

Effect of Additives on Rheological Properties of Invert Emulsions

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Abstract

This research deals with study of the effect of additives on rheological properties (yield point, plastic viscosity, and apparent viscosity) of emulsions. Twenty seven emulsion samples were prepared; all emulsions in this investigation are invert emulsions when water droplets are dispersed in diesel oil. The resulting emulsions are called water-in-oil (W/O) emulsions. 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. 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 in the same time it increase the stability of emulsions with temperature because it surrounded water droplets.

Keywords: Rheology, Emulsions

Introduction

Rheology is the study of the deformation and flow of matter under the influence of an applied stress, for example a shear stress or extensional stress.

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 its 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 [3, 4].

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 [5].

Different emulsifying agents give rise to different flow properties. The chemical nature of emulsifying agent is also important which may lead to the flocculation of the dispersed droplet, that will tend to produce plastic flow [3,6].

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 [3].

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.

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.

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 dilatants flow characteristics [8].

Experimental Work

All emulsions prepared in this investigation are invert emulsions when water droplets are dispersed in oil. The resulting emulsions are called water- in - oil emulsions (W/O). Generally, W/O-emulsions are preferred when a large amount of oil is desired.

Diesel oil was used as the external phase of all samples being tested, and distilled water was used as the dispersed phase with powdered sodium chloride to provide the salinity of the water phase.

Additives which were used as follow a soluble oil additive as emulsifying agent, barite as weighting material, lime to provide alkalinity, organophilic clay to suspend the weight material, and finally asphaltic material to provide emulsion stability at high temperature, and gel strength.

Experimental procedure

It was found that the following mixing procedure included sequence of additives and mixing periods gave 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. Nacl salt was added to beaker of water
4. Emulsifier (soluble oil additive) was added at desired concentration , concentrate drop by drop to the diesel oil in the Hamilton Beach cup while mixing, and mix for 60 minutes.
5. All powder materials and additives were weighted by using electronic balance, some of these materials are changed in tests and the others are constant as shown in table 1.

6 Lime additive was added slowly and mix for 30 minute.

7. Required volume of brine was added slowly while mixing and mix for 45 minutes.

Table 1 Constant material for all tests.

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

8. Asphaltic material additive was added and mix for 30 minutes.

9. Organophilic clay additives were added and mix for 30 minutes.

10. The total amount of barite was added 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.

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.

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

The sample cup was filled with emulsion sample prepared at 25°C (77°F) to the scribed line, and the rotor was immersed to the proper immersion depth.

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

The instrument switched to 600, 300, 200, 100, 6, and 3 rpm and the dial reading was recorded.

The procedure was repeated the above procedure to the emulsion sample after heated to 50°C (122°F), and then after heated to 75°C (167°F).

Then:

$$\eta_p = \theta_{600} - \theta_{300} \tag{1}$$

$$Y_p = \eta_p - \theta_{300} \tag{2}$$

$$\eta_a = \frac{\theta_{600}}{2} \quad (3)$$

Where

θ_{600} = Dial reading at 600 rpm

θ_{300} = Dial reading at 300 rpm

Results and Discussion

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 1 to 3 respectively. Since, the values of yield point, plastic viscosity, and apparent viscosity are plotted versus the weight of asphaltic material respectively.

The emulsions prepared were in satisfactory conditions at temperatures up to 75 °C (167 °F) with 35.5 gm asphaltic material, it was decided to increase the concentration of asphaltic material to 40.5 and 45.5gm, with three different volumes percentages of barite (0.46%, 0.65% and 0.84%) 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.

Effect of Barite on Rheological properties of Emulsions

The effects of barite on rheological properties (yield point, plastic viscosity and apparent viscosity) of emulsions under different temperatures are clearly shown in figures 4 to 6. Since, the values of yield point, plastic viscosity, and apparent viscosity are plotted versus the volume percentage (Vol. %) of barite, respectively.

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.

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 7 to (9). Since, the values of yield point, plastic viscosity, and apparent viscosity are plotted versus the volume percentage (Vol. %) of emulsifier (Lubrizol Becrosan), respectively.

From these figures, firstly one can notice that at room temperature 25 °C (77 °F), the increase in 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, also it increases the viscosity of the oil continuous phase.

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.

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.

