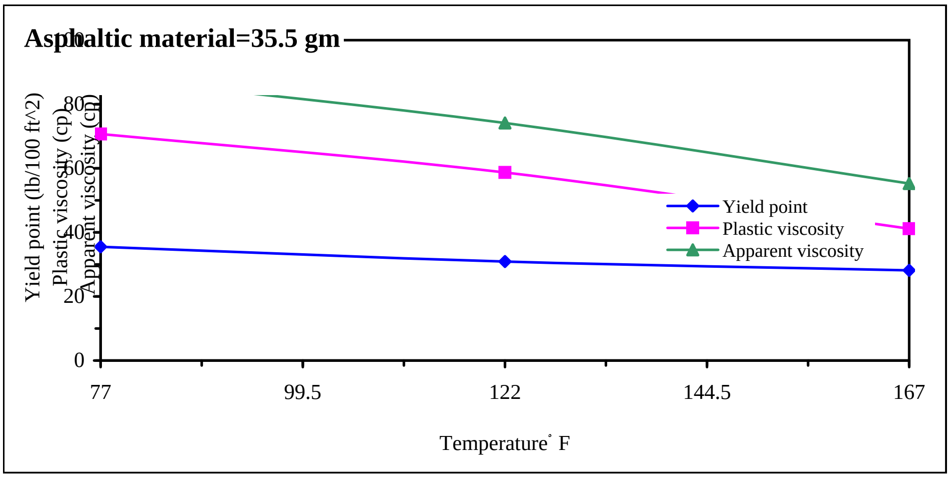
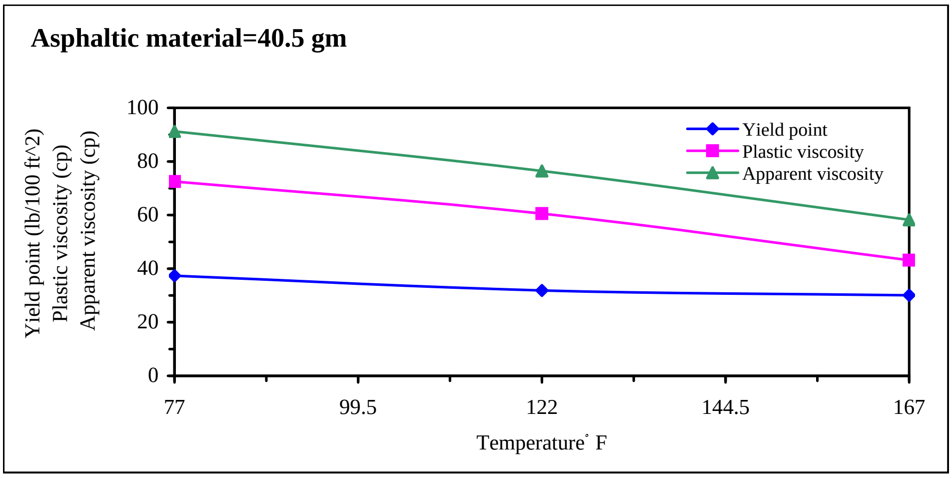


Figure (5.7) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 2.4) Vol. %





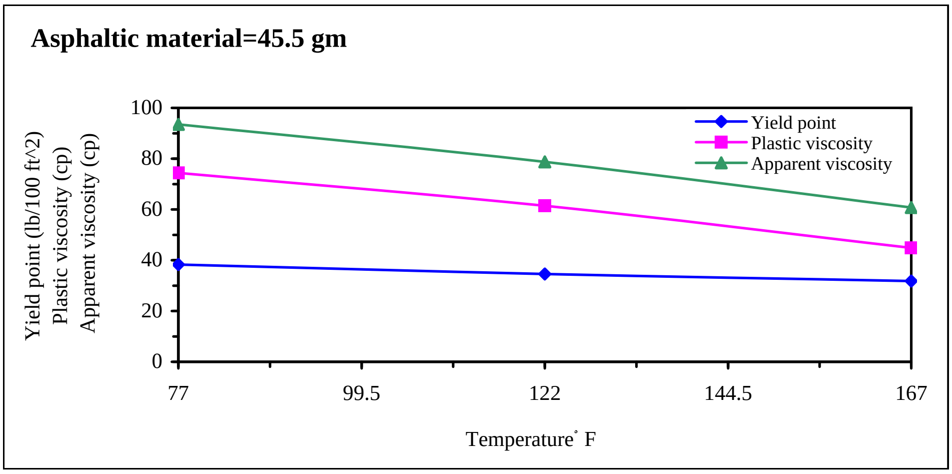
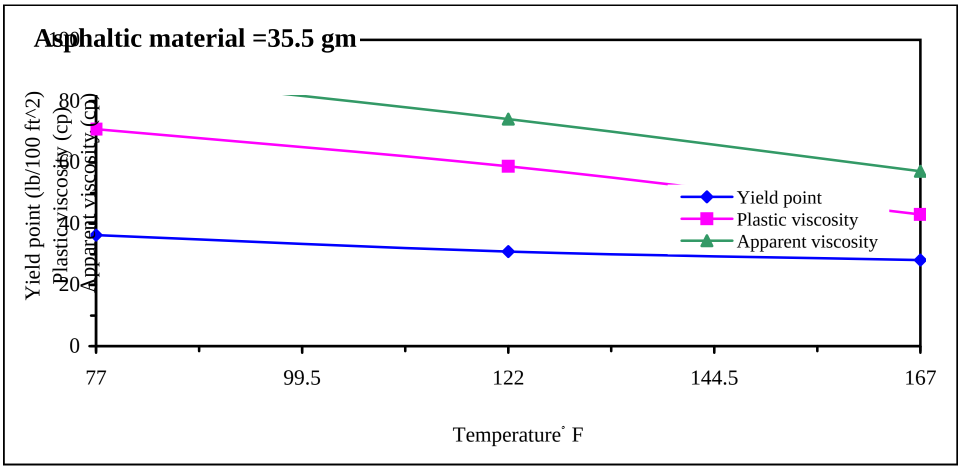
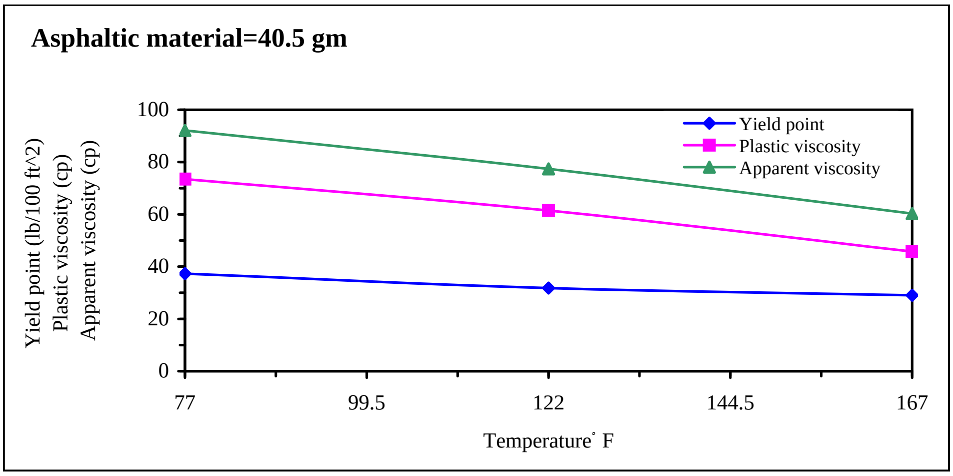


Figure (5.8) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 3.2) Vol. %





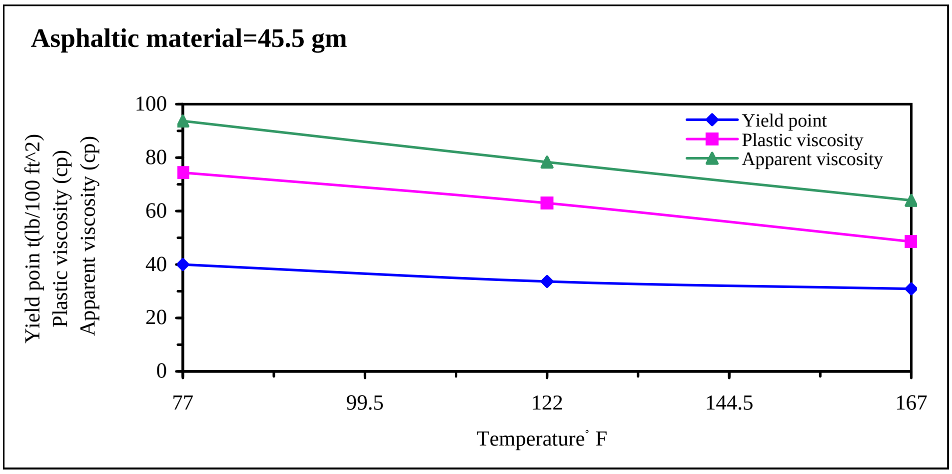


Figure (5.9) Effect of Temperature on Rheological properties of Emulsions with (Barite = 0.84 , Emulsifier = 4) Vol. %

5.3. Effect of Asphaltic material on Rheological properties of Emulsions

The effect of asphaltic material on rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions under different temperatures are clearly shown in figures (5.10) to (5.18). The values of yield point of these emulsions are plotted versus the weight of asphaltic material and presented in figures (5.10) to (5.12), also the values of plastic viscosity of these emulsions are plotted versus the weight of asphaltic material and presented in figures (5.13) to (5.15) and the apparent viscosities of emulsions are plotted versus the weight of asphaltic material and presented in figures (5.16) to (5.18).

The emulsions prepared were in satisfactory conditions at temperatures up 167 °F with 35.5 gm asphaltic material, it was decided to increase the concentration of asphaltic material to 40.5 and 45.5 gm, with three different volumes percentage of barite to demonstrate its effect on rheological properties of emulsion with temperature.

From these Figures, one can notice that the increase in weight of asphaltic material tends to increase the yield point, plastic viscosity and apparent viscosity, the increase in the weight of asphaltic material will result in a smaller size water droplet, fully emulsified. This lead to reduce the surface tension, and provide large surface area.

The emulsified water droplets act as solid in the emulsion as stated before, therefore it will result in further increasing in friction and attraction forces between the solid particles in emulsion samples. This will cause increasing the plastic viscosity, yield point and apparent viscosity of the emulsions.

The increase in the attraction forces is more obvious even at high temperatures which increase the yield point to a certain limit.

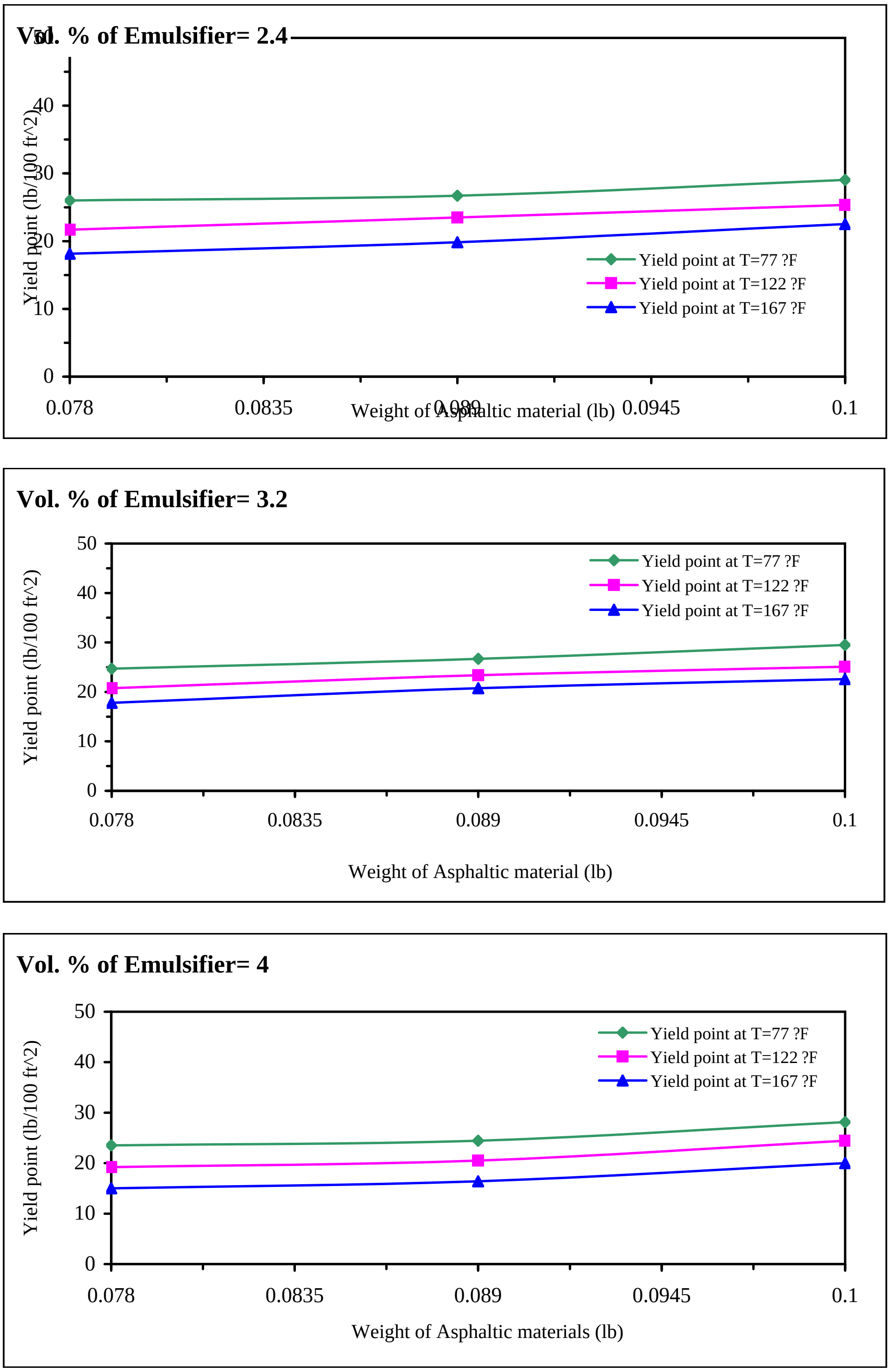
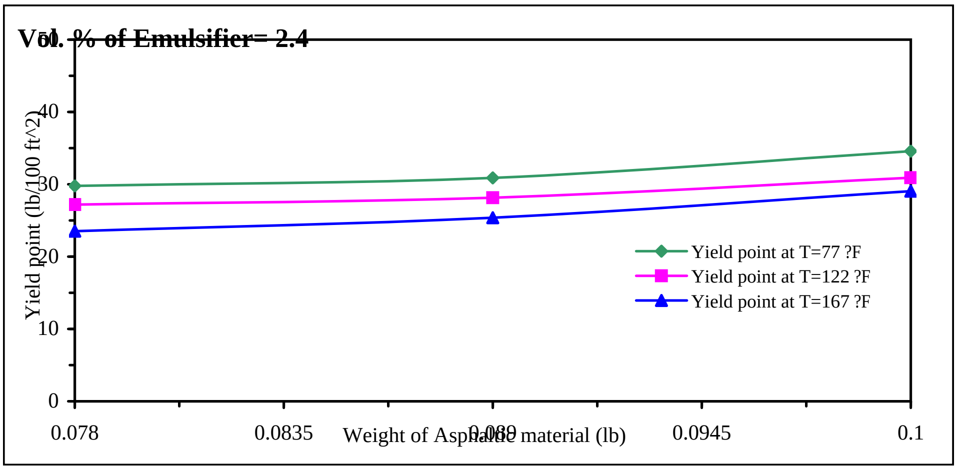
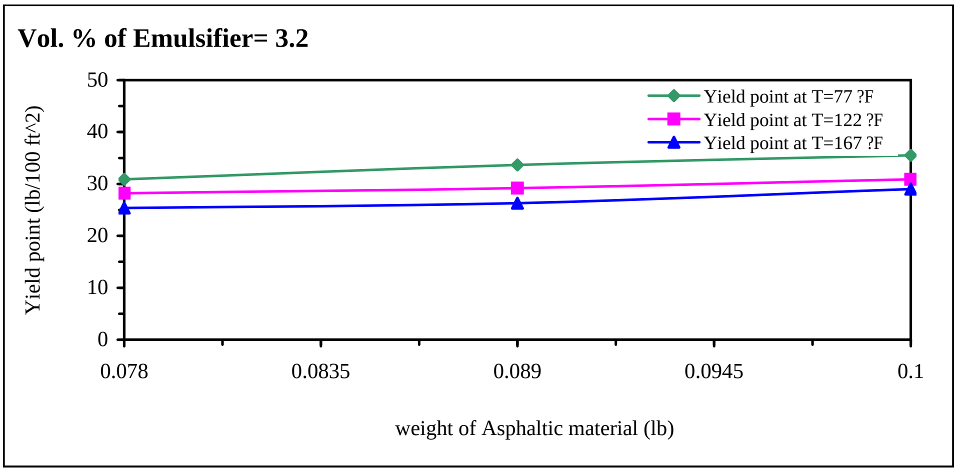


Figure (5.10) Effect of concentration of Asphaltic material on Yield point of Emulsions with Barite = 0.46 Vol. %