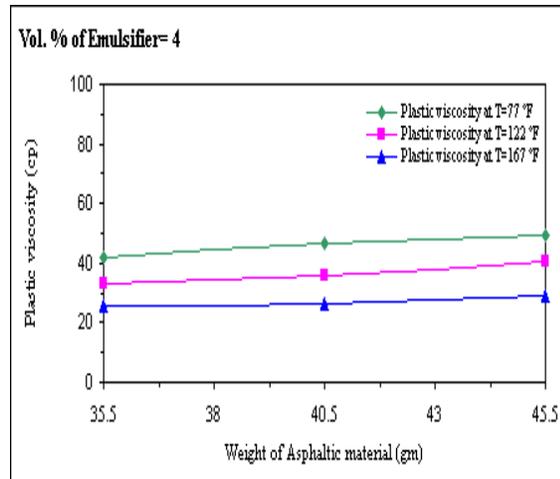
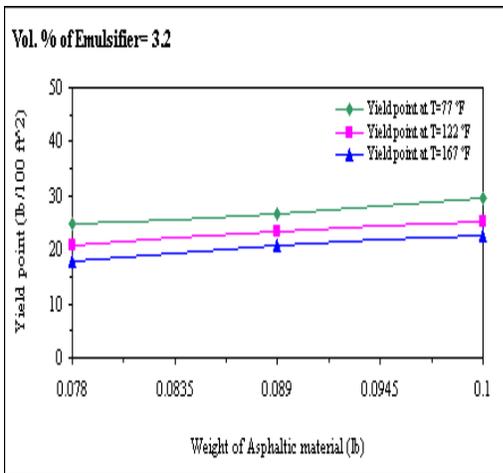
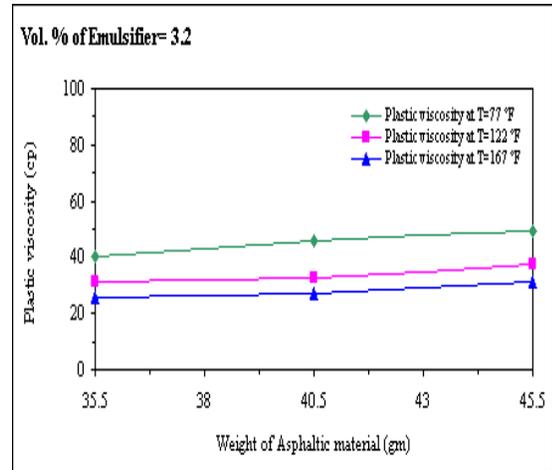
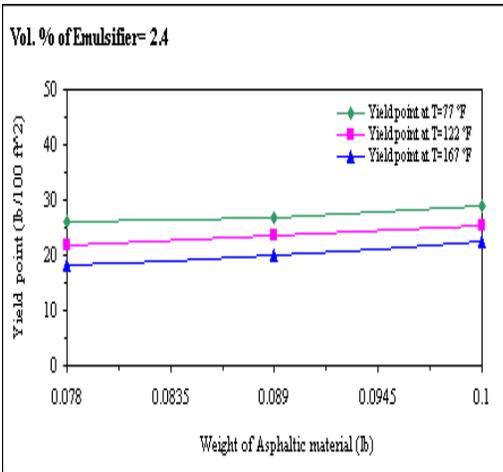
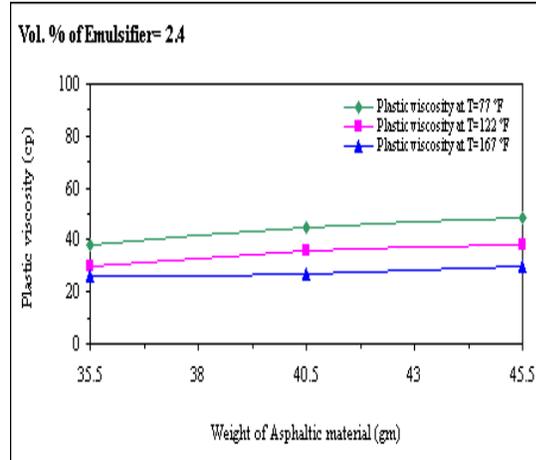
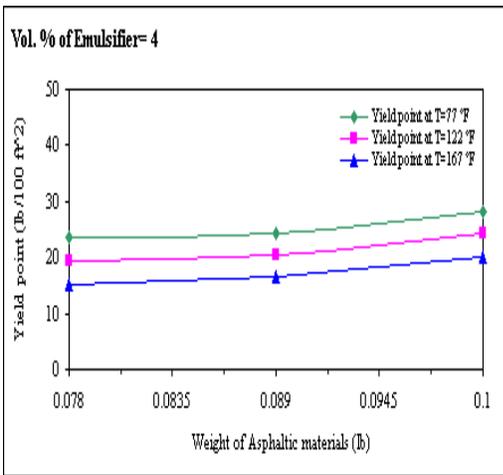


Fig. 1 Effect of concentration of Asphaltic material on Yield point of Emulsions with Barite= 0.46 Vol. %

Fig. 2 Effect of concentration of Asphaltic material on Plastic viscosity of Emulsions with Barite = 0.46 Vol. %

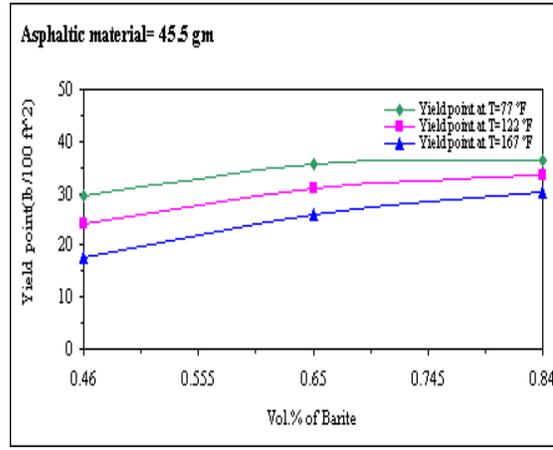
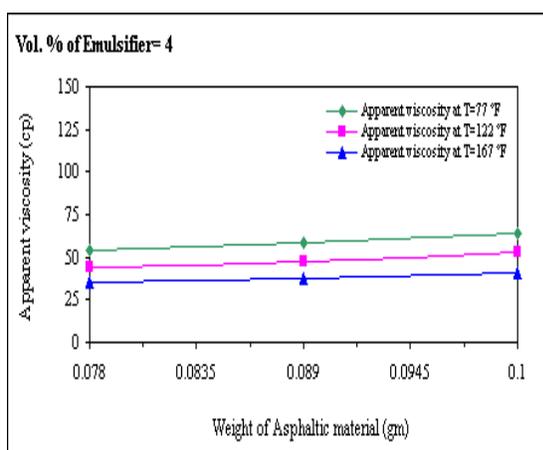
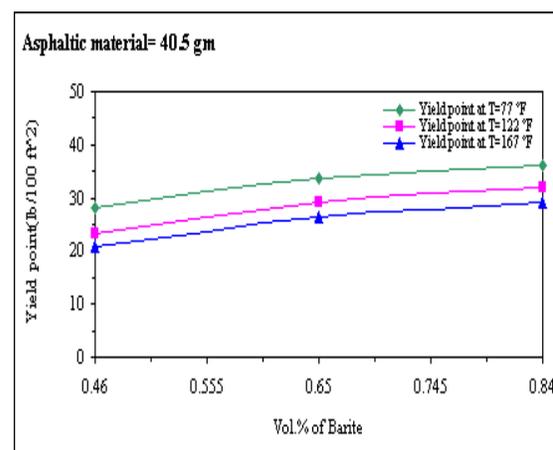
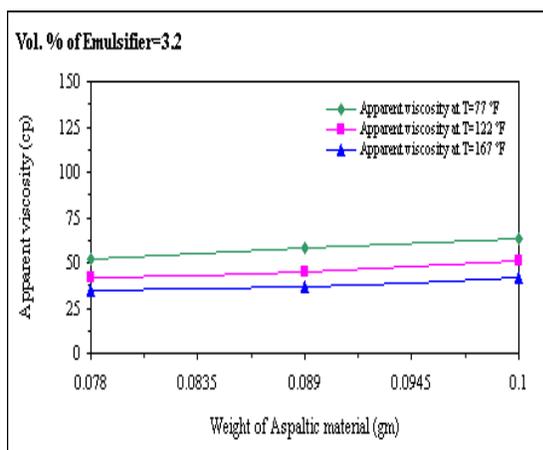
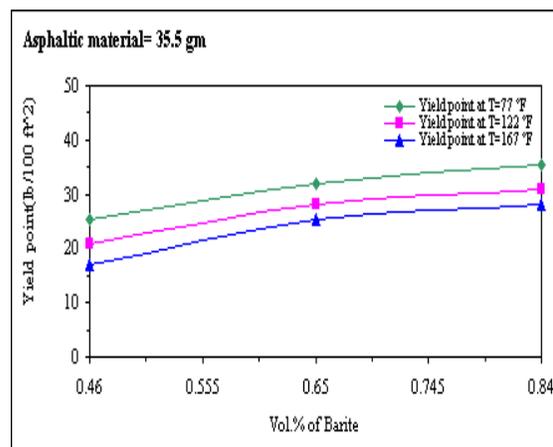
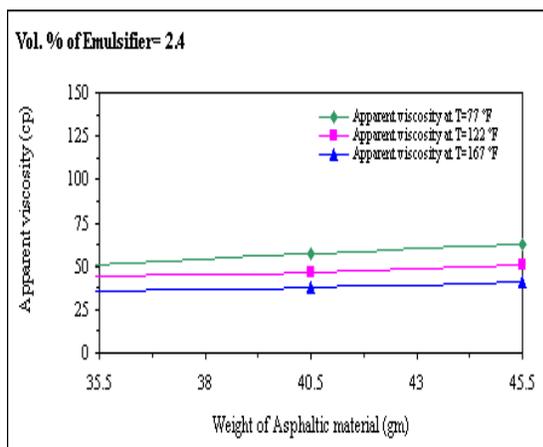