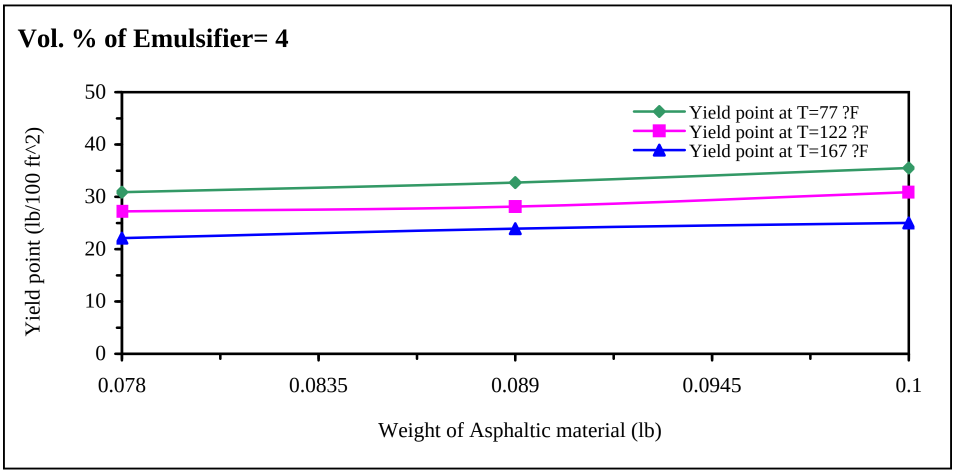
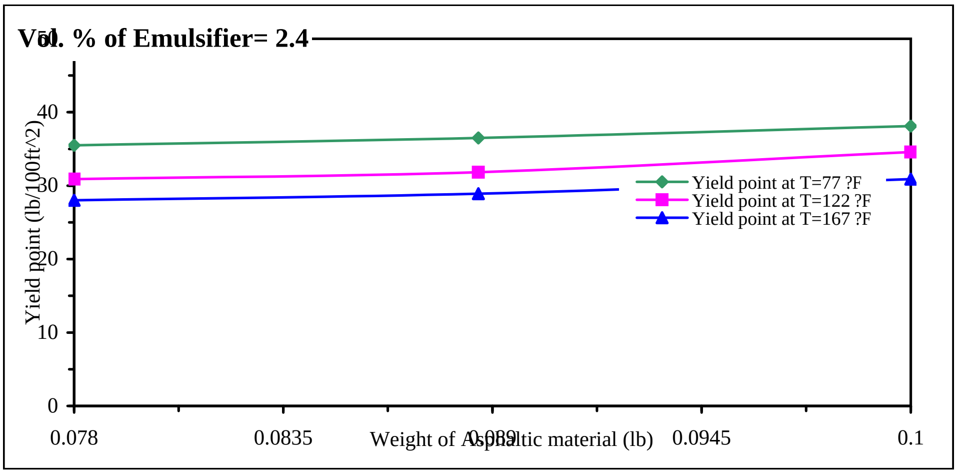
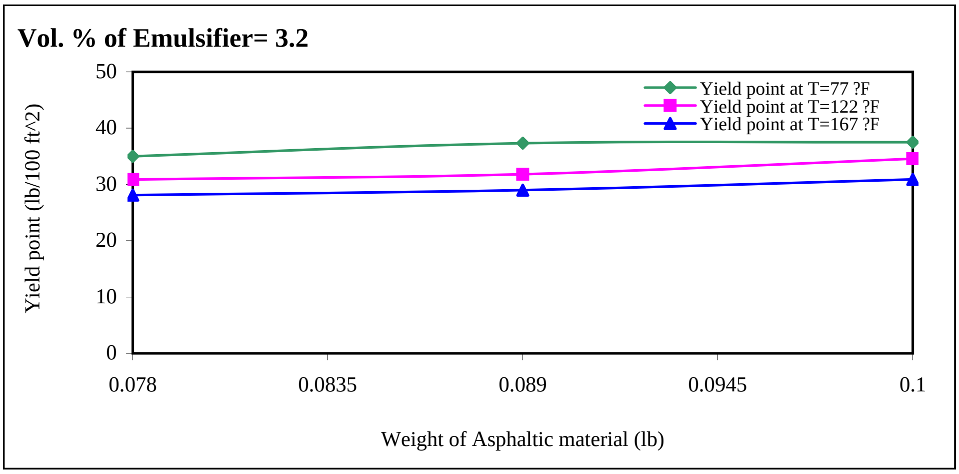


Figure (5.11) Effect of concentration of Asphaltic material on Yield point of Emulsions with Barite = 0.65 Vol. %





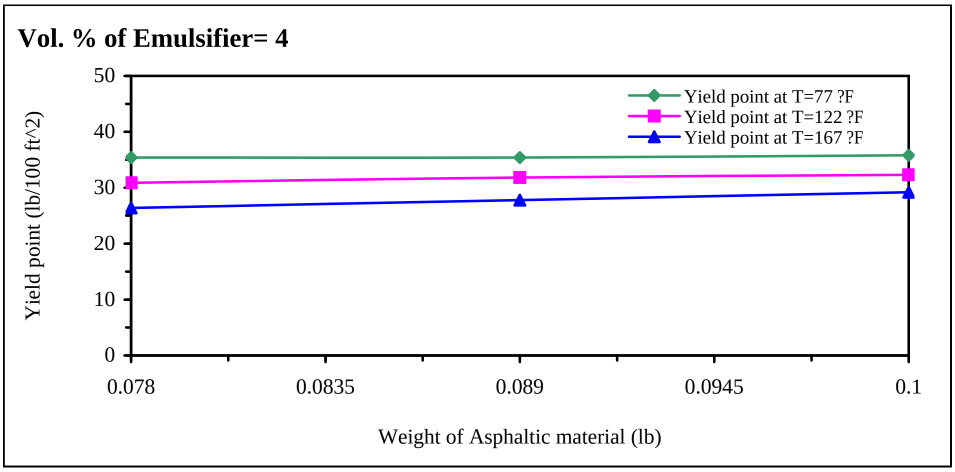
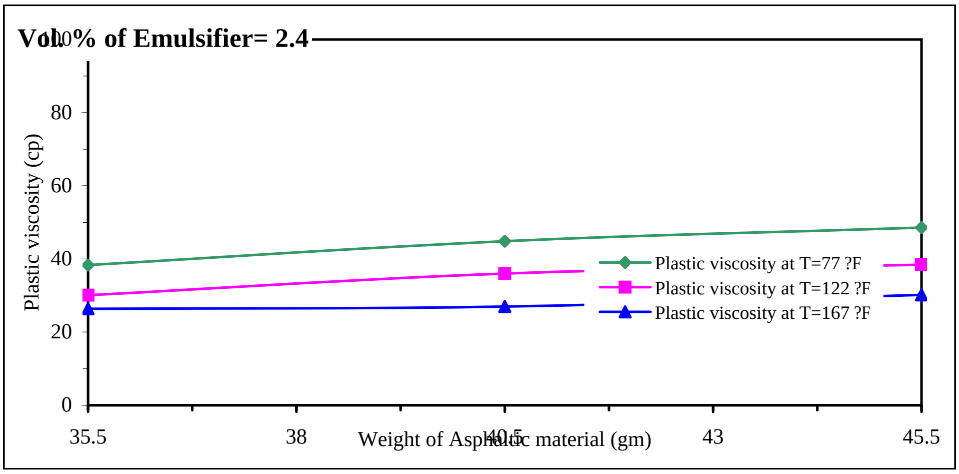
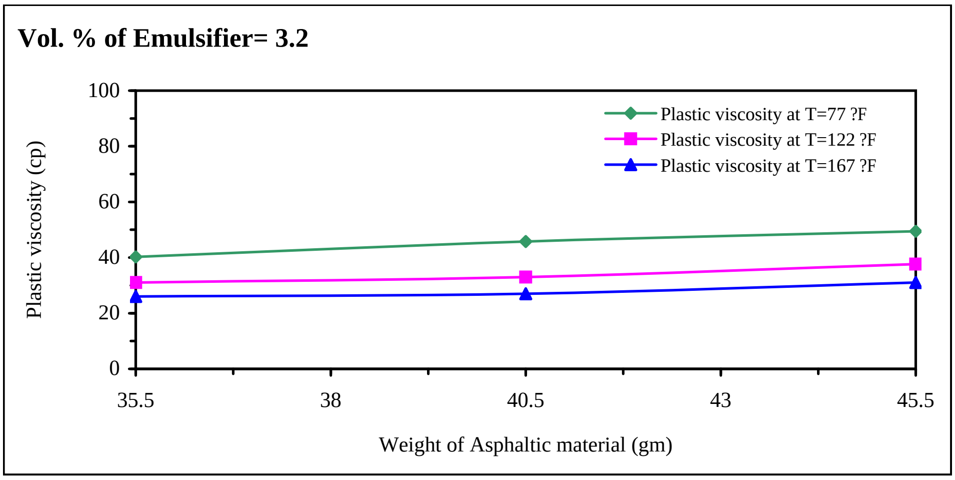


Figure (5.12) Effect of concentration of Asphaltic material on Yield point of Emulsions with Barite = 0.84 Vol. %





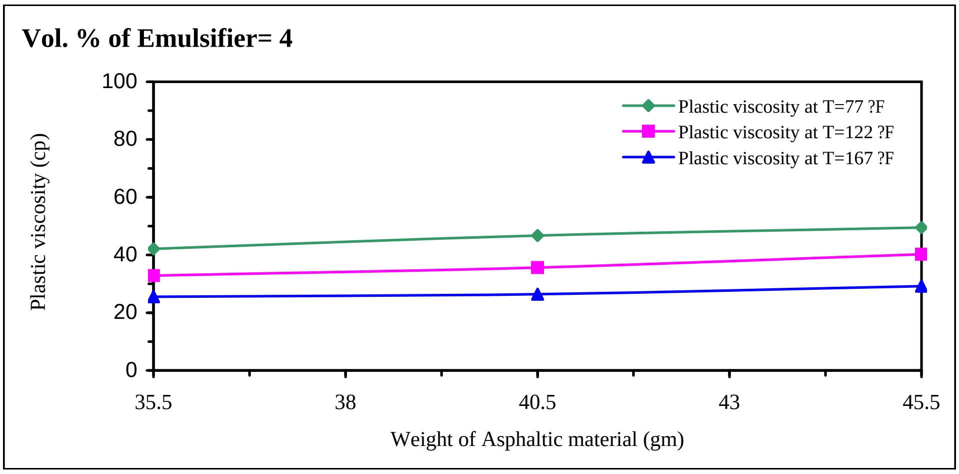
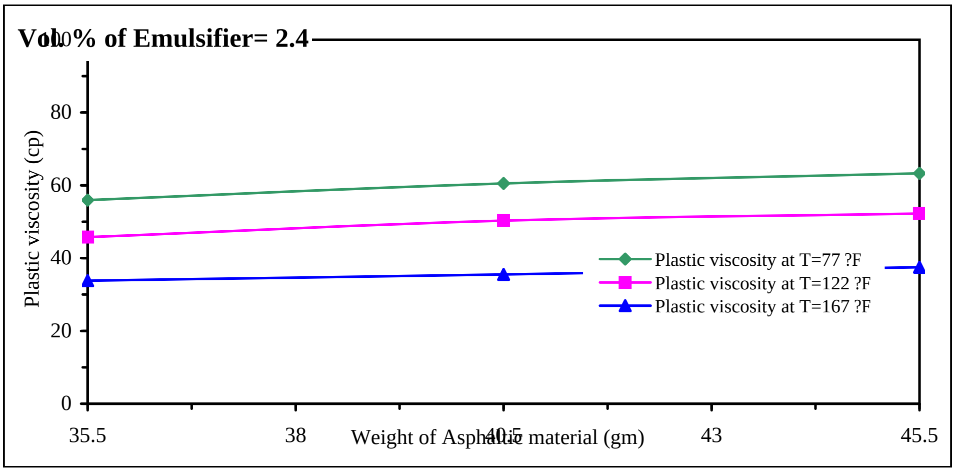
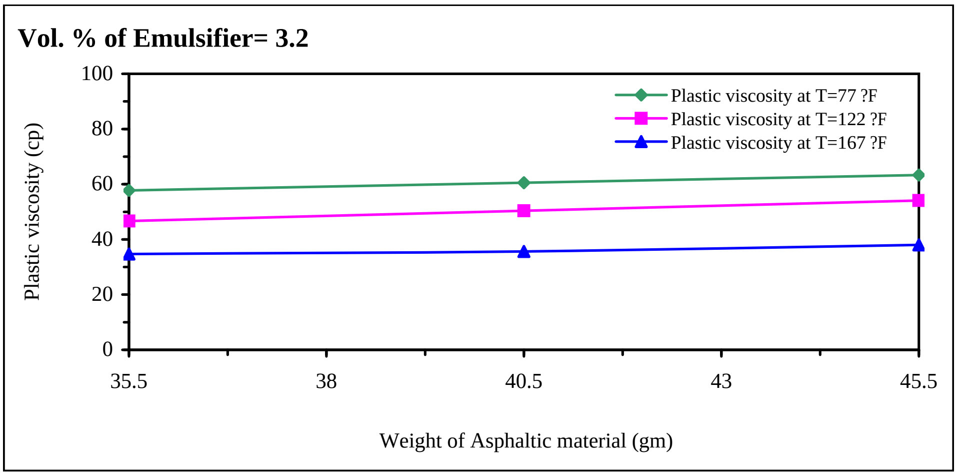


Figure (5.13) Effect of concentration of Aphaltic material on Plastic viscosity of Emulsions with Barite = 0.46 Vol. %





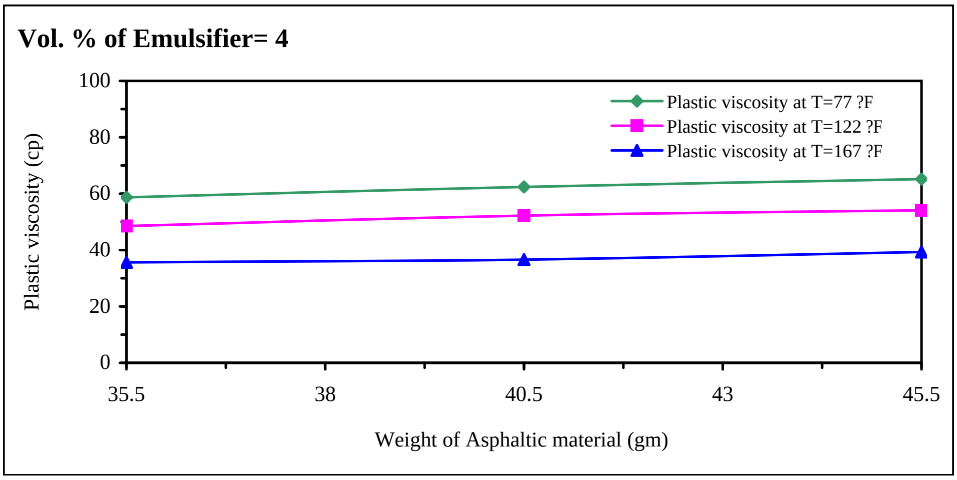
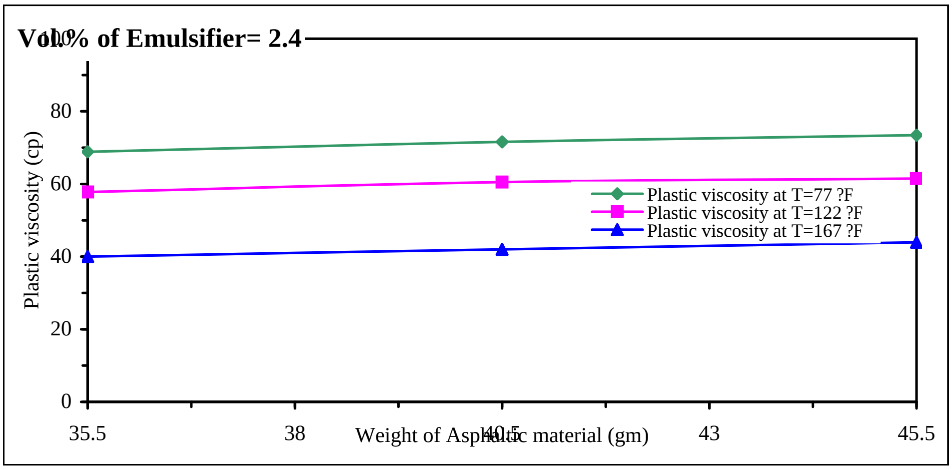
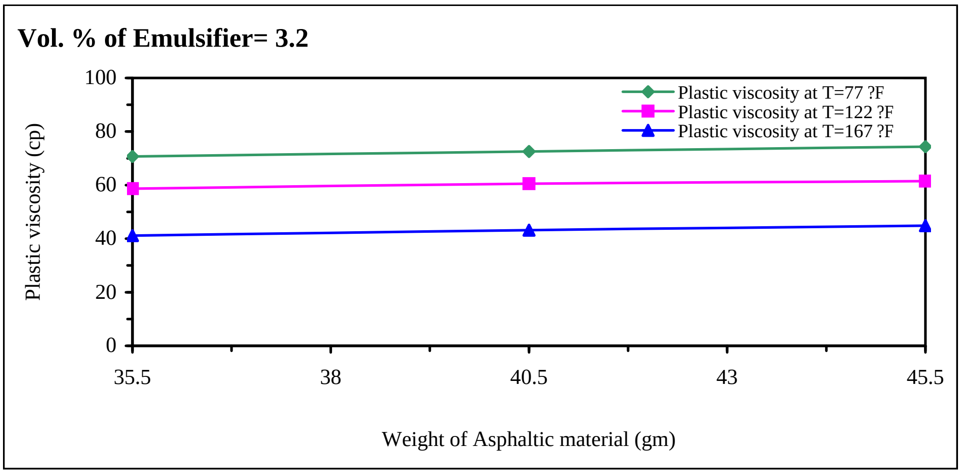


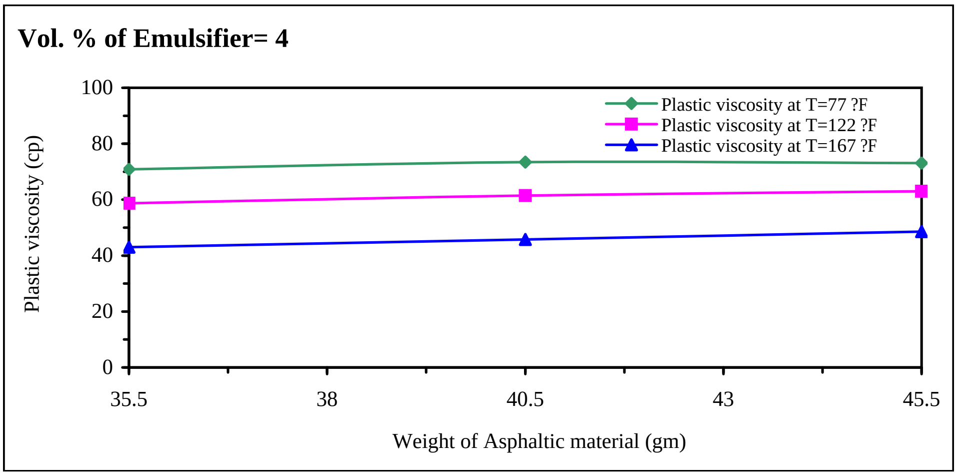
Figure (5.14) Effect of concentration of Asphaltic material on Plastic viscosity of Emulsions with Barite = 0.65 Vol. %