Fig. 3 Effect of concentration of Asphaltic material on Apparent viscosity of Emulsions with Barite = 0.46 Vol. %

Fig. 4 Effect of Vol. % of Barite on Yield point of Emulsions with Emulsifier = 3.2 Vol. %

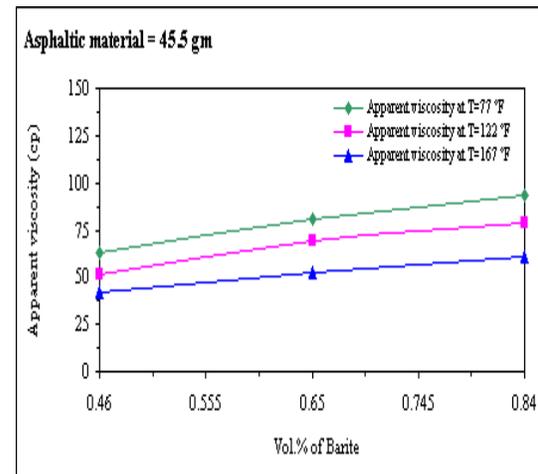
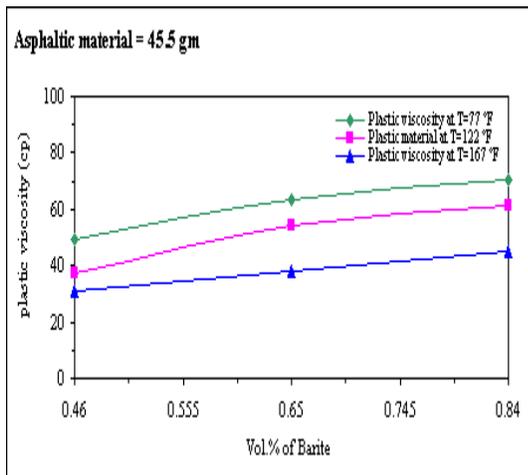
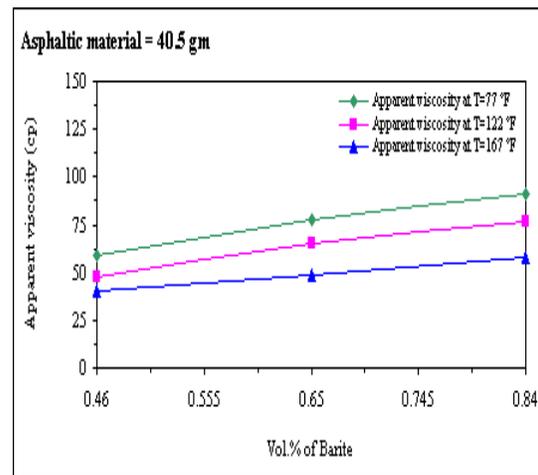
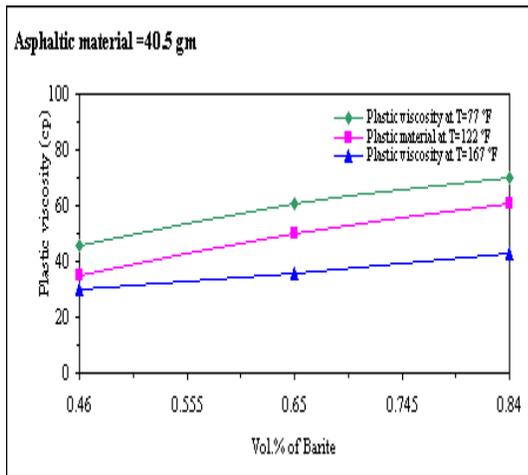
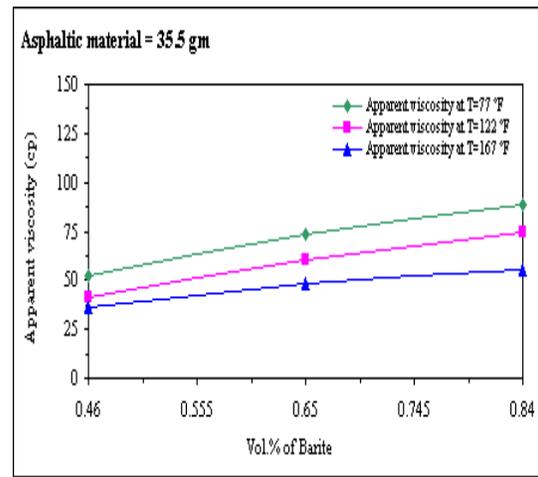
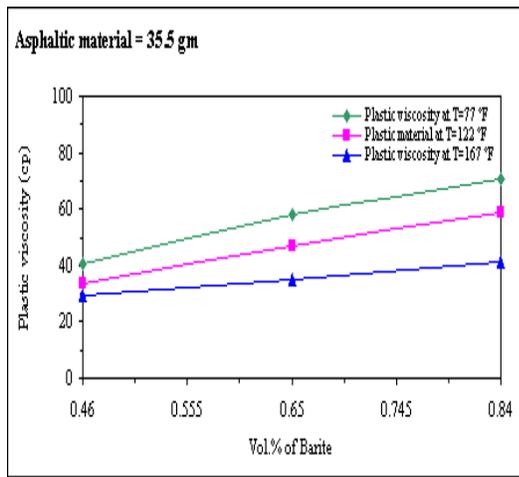


Fig. 5 Effect of Vol. % of Barite on plastic viscosity of Emulsions with Emulsifier = 3.2 Vol. %

Fig. 6 Effect of Vol. % of Barite on Apparent viscosity of Emulsions with Emulsifier = 3.2 Vol. %