Vol. % of Emulsifier= 2.4

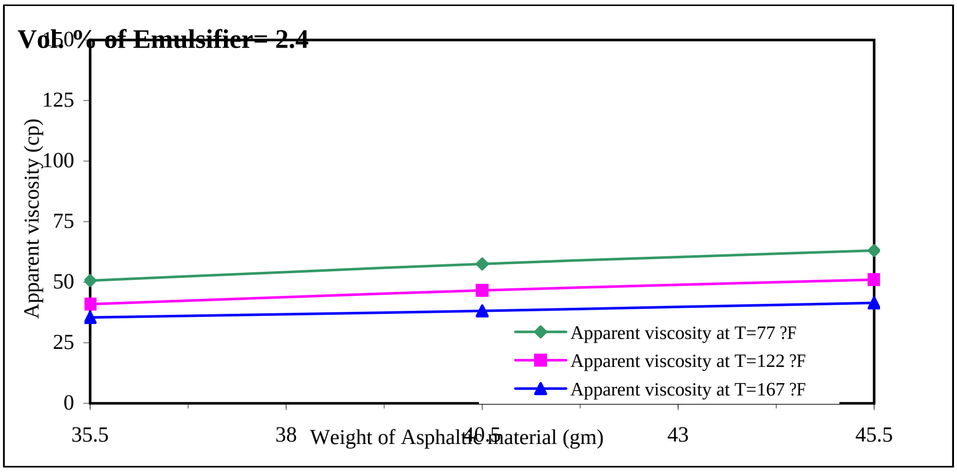


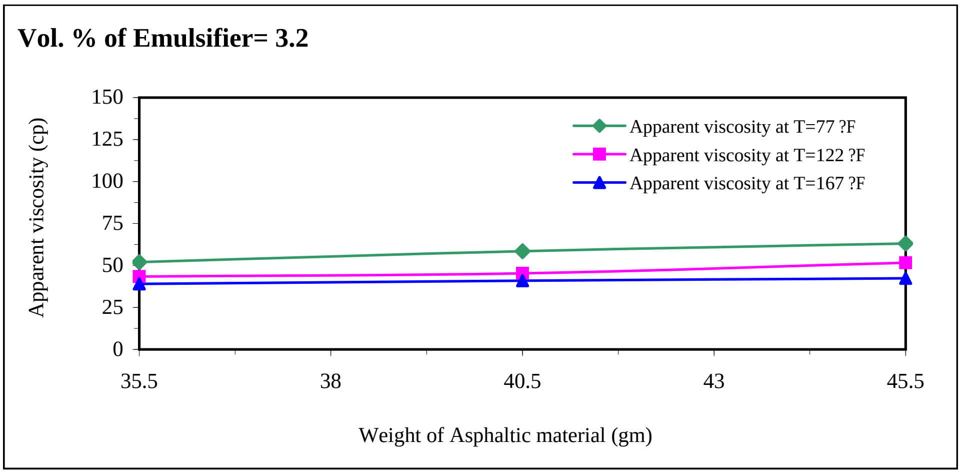
Vol. % of Emulsifier= 3.2



Vol. % of Emulsifier= 4

Figure (5.15) Effect of concentration of Asphaltic material on Plastic viscosity of Emulsions with Barite = 0.84 Vol. %





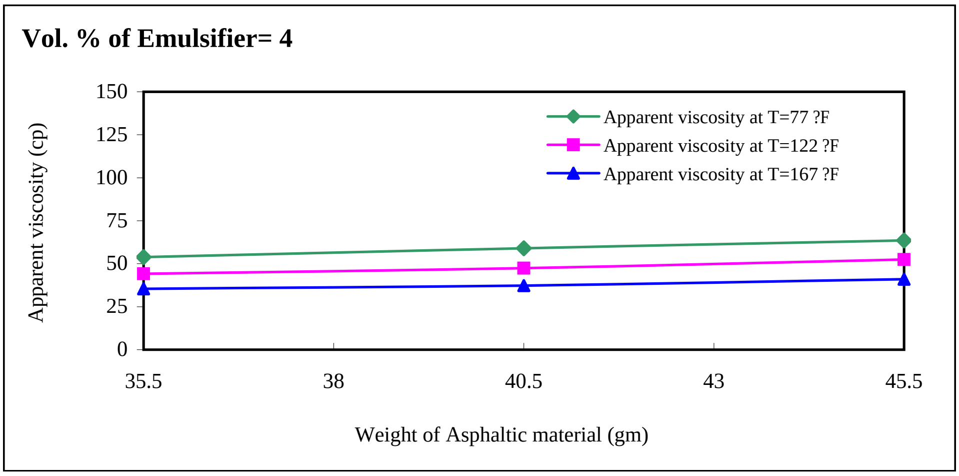


Figure (5.16) Effect of concentration of Asphaltic material on Apparent viscosity of Emulsions with Barite = 0.46 Vol. %

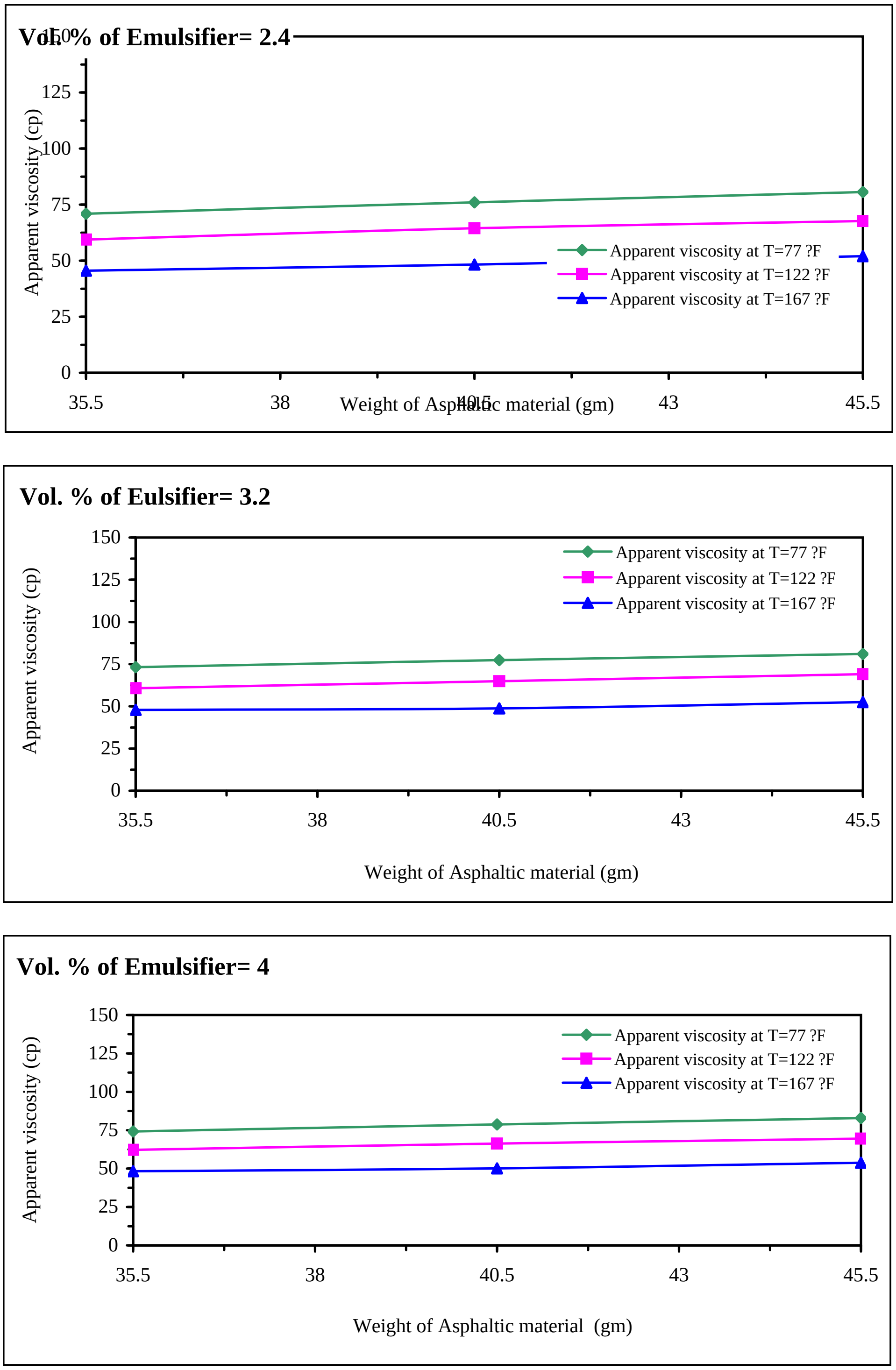


Figure (5.17) Effect of concentration of Asphaltic material on Apparent viscosity of Emulsions with Barite = 0.65 Vol. %

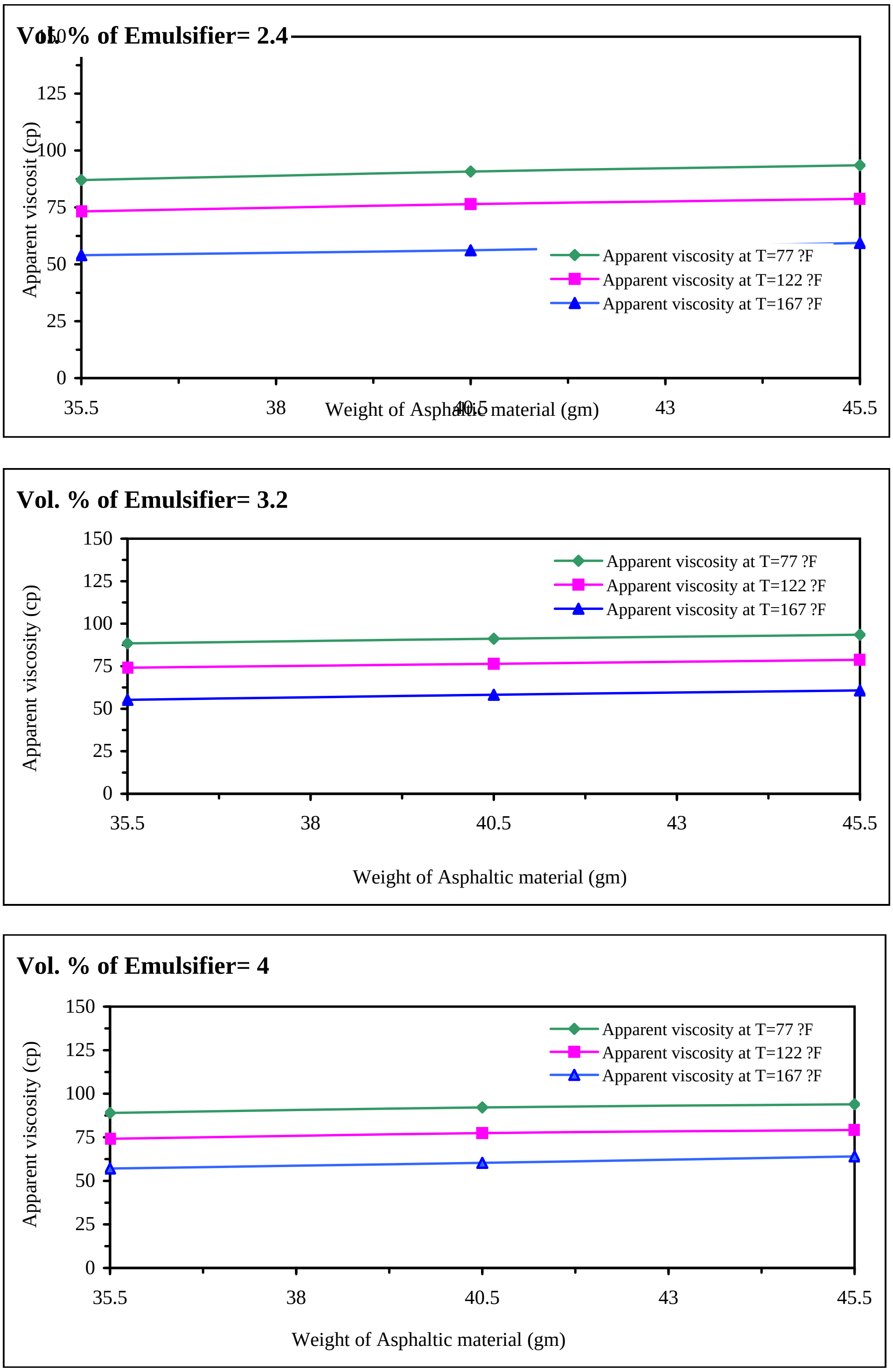


Figure (5.18) Effect of concentration of Asphaltic material on Apparent viscosity of Emulsions with Barite = 0.84 Vol. %

5.4 Effect of Barite on Rheological properties of Emulsions

The effects of barite on rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions are clearly shown in figures (5.19) to (5.27). The values of yield point of these emulsions are plotted versus the vol. % of barite and presented in figures (5.19) to (5.21), also the values of plastic viscosity of emulsions are plotted versus the vol. % of barite and presented in figures (5.22) to (5.24) and the apparent viscosity of emulsions are plotted versus the vol. % of barite and presented in figures (5.25) to (5.27).

From these figures, one can notice that the increase in the volume percentage of barite tends to increase the yield point, plastic viscosity and apparent viscosity due to the increasing in solid content. The addition of solid material will increase friction and attraction forces between the solid particles, so according to that, will result in an increase in yield point, plastic viscosity and apparent viscosity.

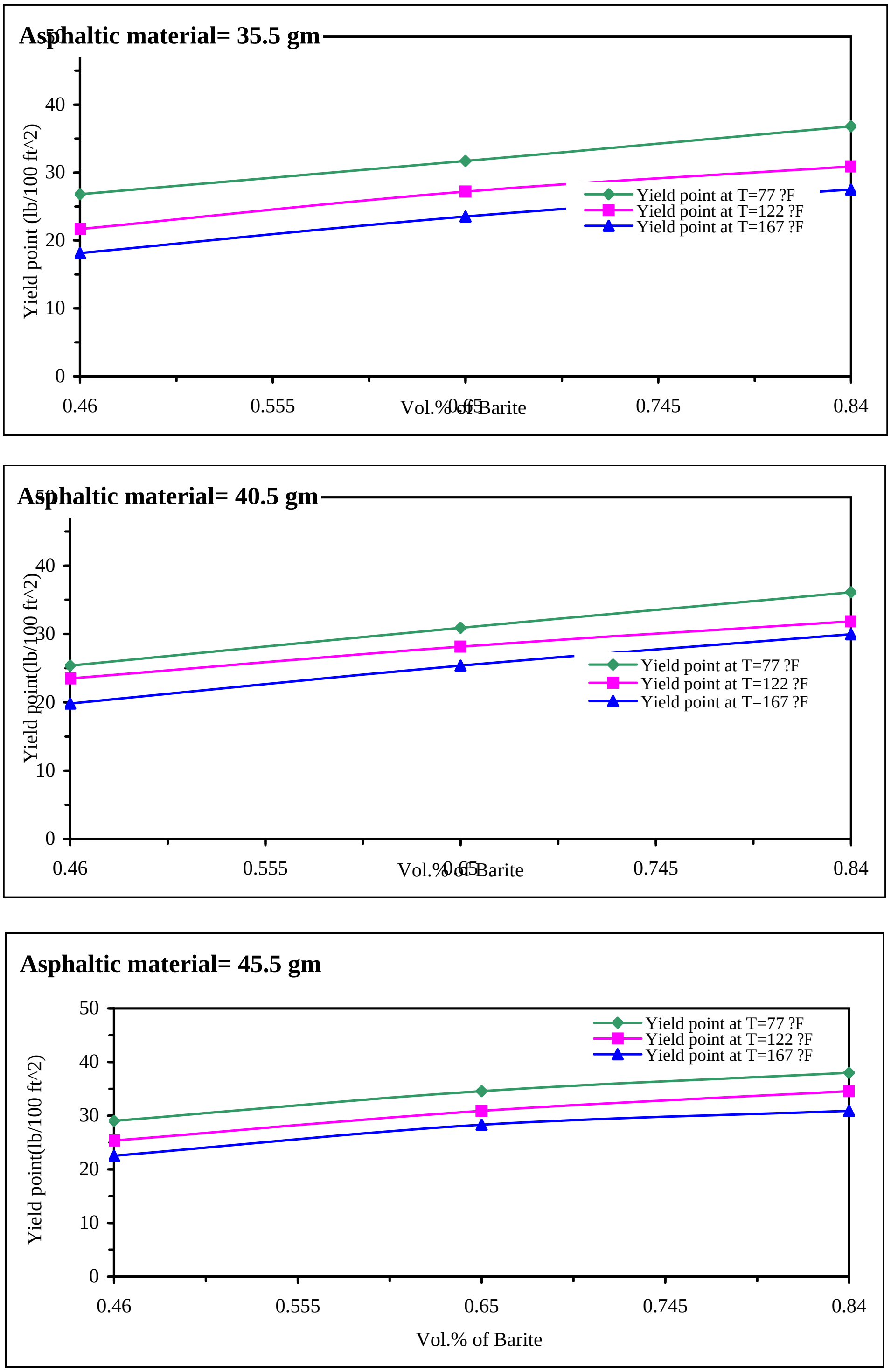
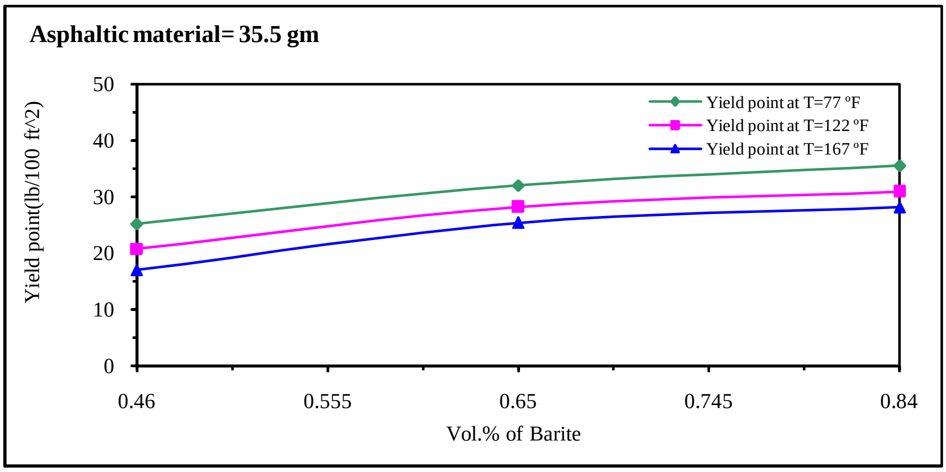
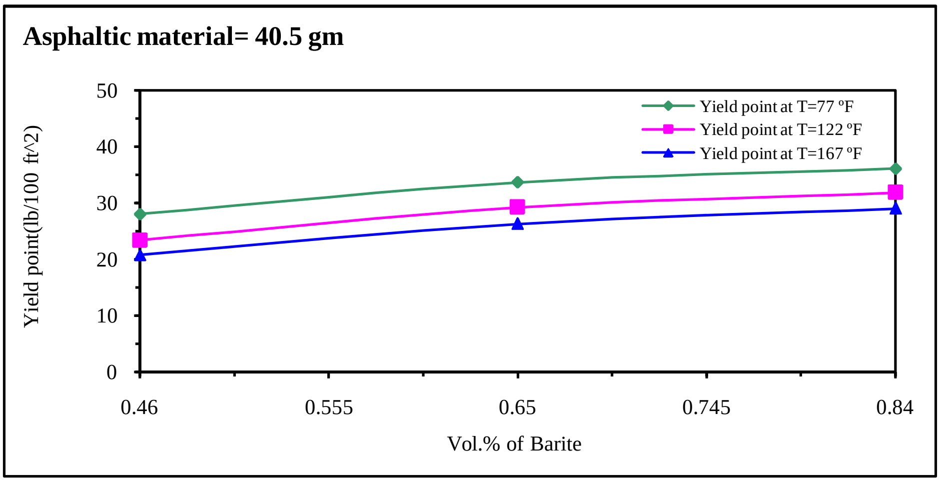


Figure (5.19) Effect of Vol. % of Barite on Yield point of Emulsions with Emulsifier = 2.4 Vol. %





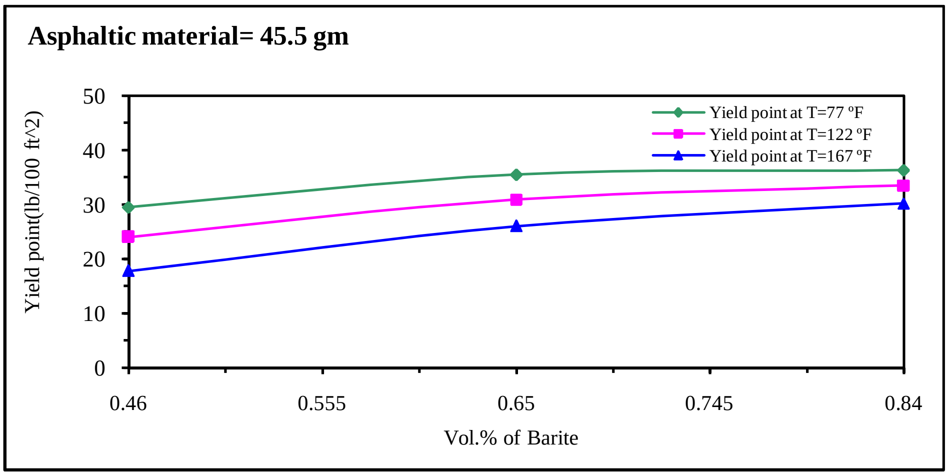
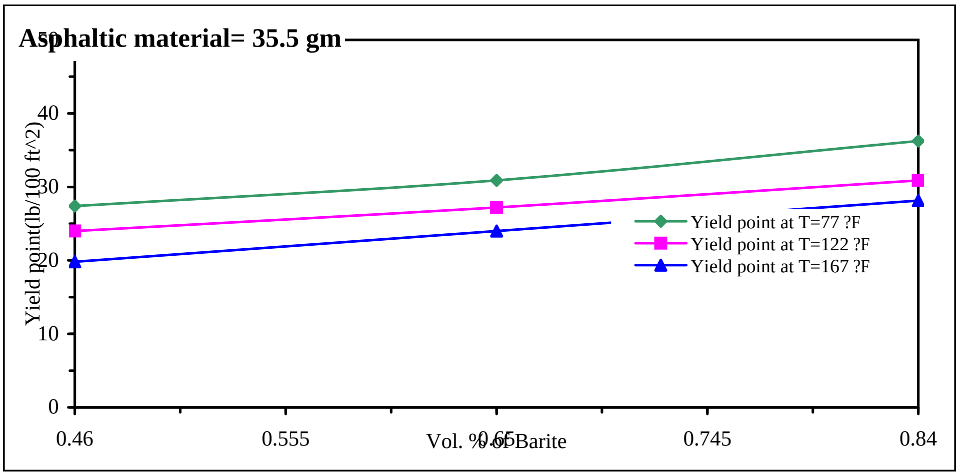
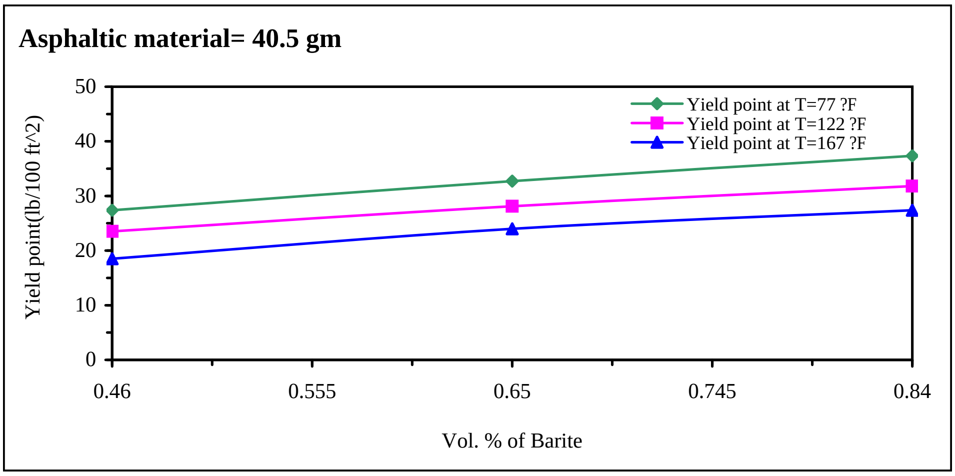


Figure (5.20) Effect of Vol. % of Barite on Yield point of Emulsions with Emulsifier = 3.2 Vol. %





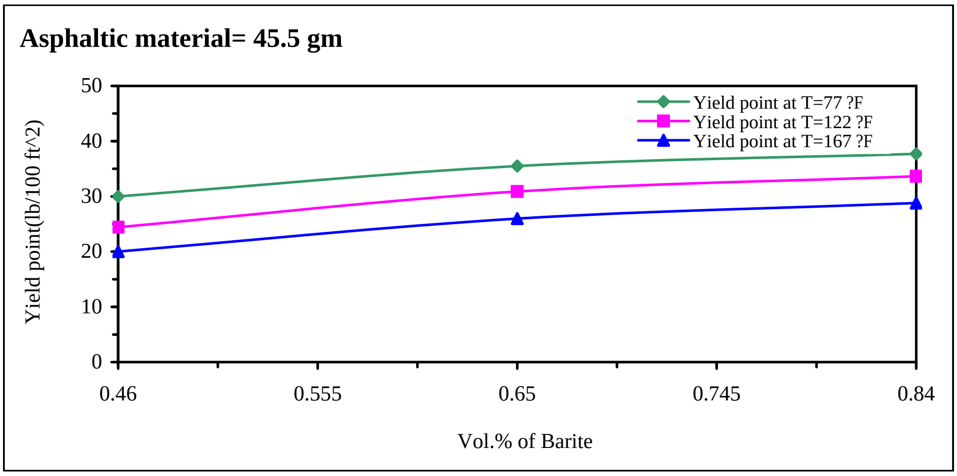


Figure (5.21) Effect of Vol. % of Barite on Yield point of Emulsions with Emulsifier = 4 Vol. %

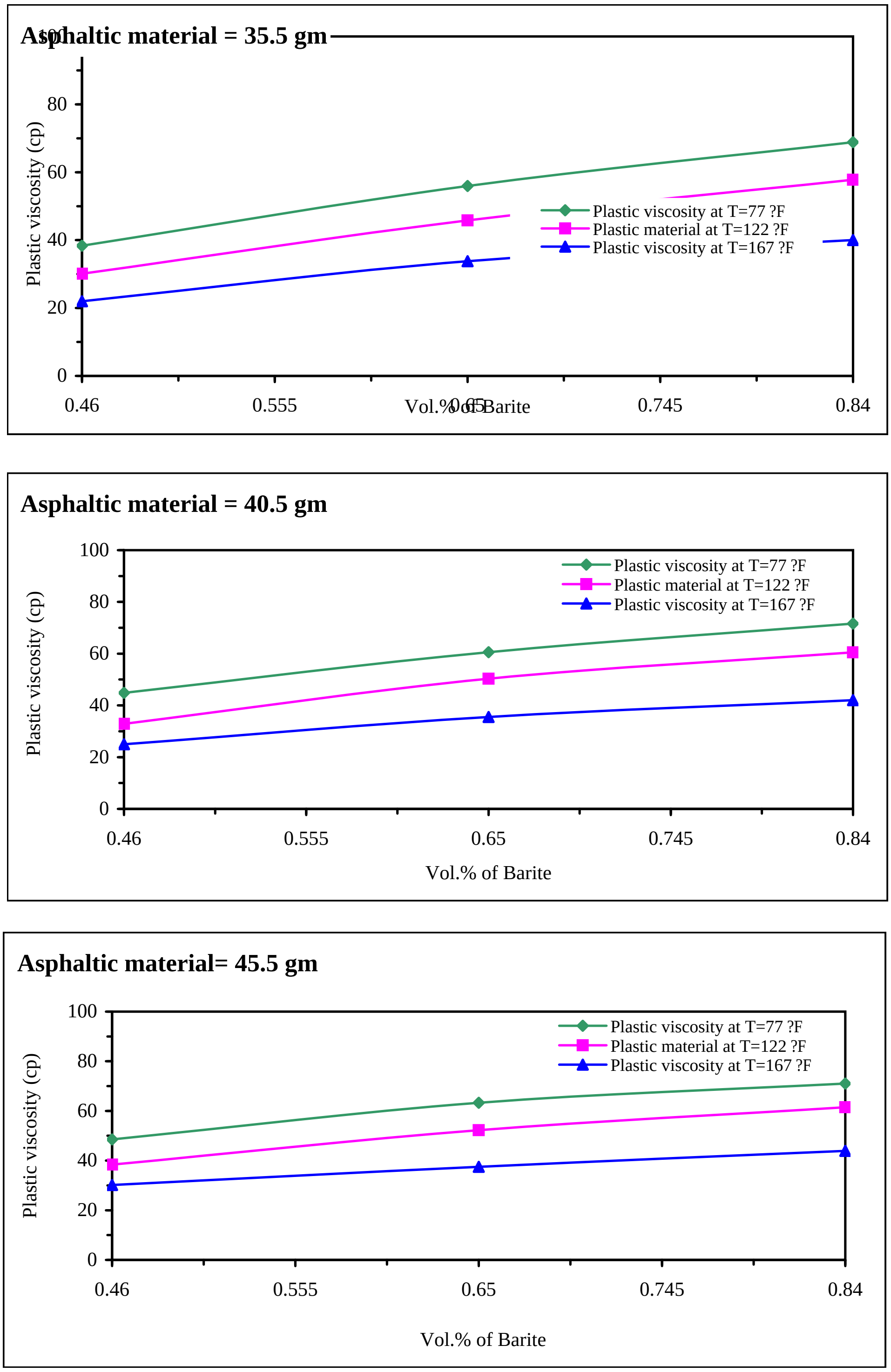


Figure (5.22) Effect of Vol. % of Barite on Plastic viscosity of Emulsions with Emulsifier = 2.4 Vol. %

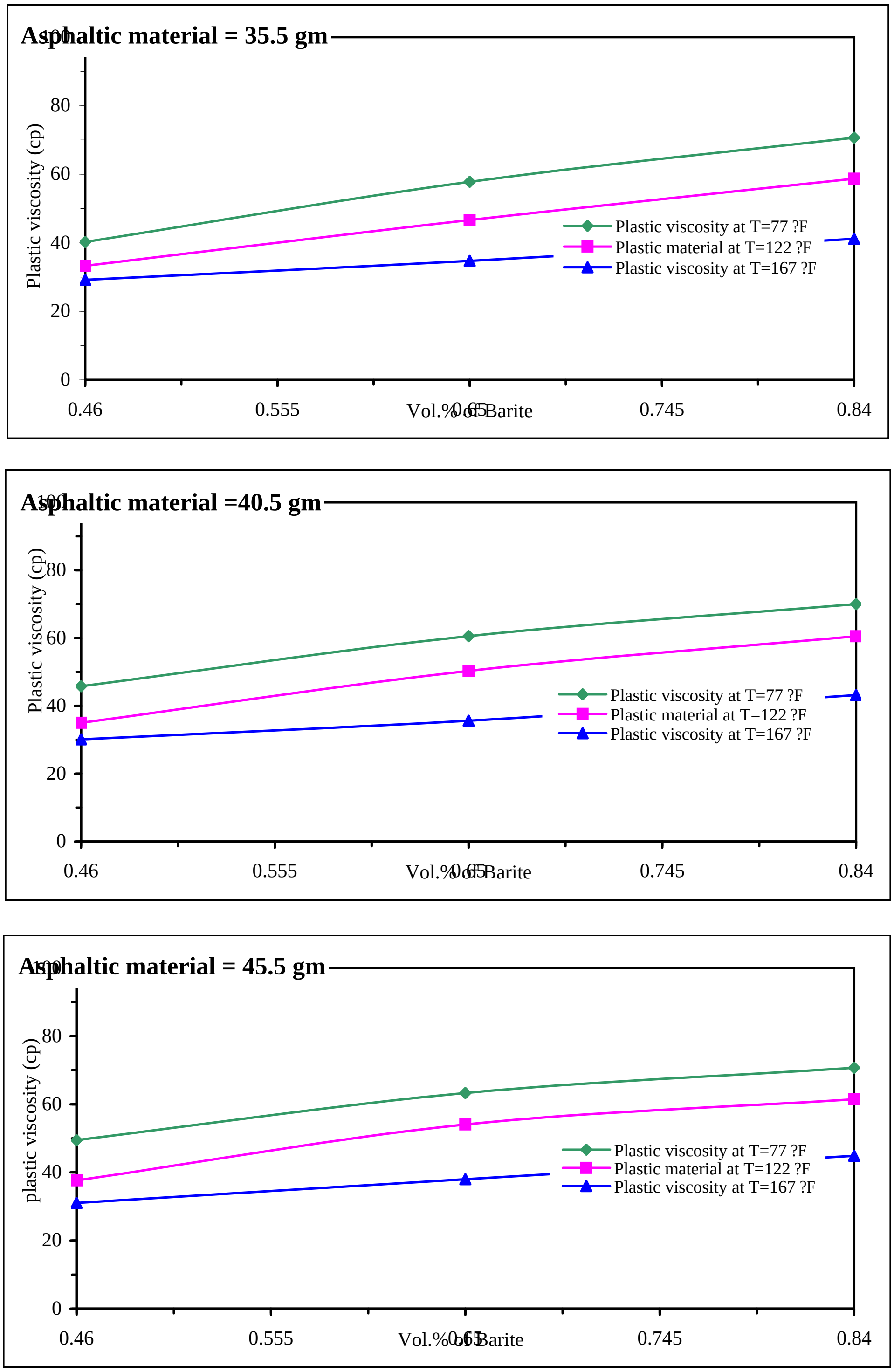
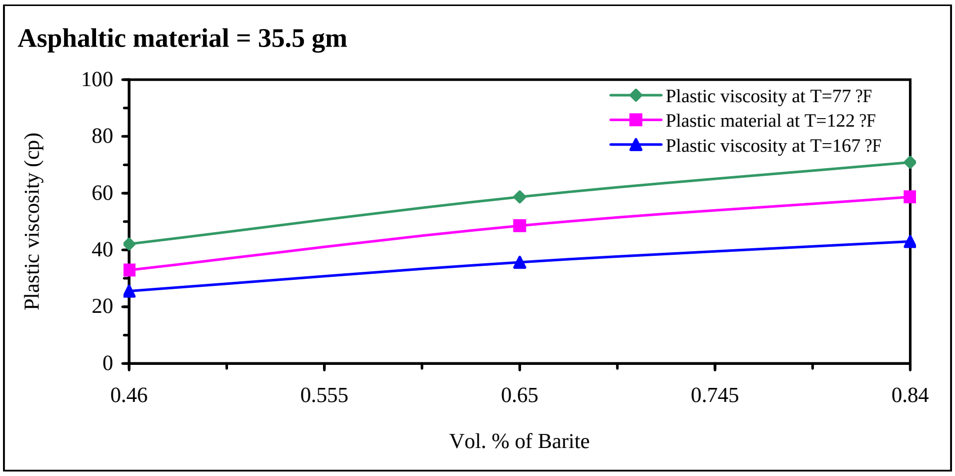
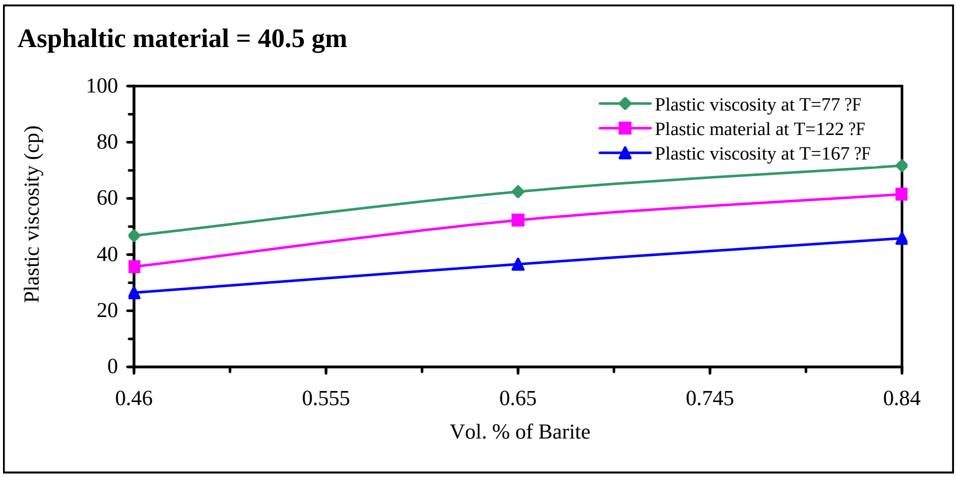


Figure (5.23) Effect of Vol. % of Barite on Plastic viscosity of Emulsions with Emulsifier = 3.2 Vol. %


Asphaltic material = 35.5 gm


Asphaltic material = 40.5 gm

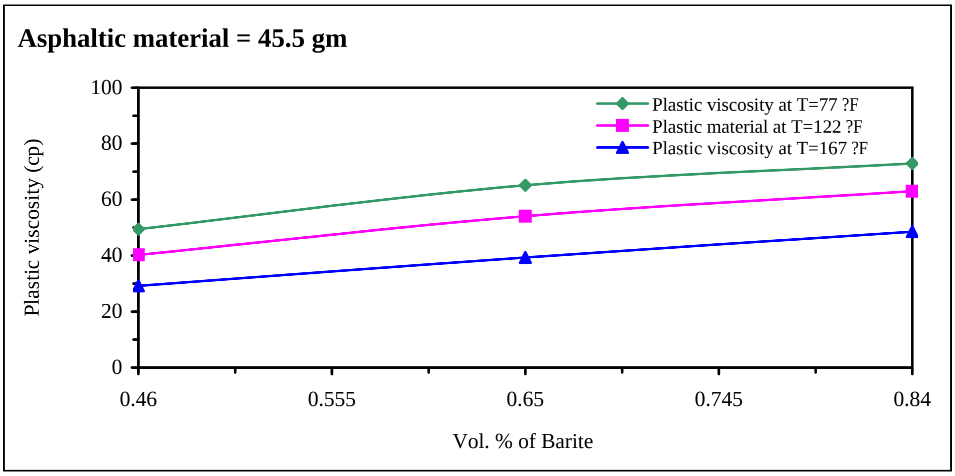
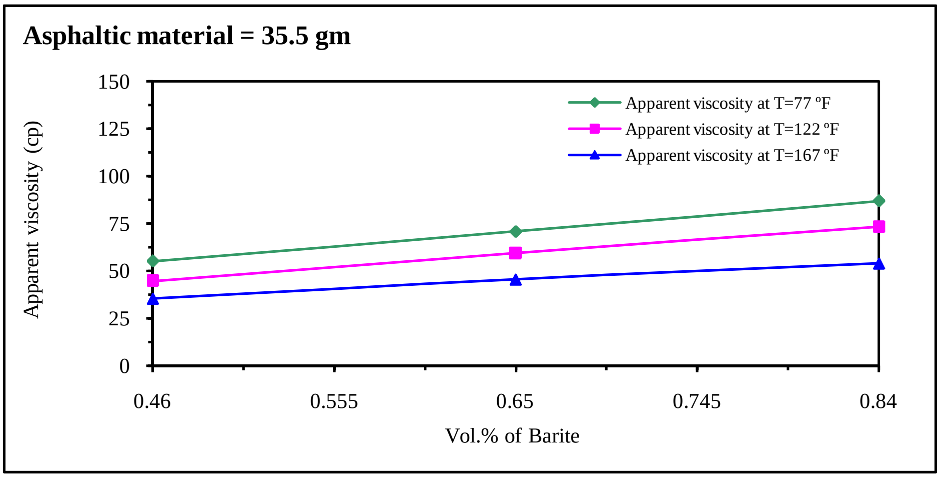
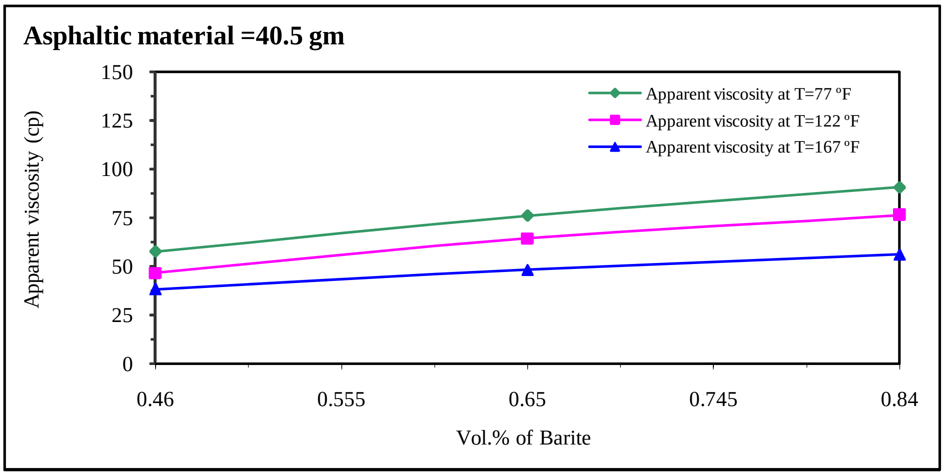