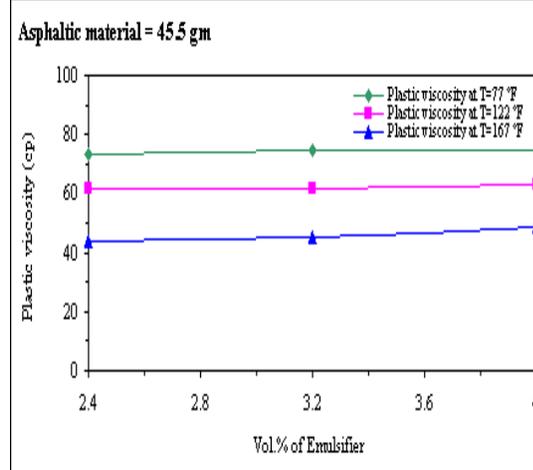
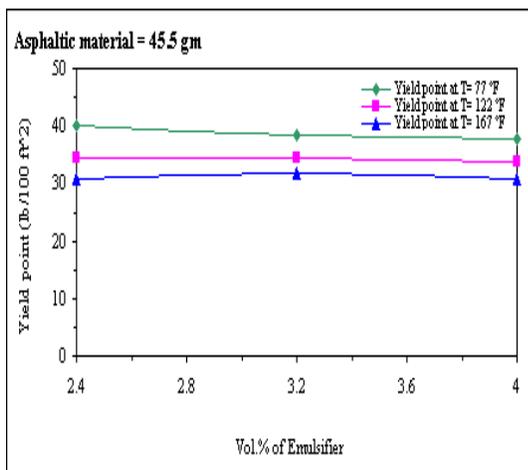
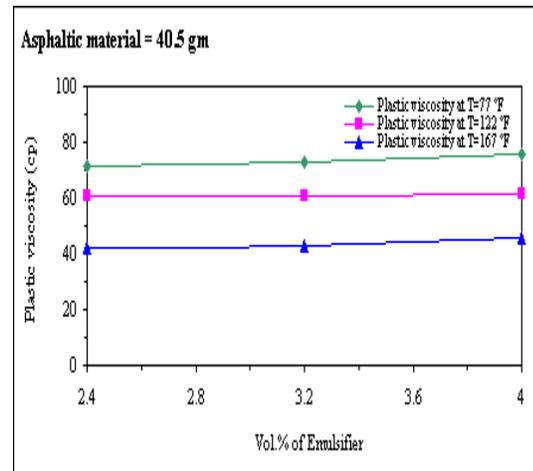
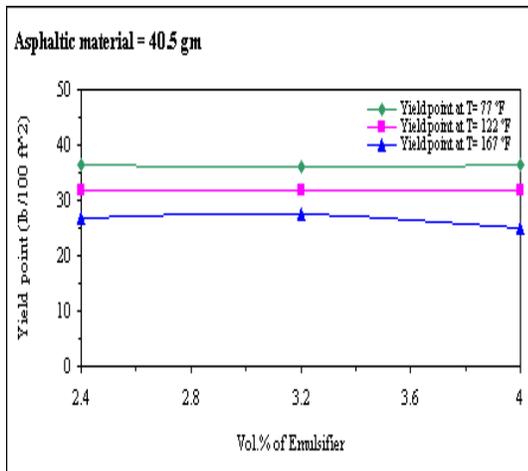
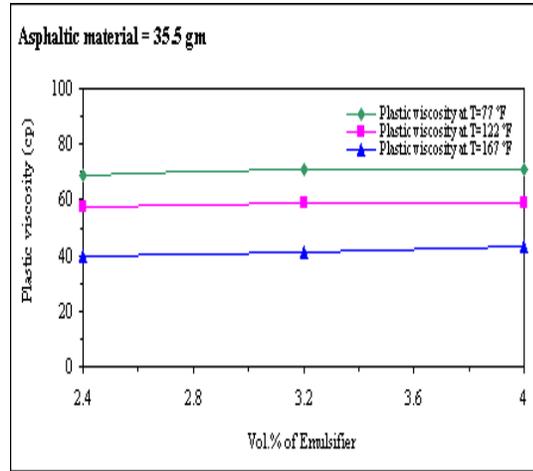
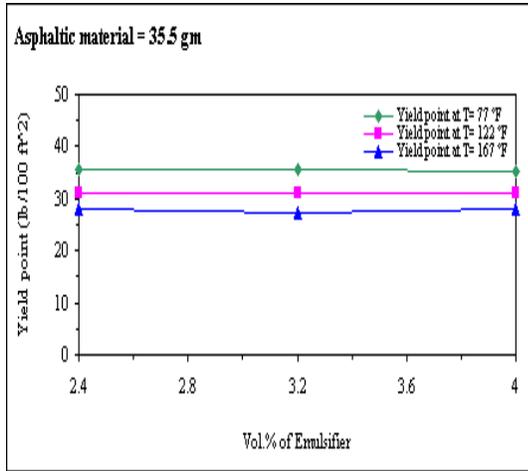


Fig. 7 Effect of Vol. % of Emulsifier on Yield point of Emulsions with Barite = 0.84 Vol. %

Fig. 8 Effect of Vol. % of Emulsifier on Plastic viscosity of Emulsions with Barite = 0.84 Vol. %