Asphaltic material = 45.5 gm

Figure (5.24) Effect of Vol. % of Barite on Plastic viscosity of Emulsions with Emulsifier = 4 Vol. %





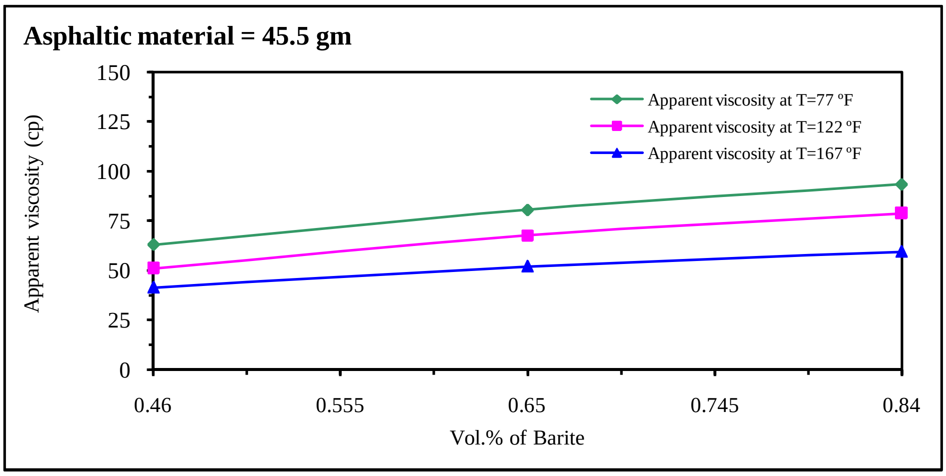


Figure (5.25) Effect of Vol. % of Barite on Apparent viscosity of Emulsions with Emulsifier = 2.4 Vol. %

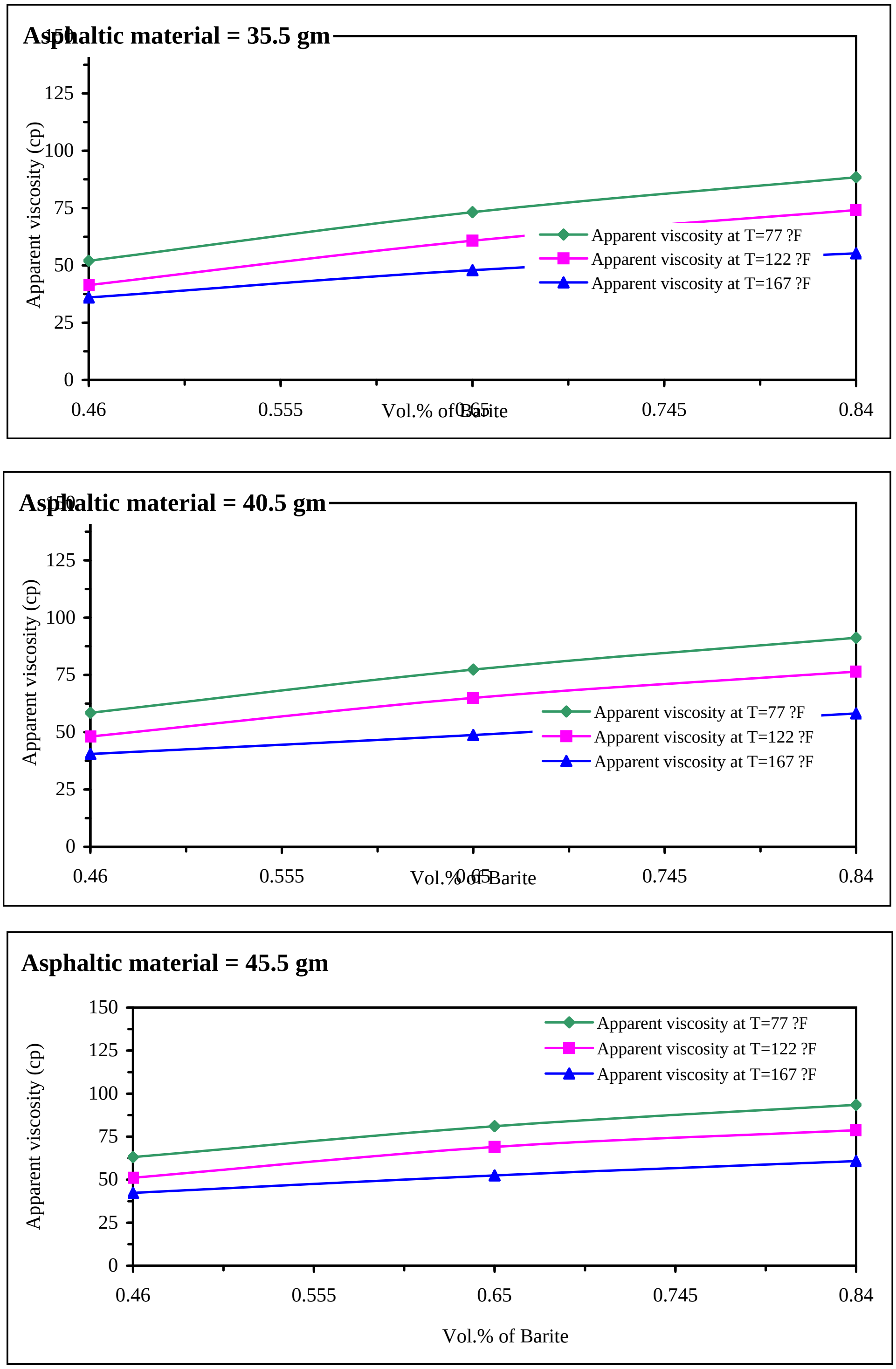


Figure (5.26) Effect of Vol. % of Barite on Apparent viscosity of Emulsions with Emulsifier = 3.2 Vol. %

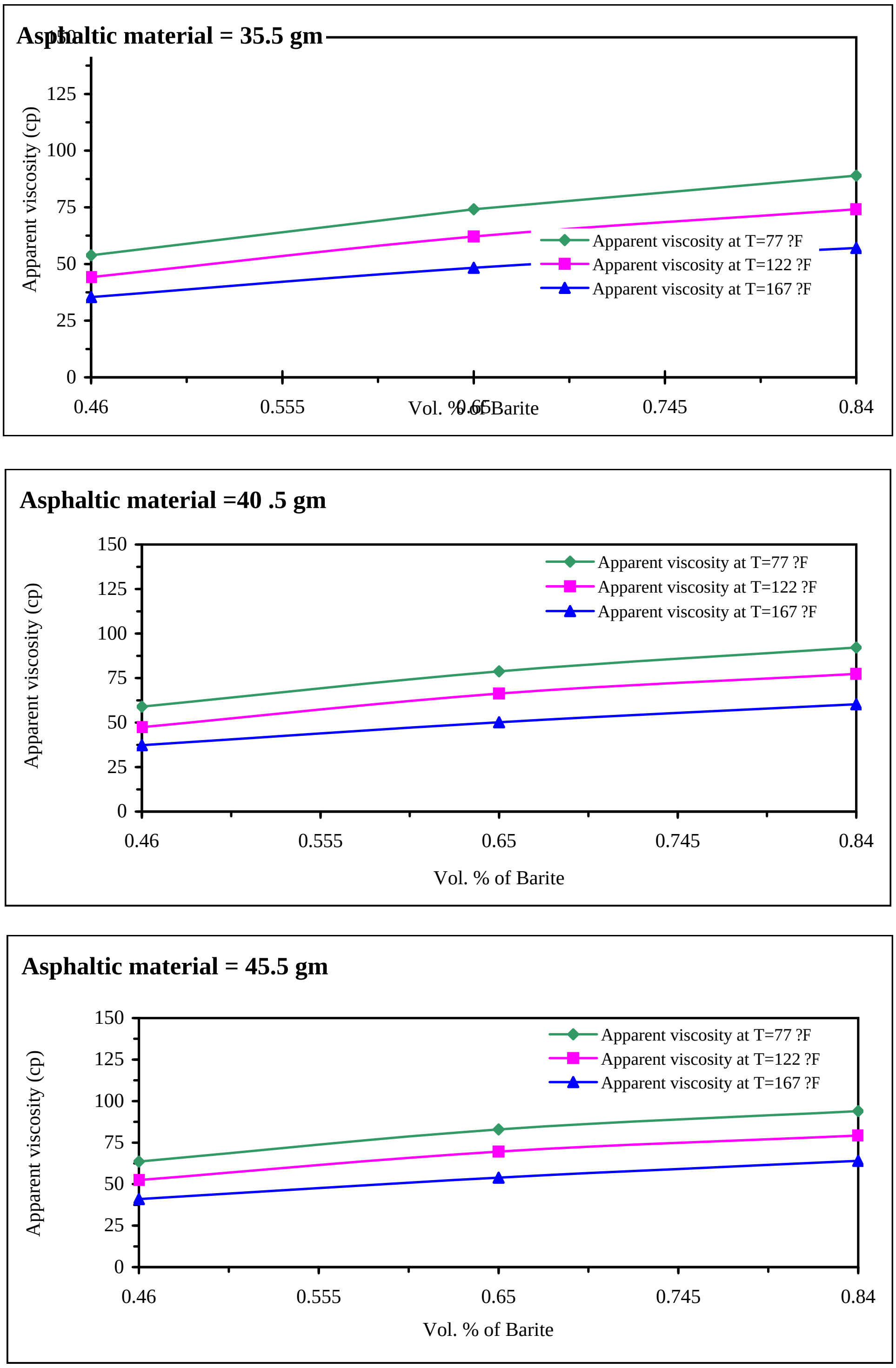


Figure (5.27) Effect of Vol. % of Barite on Apparent viscosity of Emulsions with Emulsifier = 4 Vol. %

5.5 Effect of Emulsifier on Rheological properties of Emulsions

The effects of emulsifier on rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions under different temperatures are clearly shown in figures (5.28) to (5.36). The values of yield point of these emulsion are plotted versus the vol. % of emulsifier and presented in figures (5.28) to (5.30), also the values of plastic viscosity of emulsions are plotted versus the vol. % of emulsifier and presented in figures (5.31) to (5.33) and the apparent viscosity of emulsions are plotted versus the vol. % of emulsifier and presented in figures (5.34) to (5.36).

From these figures, firstly one can notice that at room temperature 25 °C (77 °F), the increase the volume percentage of emulsifier tends to increase the yield point, plastic viscosity and apparent viscosity because the emulsifier is effective by forming a mechanical barrier that surrounded water droplets and the emulsifier sufficient to coat all the water droplets.

Insufficient emulsifier concentration will result in a break down of emulsion with increasing temperature that will lead to a free water phase in the mud, which causes water-wetting of solid constituents in the emulsions, especially barite. Water-wetting of barite causes it to be settled, that will increase the rheological properties.

It was noticed that the increase in volume percentage of emulsifier has no appreciable effect on the values of plastic viscosity, yield point and apparent viscosity but it resulted in a stronger with better tolerance to temperature. This effect may be more pronounced for a large quantity of emulsifiers.

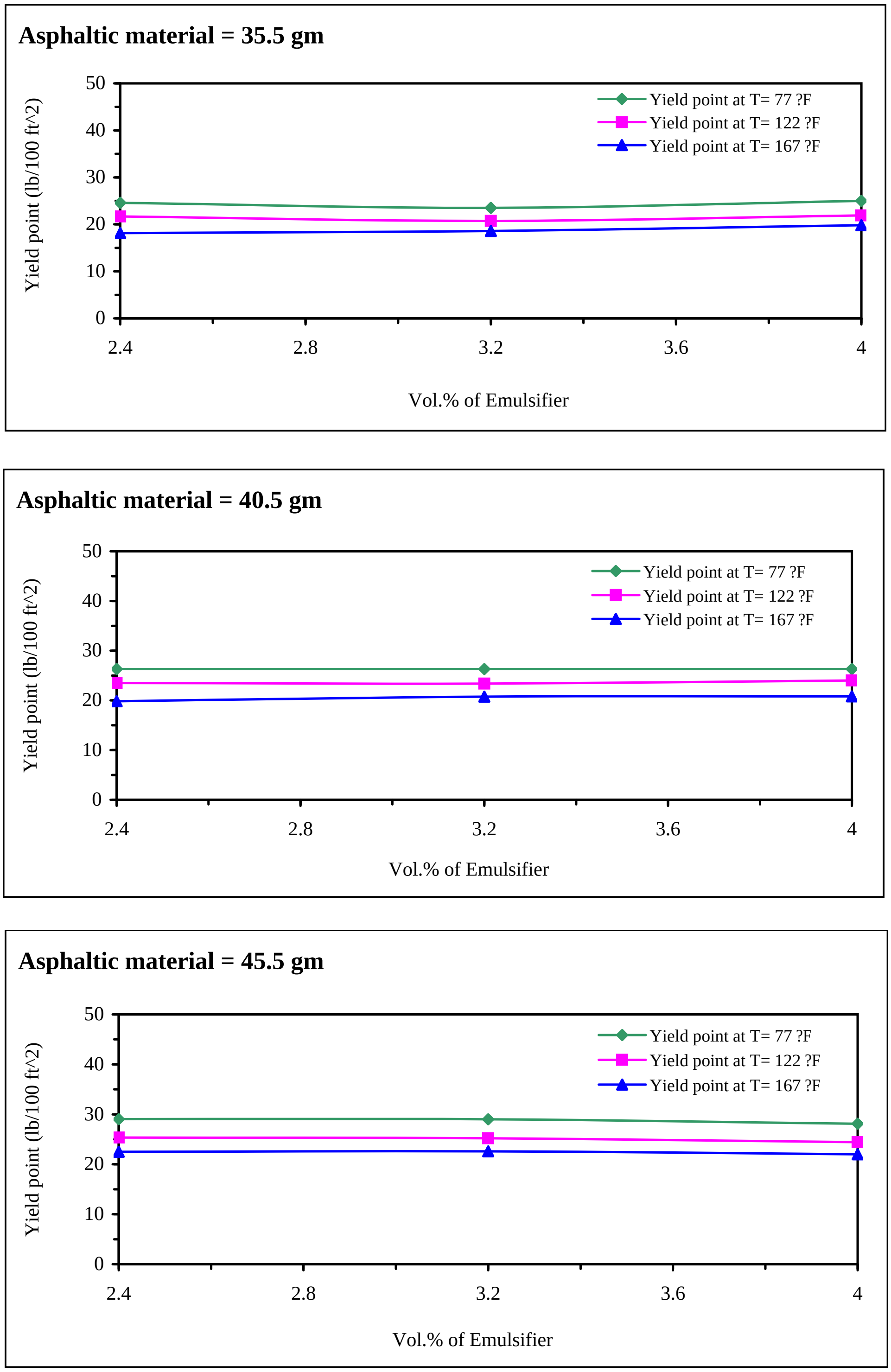


Figure (5.28) Effect of Vol. % of Emulsifier on Yield point of Emulsions with Barite = 0.46 Vol. %

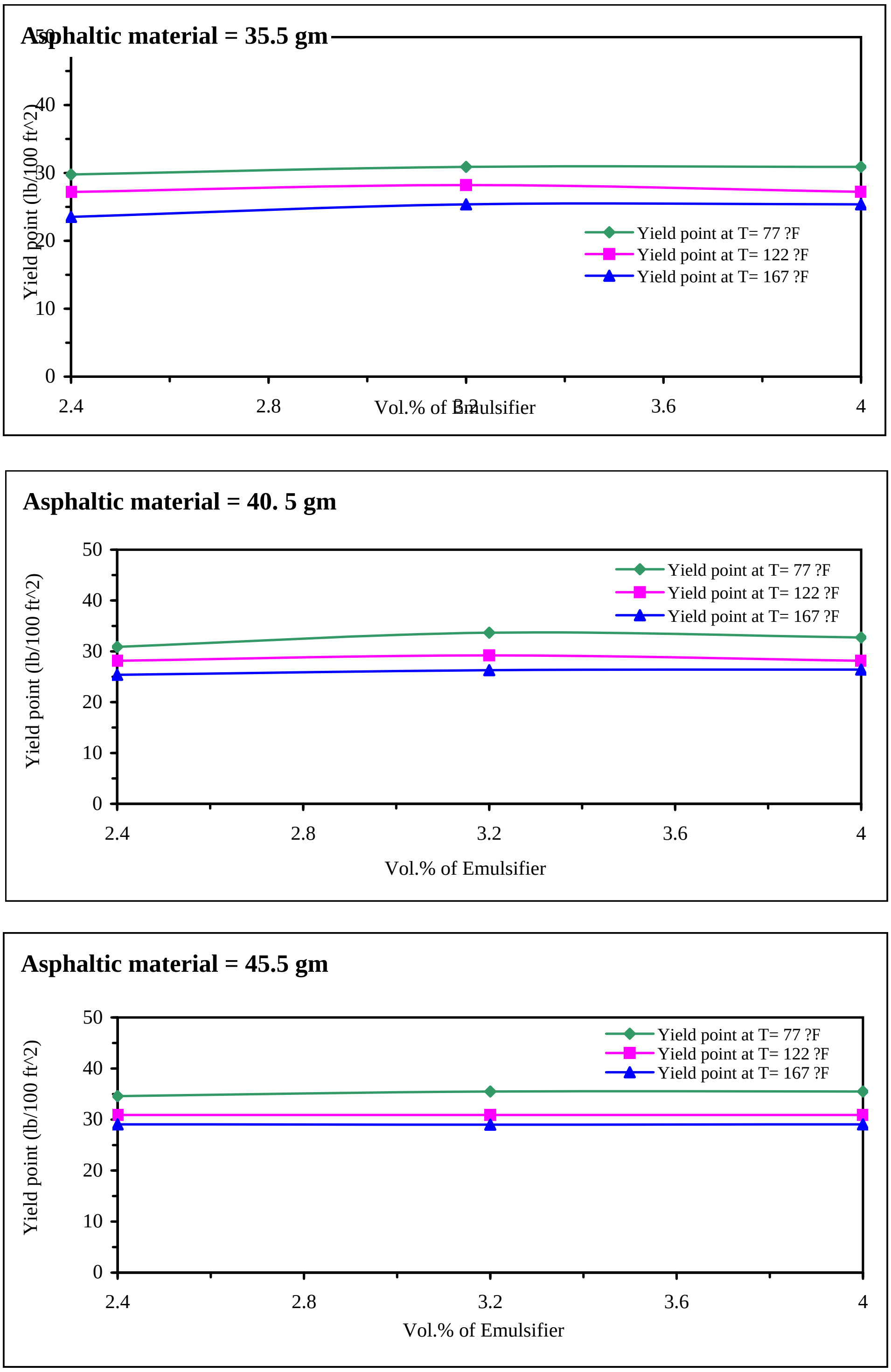


Figure (5.29) Effect of Vol. % of Emulsifier on Yield point of Emulsions with Barite = 0.65 Vol. %

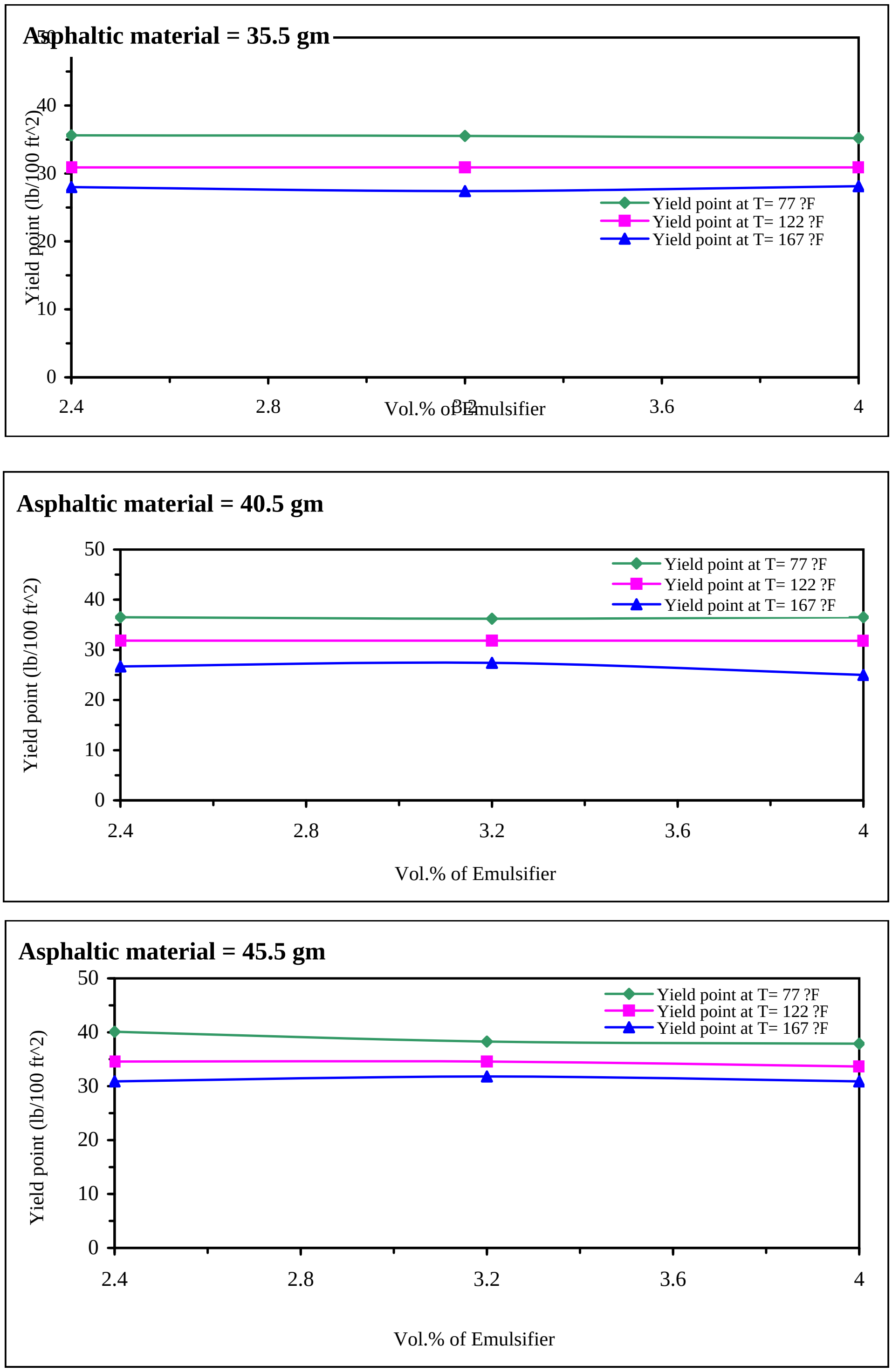


Figure (5.30) Effect of Vol. % of Emulsifier on Yield point of Emulsions with Barite = 0.84 Vol. %

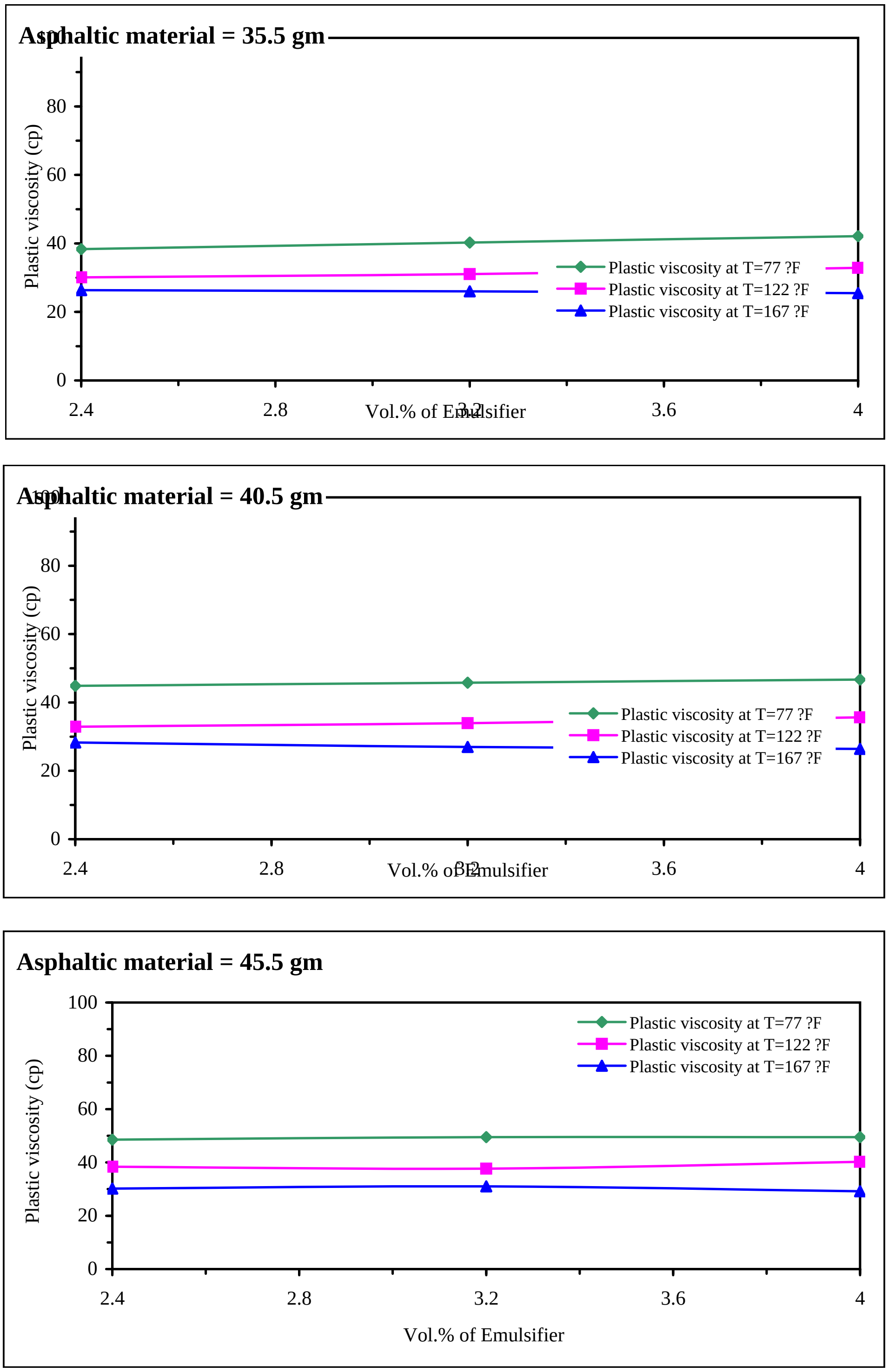


Figure (5.31) Effect of Vol. % of Emulsifier on Plastic viscosity of Emulsions with Barite = 0.46 Vol. %

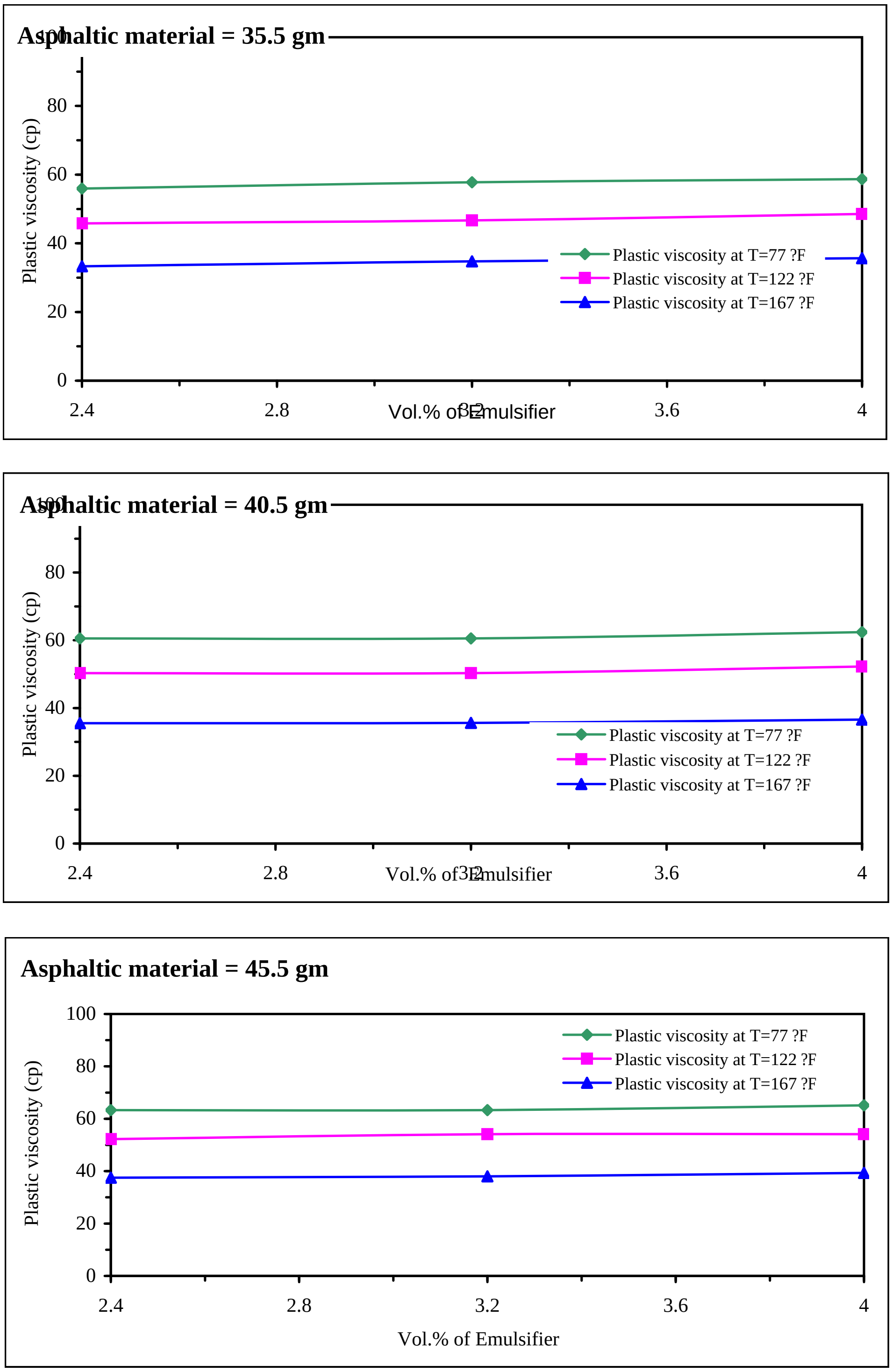
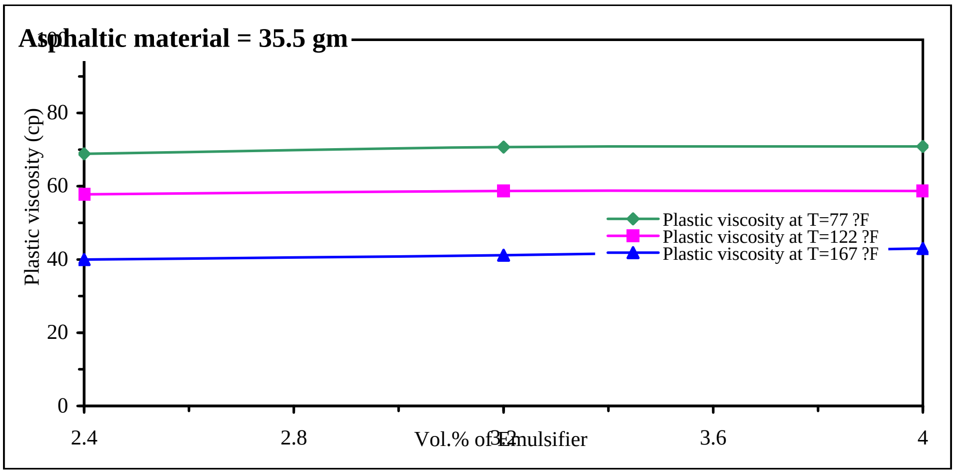
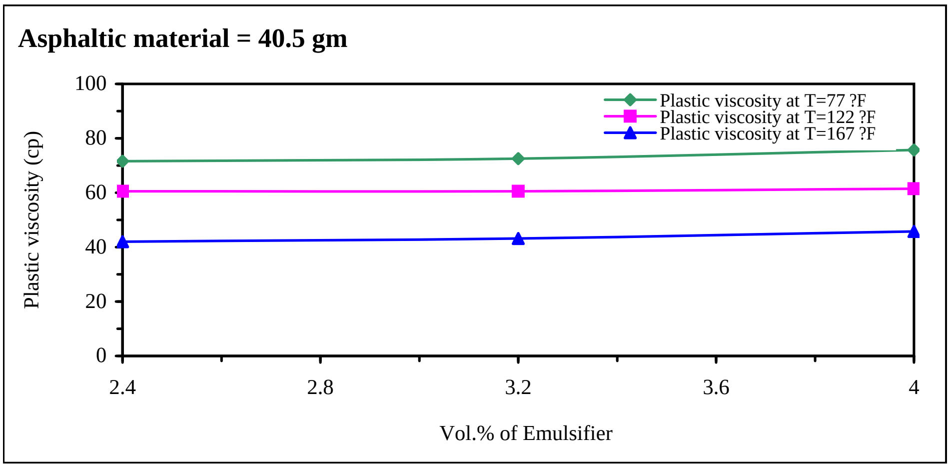


Figure (5.32) Effect of Vol. % of Emulsifier on Plastic viscosity of Emulsions with Barite = 0.65 Vol. %





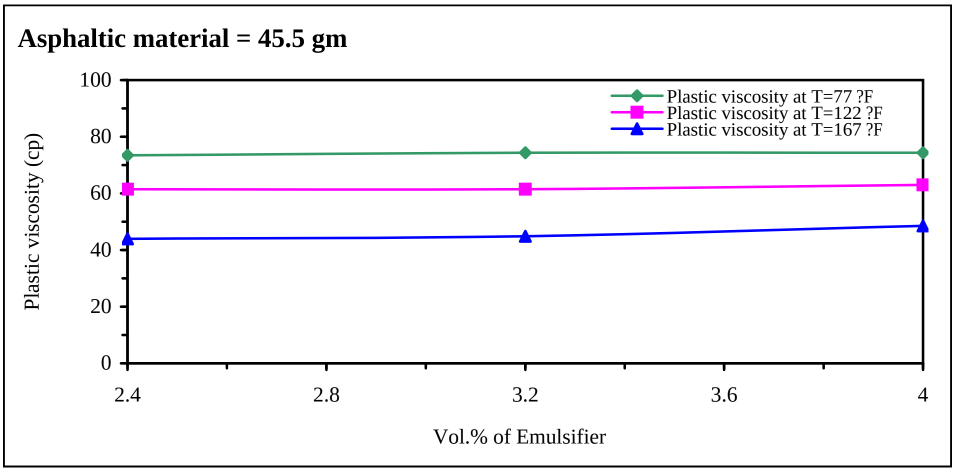
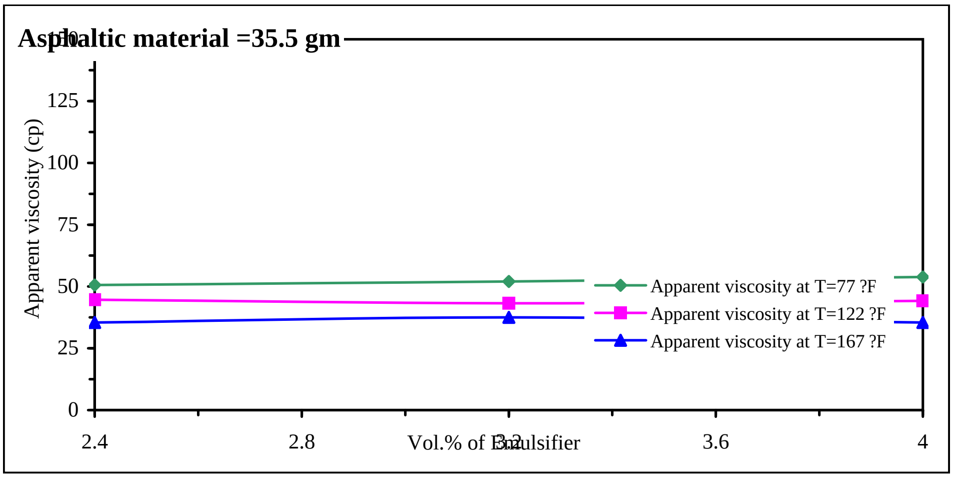
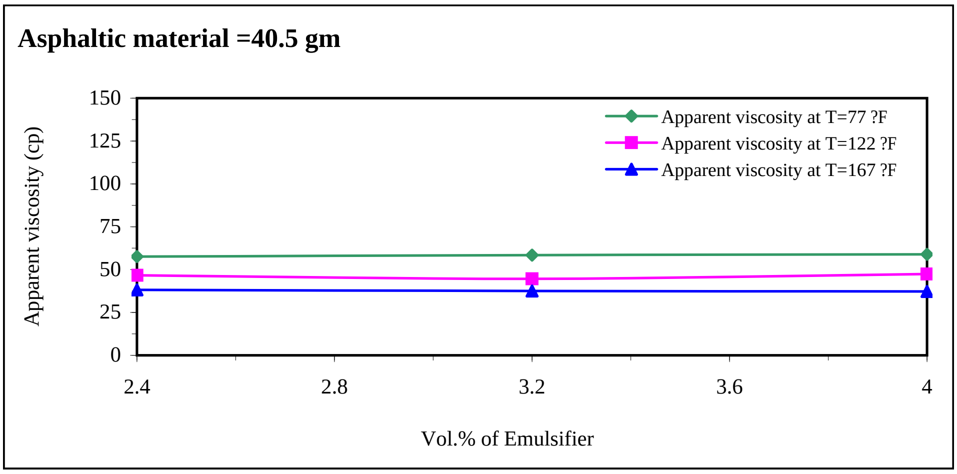