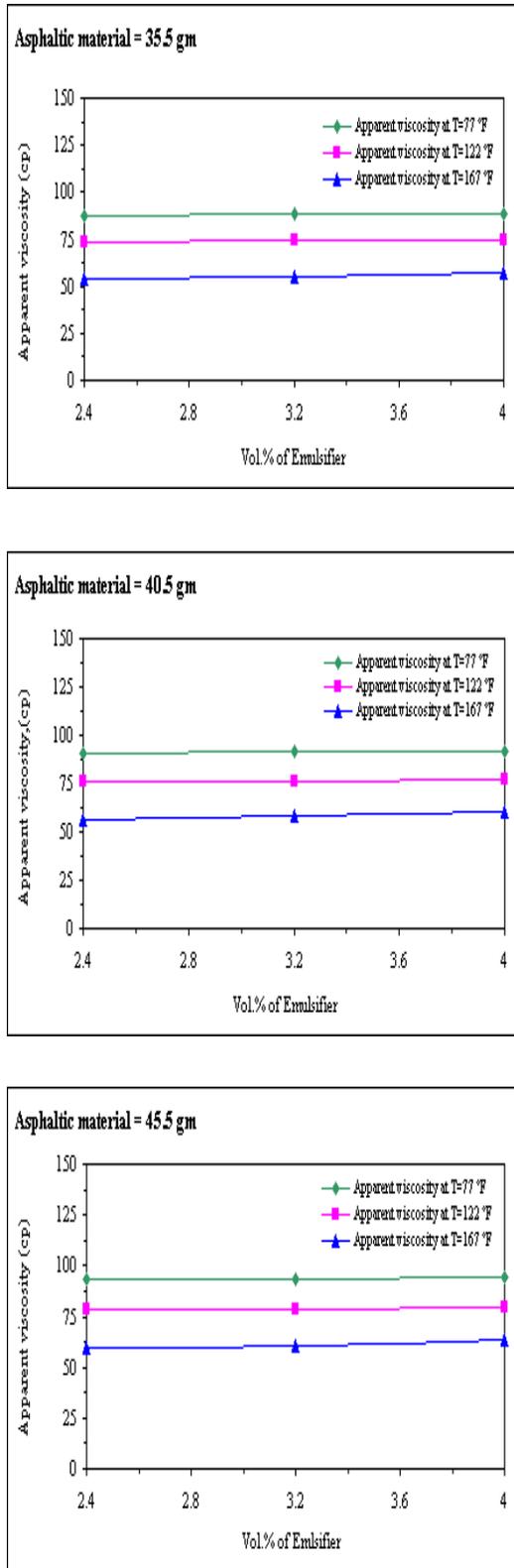


Fig. 9 Effect of Vol. % of Emulsifier on Apparent viscosity of Emulsions with Barite = 0.84 Vol. %

Conclusions

From the present study, one can conclude the followings:

- 1) The increase in the concentration of asphaltic material tends to increase the yield point, plastic viscosity and apparent viscosity of emulsions.
- 2) The increase in the volume percentage of barite tends to increase the yield point, plastic viscosity, and apparent viscosity of emulsions.
- 3) The emulsifier should 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 emulsions at 122, 167 °F, but its effect is clearly shown at room temperature (25°C) 77°F.

Nomenclature

Symbol	Meaning	Unit
η_p	Bingham plastic viscosity	cp
Y_p	Yield point	lb/100 ft ²
η_a	Apparent viscosity	cp
θ	Dial reading	deg

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تأثير الإضافات على الخواص الريولوجية للمستحلبات العكسية

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الخلاصة

يهتم هذا البحث بدراسة تأثير الاضافات على الخواص الريولوجية (نقطة الخضوع , اللزوجة اللدائنية واللزوجة الظاهرية) للمستحلبات .
تم تحضير 27 نموذج مستحلب , حيث كل المستحلبات المحضرة هي مستحلبات عكسية عندها تكون قطرات الماء منتشرة خلال زيت الديزل والنتيجة تسمى مستحلبات ماء – في – نפט .
وجد إن تأثير الإضافات على الخواص الريولوجية للمستحلبات هي كالآتي :زيادة تركيز المادة الاسفلتية يزيد من الخواص الريولوجية للمستحلبات , زيادة النسبة الحجمية للبارايت يزيد من الخواص الريولوجية للمستحلبات ايضا وزيادة النسبة الحجمية لعامل الاستحلاب له تأثير قليل على قيم الخواص الريولوجية ولكنه يزيد من استقرارية المستحلبات مع درجة الحرارة وذلك لأنه يحيط بقطرات الماء.