Figure (5.33) Effect of Vol. % of Emulsifier on Plastic viscosity of Emulsions with Barite = 0.84 Vol. %





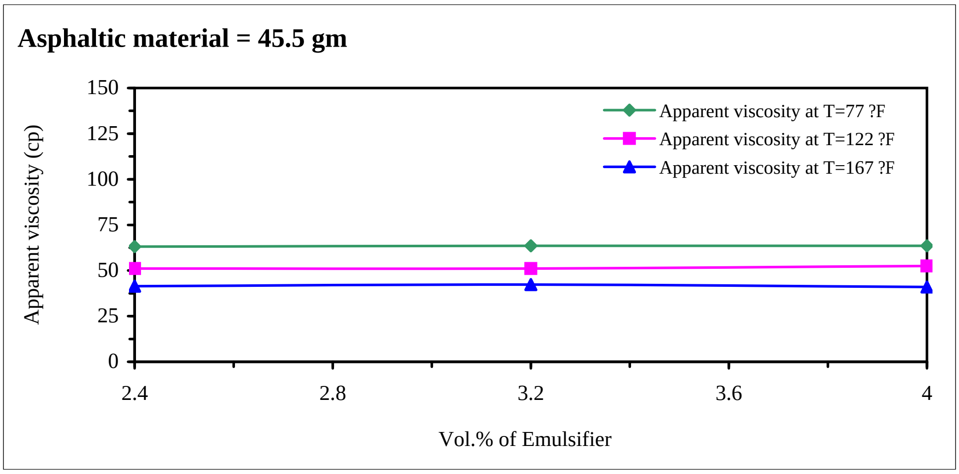


Figure (5.34) Effect of Vol. % of Emulsifier on Apparent viscosity of Emulsions with Barite = 0.46 Vol. %

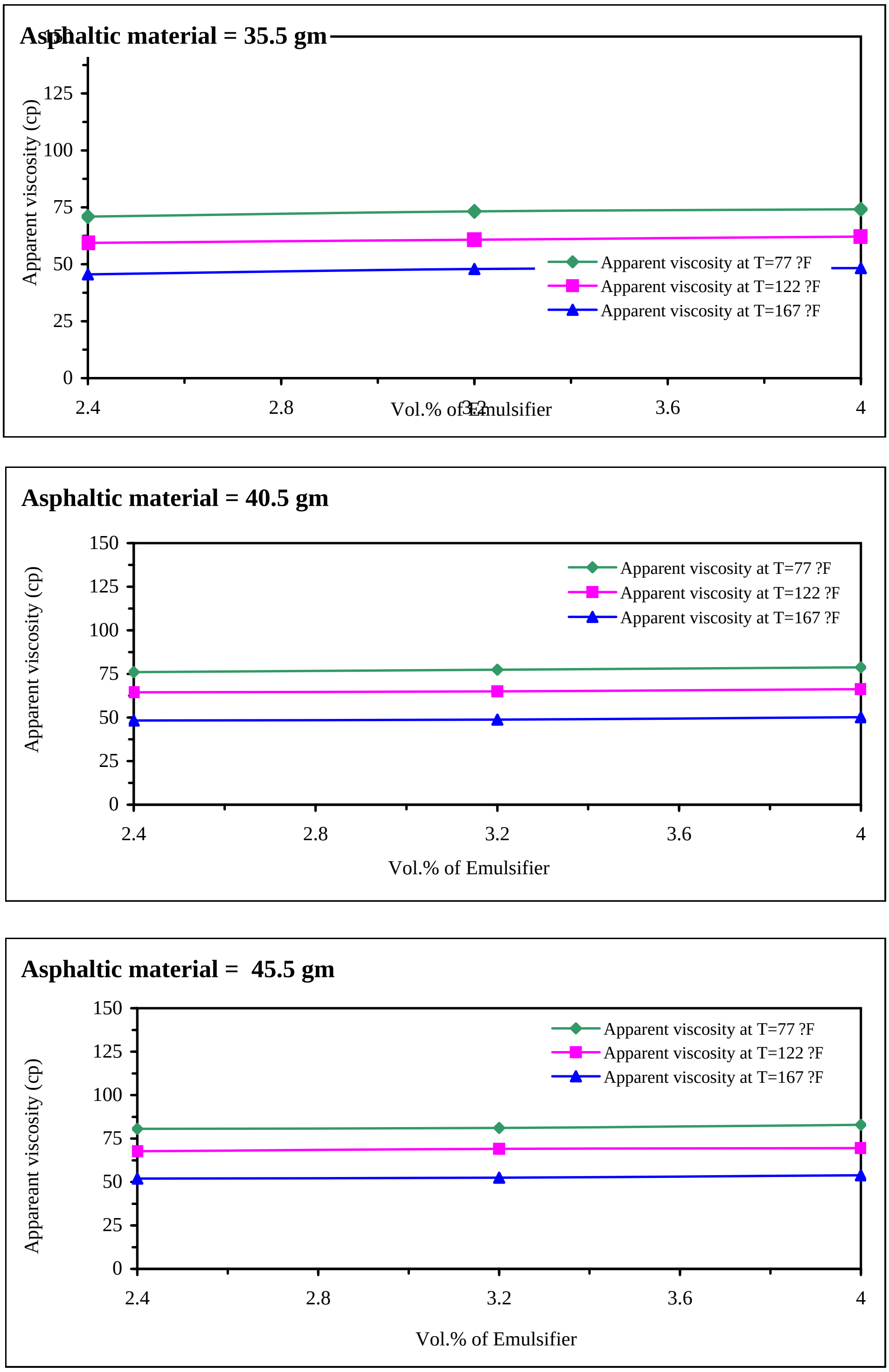


Figure (5.35) Effect of Vol. % of Emulsifier on Apparent viscosity of Emulsions with Barite = 0.65 Vol. %

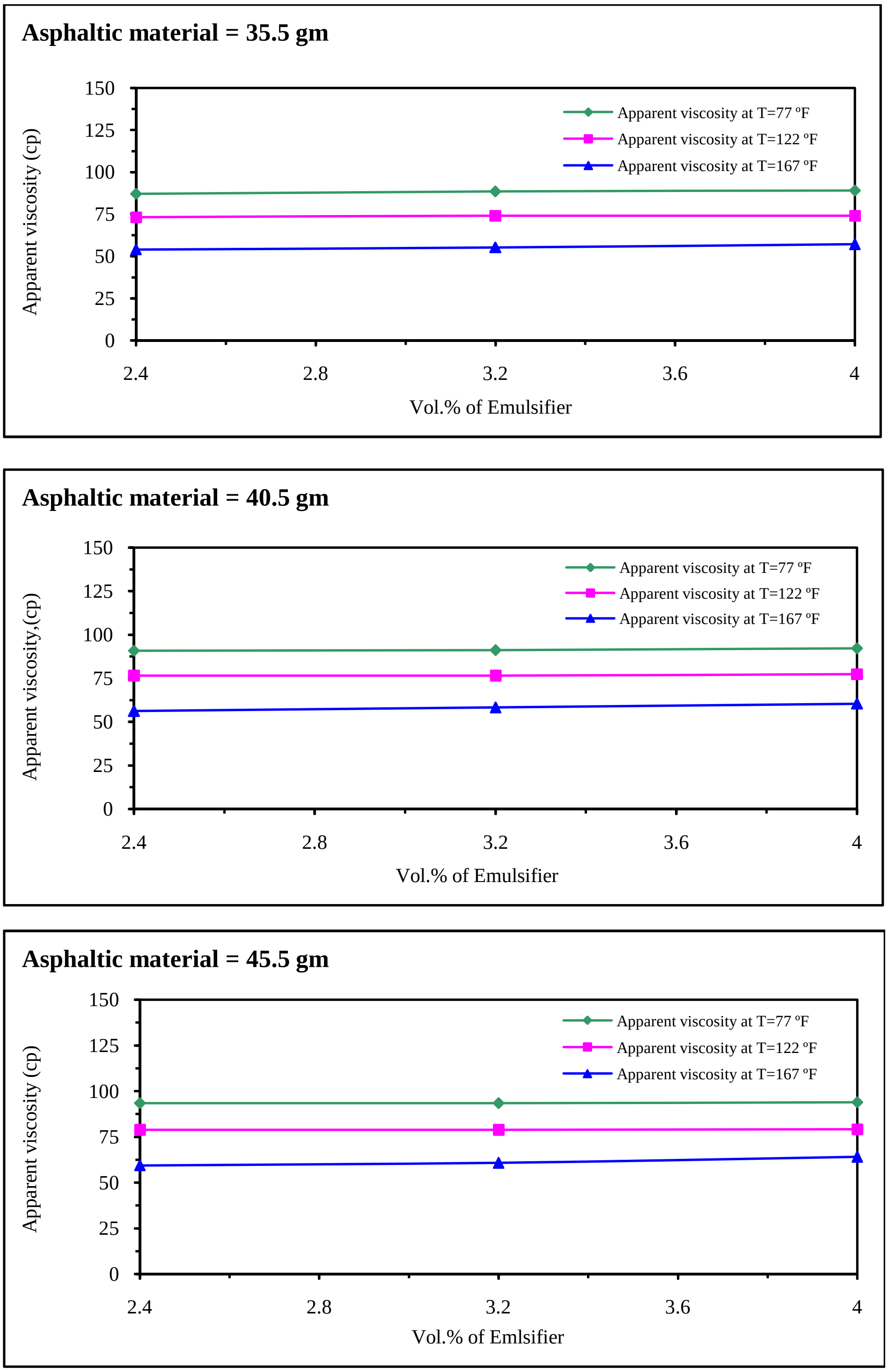


Figure (5.36) Effect of Vol. % of Emulsifier on Apparent viscosity of Emulsions with Barite = 0.84 Vol. %

5.6 Flow Model Selection

The selection of the flow model that best fit the rheological behavior is useful for treating experimental data or for describing flow behavior.

In this work a new method is used, which is proposed by Faith A. Morrison (2005) [54]. This method uses the Solver Add-in in Microsoft Excel® to optimize the solution.

The basic outlines of this method include:

- Arranging the experimental data in the Excel spreadsheet, by using two columns, one for shear rate and the other for shear stress.

- Create a column that has a predicted value of shear stress calculated from a considered flow model. Since it has not know the values of any model parameters, will be started with some guesses.

- Create a new column for the square of the deviation between the actual shear stress and the predicted value. Add up all the values in the error column and put that value in a cell.

- The Solver function in the Excel® is set up to minimize the error cell mentioned above.

- Solver will replace our initial guesses with optimized values.

- Solver allow us to put constrains on the ways in which it manipulate the parameters may be negative.

Applied the experimental data which prepared in 25 °C (77 °F) by using Add-in Microsoft Excel® and the result was the best by using Bingham plastic model.

By using Add-in Microsoft Excel® the experiments at 25 °C (77 °F) will be taken because the experiments at 50 °C (122 °F) and 75 °C (167 °F) give the same results, which is the Bingham plastic model best fits the experimental results.

The results by using the Add-in Microsoft Excel® are shown in tables (5.10) to (5.18) and figures (5.37) to (5.39).

Table (5.10) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.46 , Emulsifier = 2.4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.1942	0.1924	0.0037	0.0538
40.5	2.2632	0.1540	0.0079	0.0518
45.5	2.2336	0.1492	0.0167	0.0663

Table (5.11) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.46 , Emulsifier = 3.2) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.1763	0.1684	0.0042	0.0438
40.5	2.2652	0.1545	0.0086	0.0531
45.5	2.3441	0.1443	0.0174	0.0644

Table (5.12) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.46 , Emulsifier = 4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.1891	0.1654	0.0038	0.0435
40.5	2.2747	0.1512	0.0098	0.0533
45.5	2.3502	0.1419	0.0171	0.0633

Table (5.13) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.65 , Emulsifier = 2.4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.1834	0.2278	0.0278	0.1020
40.5	2.2523	0.2032	0.0360	0.1041
45.5	2.2743	0.1948	0.0319	0.0986

Table (5.14) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.65 , Emulsifier = 3.2) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.1812	0.2450	0.0326	0.1156
40.5	2.2714	0.1876	0.0265	0.0896
45.5	2.2783	0.1940	0.0328	0.0991

Table (5.15) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.65 , Emulsifier = 4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.2041	0.2188	0.0236	0.1340
40.5	2.2820	0.1806	0.0248	0.0857
45.5	2.3065	0.1783	0.0316	0.0923

Table (5.16) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.84 , Emulsifier = 2.4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.2246	0.1864	0.0157	0.0736
40.5	2.2625	0.1936	0.0258	0.0918
45.5	2.2760	0.1917	0.0286	0.0946

Table (5.17) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.84 , Emulsifier = 3.2) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.2329	0.1837	0.0164	0.0739
40.5	2.2601	0.1822	0.0188	0.0791
45.5	2.2813	0.1914	0.0306	0.0965

Table (5.18) Model selection for Emulsions using Add-in Microsoft Excel at room temperature 77 °F (25 °C) with (Barite = 0.84 , Emulsifier = 4) Vol. %

Weight of Asphaltic material (gm)	Sum of Square Error			
	Newtonian Eqn.(3.1)	Power Law Eqn.(3.3)	Bingham Eqn.(3.2)	Casson Eqn.(3.5)
35.5	2.2480	0.1787	0.0162	0.0727
40.5	2.2606	0.1877	0.0220	0.0852
45.5	2.2907	0.1838	0.0282	0.0914

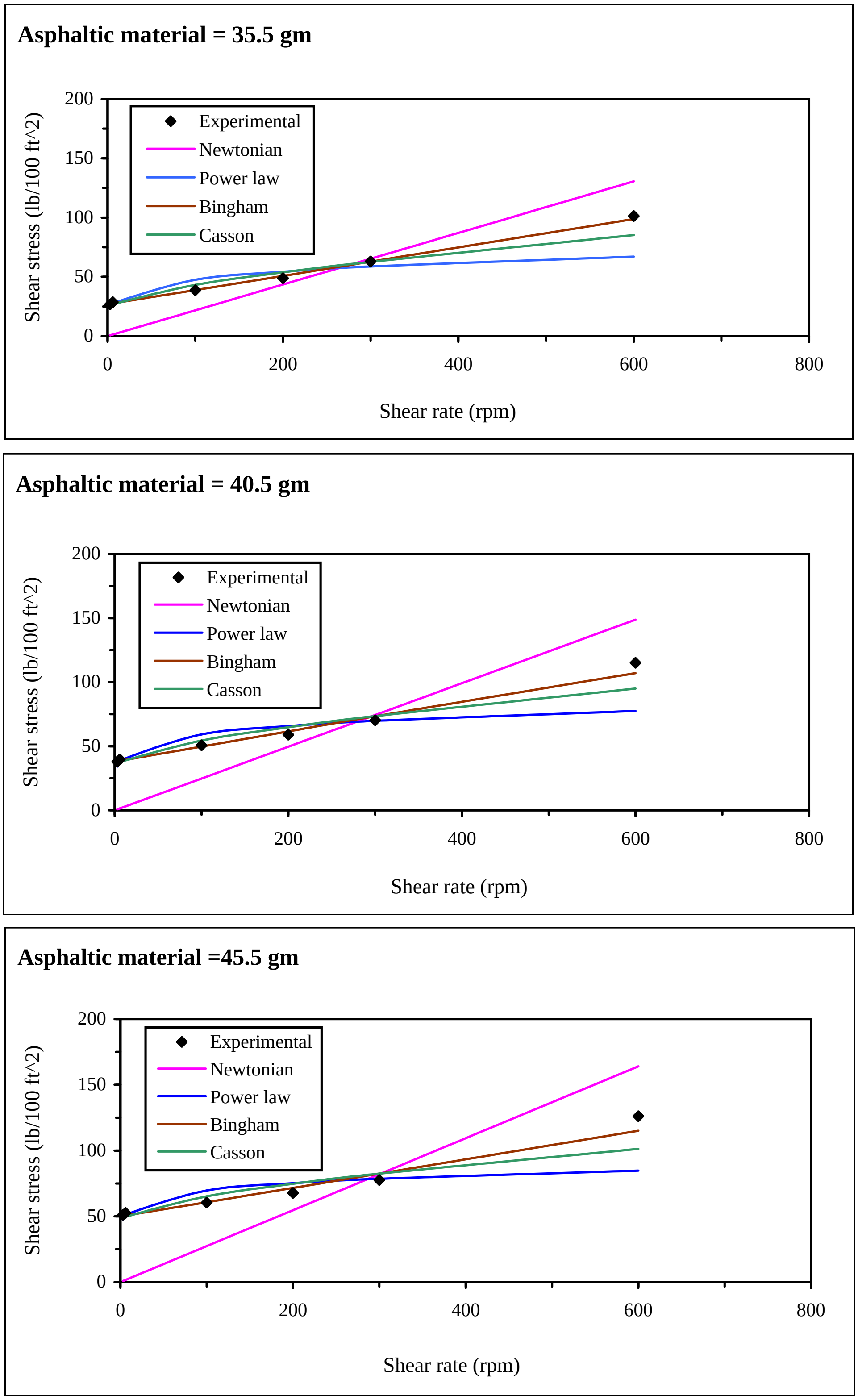


Figure (5.37) Experimental results and flow models representation with (Barite = 0.46 , Emulsifier = 2.4) Vol. %

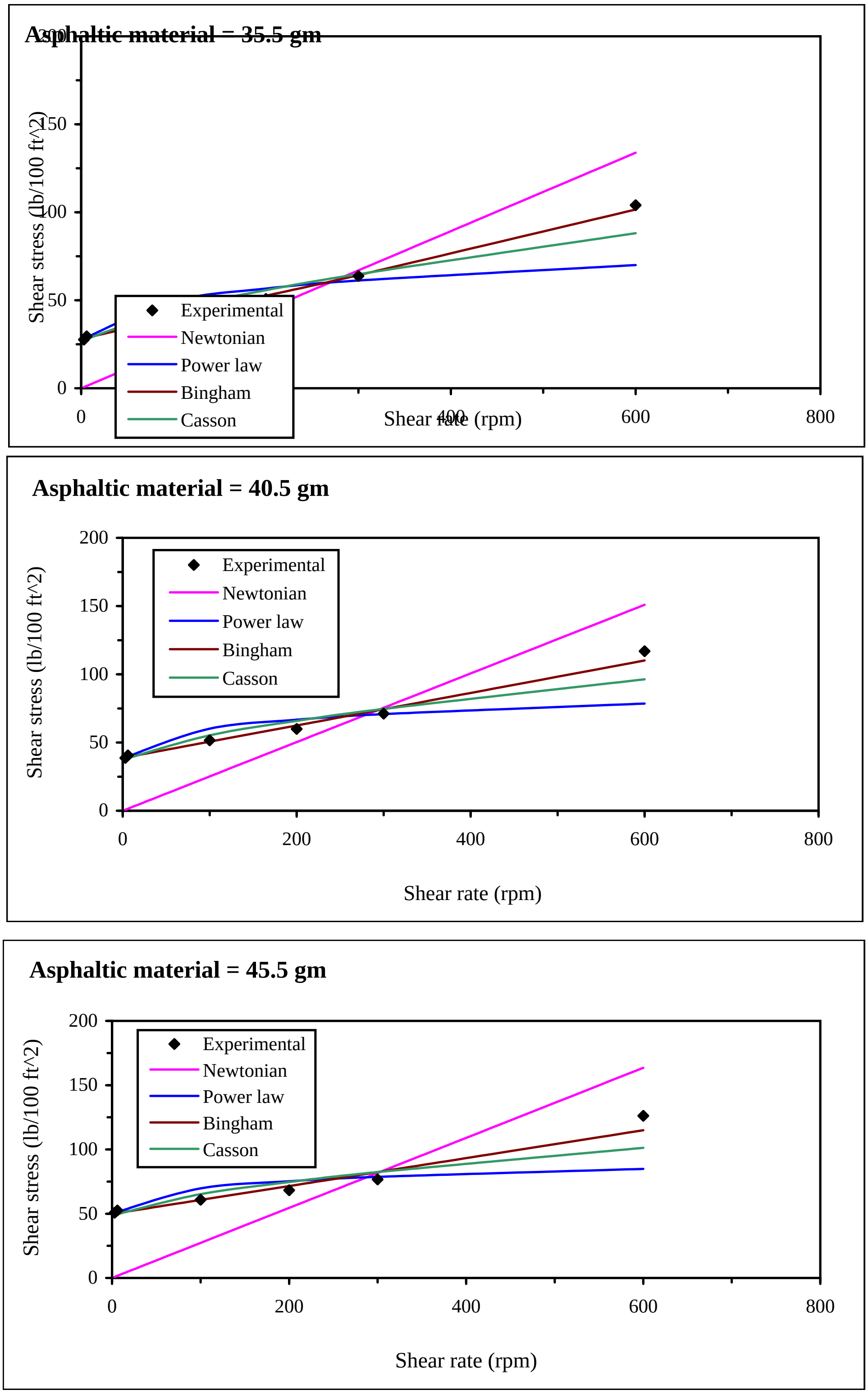
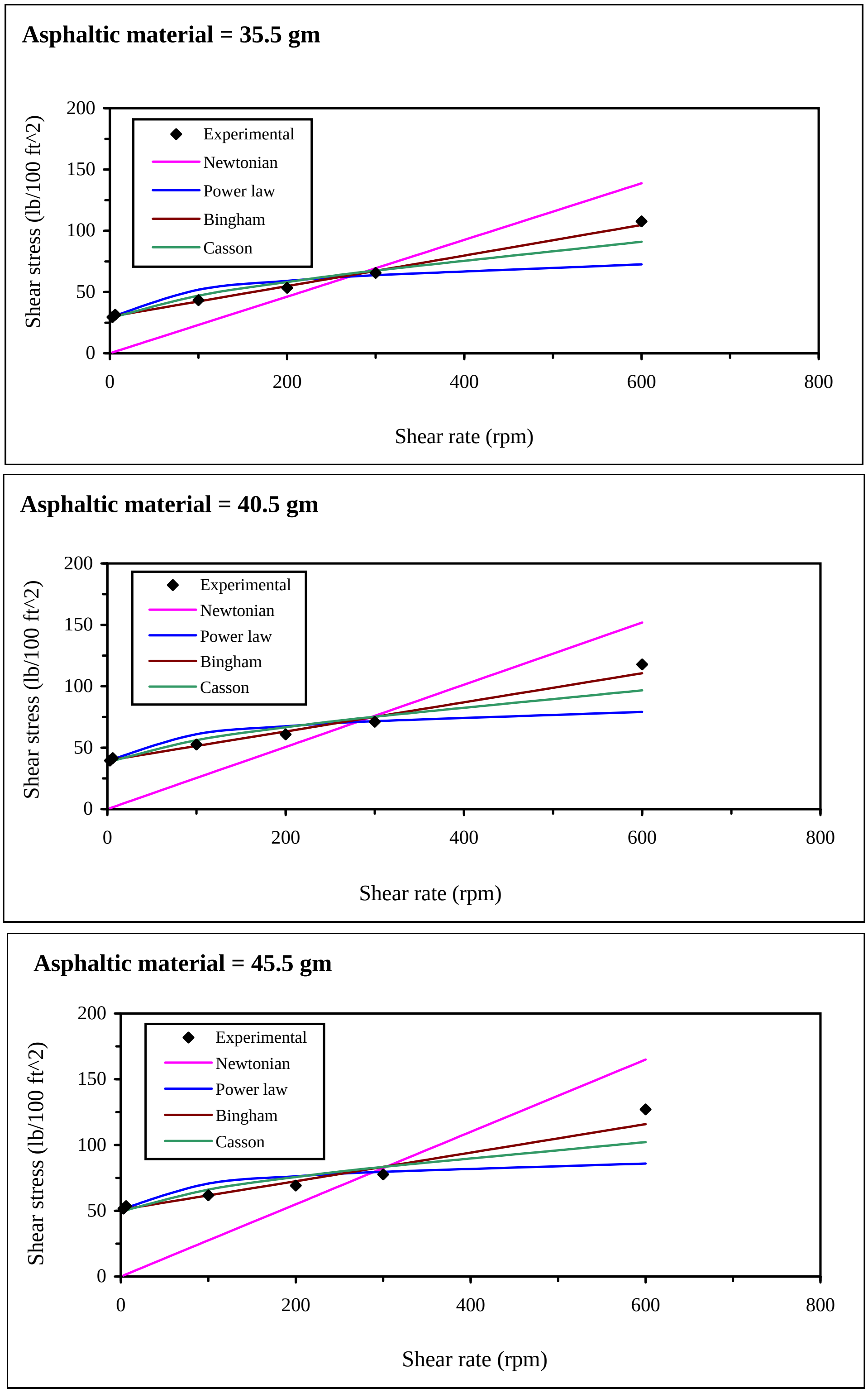


Figure (3.38) Experimental results and flow models representation with (Barite = 0.46 , Emulsifier = 3.2) Vol. %


Asphaltic material = 35.5 gm

Asphaltic material = 40.5 gm

Asphaltic material = 45.5 gm

Figure (3.39) Experimental results and flow models representation with (Barite = 0.46 , Emulsifier = 4) Vol. %

Chapter Six

Conclusions and Recommendations

6.1 Conclusions

From the present study, one can conclude the followings:

1. The increase in temperature will decrease the rheological properties (yield point, plastic viscosity and apparent viscosity) of (W/O) invert emulsion.

2. The increase in concentration of asphaltic material tends to increase the (yield point, plastic viscosity and apparent viscosity) of (W/O) invert emulsion.

3. The increase in the volume percentage of barite tends to increase the (yield point, plastic viscosity and apparent viscosity) of (W/O) invert emulsion.

4. The emulsifier showed be added in a sufficient quantity to get a stable emulsion with temperature since it surrounded water droplets. It has a little effect on the rheological properties of invert emulsions at (122 ,167) °F, but it's effect is clearly shown at room temperature (25 °C) 77 °F.

6. By using the Solver Add-in-Microsoft Excel ®, the Bingham plastic model was found to be the best fits the experimental results.

6.2 Recommendations For Future Works

The following recommendations were drawn from the experimental work:

1. Study the effect of high temperature on the stability of emulsions or the rheological properties of emulsions.

2. Study the effect of temperature and additives on rheological properties of direct emulsions (O/W) where the water is the external phase and the oil is the dispersed phase.

3. Study the effect of other additives on the rheological properties of emulsions such as, organophilic clay, lime and water.

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Appendix-A

Experimental Data

Table (A-1)i Shear Stress versus Shear Rate with (Barite = 0.46 , Emulsifier = 2.4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	101.26	81.90	70.84
300	62.93	51.79	44.49
200	48.87	42.41	33.19
100	38.72	35.04	26.74
6	28.58	26.74	18.44
3	26.74	24.89	16.59

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	115.09	93.28	76.37
300	70.23	58.39	48.1
200	59.01	47.94	37.80
100	50.71	40.57	30.43
6	39.65	33.19	23.05
3	37.86	31.35	21.21

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	126.16	102.19	82.90
300	77.60	63.77	52.71
200	67.77	56.98	47.94
100	60.39	49.79	39.65
6	52.55	40.57	34.41
3	51.17	38.72	31.57

Table (A-2)i Shear Stress versus Shear Rate with (Barite = 0.46 , Emulsifier =3.2) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	104.03	82.82	78.21
300	63.77	51.78	49.02
200	50.71	43.33	35.96
100	41.49	36.88	27.66
6	29.50	27.66	20.28
3	27.66	25.82	18.44

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	116.94	89.28	80.98
300	71.15	56.32	50.87
200	59.63	49.79	39.65
100	51.93	42.41	32.27
6	40.57	35.19	24.89
3	38.72	33.19	23.05

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	126.16	103.19	84.67
300	76.68	64.19	53.63
200	68.23	57.16	48.87
100	60.85	49.79	40.57
6	52.55	40.57	34.11
3	50.72	38.72	32.27

Table (A-3)i Shear Stress versus Shear Rate with (Barite = 0.46 , Emulsifier = 4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	107.72	88.36	70.84
300	65.62	55.48	45.33
200	53.48	44.26	35.96
100	43.34	36.88	26.74
6	31.39	28.58	19.36
3	29.50	27.66	17.52

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	117.86	94.81	74.53
300	71.15	59.16	48.1
200	60.85	49.41	39.65
100	52.55	42.41	29.50
6	41.49	35.04	23.97
3	39.45	33.19	22.59

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	127.08	104.95	81.92
300	77.6	64.69	52.71
200	69.15	59.01	47.94
100	61.77	51.63	39.65
6	53.48	42.41	35.04
3	51.63	40.57	33.19

Table (A-4)i Shear Stress versus Shear Rate with (Barite = 0.65 , Emulsifier = 2.4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	141.83	118.78	91.12
300	85.90	72.99	57.32
200	64.54	61.77	47.94
100	56.26	52.55	38.72
6	47.94	41.49	29.50
3	44.26	39.64	27.66

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	151.96	128.93	96.85
300	91.43	78.53	61.09
200	73.76	68.23	58.01
100	68.23	59.93	53.48
6	59.01	52.55	46.10
3	57.16	50.71	44.26

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	161.19	135.38	104.03
300	97.89	83.14	66.54
200	78.83	73.76	59.93
100	71.92	66.38	55.32
6	64.54	59.93	48.87
3	62.69	58.09	47.02

Table (A-5)i Shear Stress versus Shear Rate with (Barite = 0.65 , Emulsifier =3.2) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	146.44	121.55	94.81
300	88.67	74.88	60.09
200	67.30	62.69	47.94
100	57.16	53.94	38.72
6	50.71	48.87	29.50
3	48.87	47.02	27.66

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	154.74	129.85	97.58
300	94.20	79.53	61.93
200	75.61	68.69	50.31
100	69.15	60.85	45.39
6	59.93	53.02	32.02
3	58.09	51.63	30.19

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	162.11	139.07	105.12
300	98.81	84.98	67.01
200	79.29	75.60	61.77
100	72.84	68.23	57.16
6	65.46	61.77	50.71
3	63.62	59.93	48.87

Table (A-6)i Shear Stress versus Shear Rate with (Barite = 0.65 , Emulsifier = 4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	148.29	124.31	96.65
300	89.59	75.76	61.01
200	70.07	64.54	51.63
100	59.93	55.32	42.41
6	51.63	44.26	33.19
3	49.79	42.41	30.35

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	157.51	132.61	100.34
300	95.12	80.37	63.77
200	78.37	70.53	59.93
100	70.99	61.77	55.32
6	61.77	55.32	47.94
3	59.93	53.48	45.10

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	165.80	139.07	107.72
300	100.65	84.98	68.38
200	82.98	78.37	61.77
100	77.45	70.07	57.16
6	69.15	63.62	50.77
3	67.31	61.77	48.87

Table (A-7)i Shear Stress versus Shear Rate with (Barite = 0.84 , Emulsifier = 2.4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	174.10	146.44	108.12
300	105.26	88.67	68.01
200	82.98	74.68	59.93
100	73.76	65.46	53.47
6	58.08	56.01	46.10
3	56.24	52.90	44.26

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	181.48	152.89	112.33
300	109.87	92.36	71.15
200	89.43	82.98	64.54
100	79.29	75.60	56.24
6	70.07	66.38	51.63
3	68.23	64.54	49.79

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	187.01	157.51	118.78
300	113.56	96.04	74.84
200	93.12	88.51	68.69
100	82.98	76.53	59.93
6	75.14	72.84	56.24
3	72.84	70.99	54.39

Table (A-8)i Shear Stress versus Shear Rate with (Barite = 0.84 , Emulsifier = 3.2) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	176.87	148.29	110.48
300	106.19	89.59	69.31
200	84.82	76.07	61.77
100	75.60	66.85	55.32
6	59.93	49.79	41.49
3	58.09	47.94	39.65

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	182.40	152.89	116.41
300	109.87	92.36	73.23
200	90.36	83.90	65.46
100	79.73	76.53	57.16
6	67.31	70.99	52.55
3	65.46	69.15	50.71

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	187.01	157.51	121.55
300	112.64	96.04	76.68
200	93.31	88.97	69.15
100	83.44	76.72	60.85
6	75.60	73.29	56.70
3	74.22	71.92	55.32

Table (A-9)i Shear Stress versus Shear Rate with (Barite = 0.84 , Emulsifier = 4) Vol. %

1- Asphaltic material = 35.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	177.97	148.29	114.17
300	107.11	89.59	71.15
200	86.67	78.37	63.62
100	77.45	68.69	57.16
6	61.77	52.09	44.79
3	60.67	49.79	42.41

2- Asphaltic material = 40.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	184.24	154.74	120.63
300	110.79	93.28	74.84
200	91.28	85.29	70.07
100	80.21	77.45	62.69
6	69.69	71.92	58.09
3	67.31	70.07	56.24

3- Asphaltic material = 45.5 gm

Shear rate (rpm)	Shear stress (lb/100 ft^2) at T=77 °F	Shear stress (lb/100 ft^2) at T=122 °F	Shear stress (lb/100 ft^2) at T=166 °F
600	187.93	158.43	128.01
300	113.56	96.04	79.45
200	94.97	90.36	70.07
100	84.83	77.45	62.69
6	76.97	74.22	58.09
3	74.60	72.84	56.24

الخلاصة

ان الهدف الاساسي من هذا البحث هو دراسة تاثير درجة الحرارة على الخواص الريولوجية (اللزوجة البلاستيكية، نقطة المطاوعة و اللزوجية الظاهرية) للمستحلبات وباستخدام اضافات مختلفة للحصول على افضل خواص ريولوجية.

تم تحضير 27 نموذج من المستحلب وان كل المستحلبات في هذا البحث هي مستحلبات عكسية (invert emulsions) اي قطرات الماء مفرقة في زيت الديزل، والمستحلب الناتج يدعى ماء في النفط (ماء/نفط) مستحلب عكسي.

وان هذه المستحلبات تحتوي على ثلاث نسب مئوية مختلفة من حجم البرايت (barite) ، مع ثلاث نسب مئوية مختلفة من حجم عامل الاستحلاب (Emulsifier) ، وثلاث أوزان مختلفة من المادة الإسفلتية (Asphaltic material)، تحت درجة حرارة (77، 122 و167) ° F.

تم دراسة الخواص الريولوجية باستخدام جهاز (Fann VG-35 A) وذلك بقياس اجهاد القص (shear stress) المصاحب لكل معدل قص (shear rate).

تم استخدام برنامج مايكروسوفت ايكسيل لايجاد افضل موديل يمثل النتائج العلمية. وقد وجد بان الموديل (Bingham Plastic) هو الافضل.

وقد تم ايجاد ان الزيادة في درجة الحرارة يسبب نقصان في الخواص الريولوجية (اللزوجة البلاستيكية، نقطة المطاوعة و اللزوجية الظاهرية) للمستحلبات ويعتمد على التغير في لزوجة الطور المستمر(continuous phase) للمستحلبِ وهو زيتُ ديزل.

وكذلك تم إيجاد تأثير الإضافات على الخواص الريوليجية لمستحلبات كالاتي: ان الزيادة في وزن المادة الإسفلتية (Asphaltic material) يؤدي الى زيادة الخواص الريوليجية للمستحلبات ، وان زيادة النسبة المئوية الحجمية لبرايت (Barite) تؤدي الى زيادة الخواص الريوليجية لمستحلبات وان زيادة النسبة المئوية الحجمية لعامل الاستحلاب (Emulsifier) له تأثير صغير على قيم الخواص الريولوجية، ولكنه يزيد من استقراريه ا لمستحلبات مع درجة الحرارة بسب إحاطته بقطرات الماء.

شكر وتقدير

أود ان اعبر عن خالص شكري وتقديري وامتناني العميق للمشرف الدكتور **مهند عبد الرزاق** لما قدمه لي من توجيهات قيمة طوال فترة انجاز البحث.

أود ايضاً ان اتوجه بالشكر الى رئيس قسم الهندسة الكمياوية الأستاذ الدكتور **قاسم جبار السليمان** لارشاداته ونصائحه السديدة.

ولا أنسى ان اتقدم بالشكر و الامتنان الى كل من لازمني طوال فترة البحث وخلال اصعب الظروف الى أعز من في الوجود **أمي** و **أبي** و **أخي** و **أخواتي**.

سمر علي عبد محمد

تأثير الإضافات ودرجة الحرارة على السلوك الريولوجي للمستحلبات العكسية

(ماء/نفط)

رسالة

مقدمة الى كلية الهندسة في جامعة نهرين

وهي جزء من متطلبات نيل درجة ماجستير علوم

في الهندسة الكيمياوية

من قبل

سـمر علي عبد محمد

(بكالوريوس علوم في الهندسة الكيمياوية ٢٠٠٤)

محرم ١٤٣٠ هـ

كانون الثاني ٢٠٠٩ م