

Effect of Mixing Time and Temperature on the Rheology of Water/Oil Emulsion

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ABSTRACT

A study of temperature effect with a significant impact on rheology fluid, mixing time, and also volume fractions was carried out. In this study, the w/o emulsions were prepared into three volume ratios (30-70%, 40-60% and 50-50% w/o) and at mixing time (5, 15 and 30 minutes) by using one type of crude oil (Kirkuk). The w/o emulsions were stabilized, then characteristics were measured. The effective viscosity of water-in-oil emulsions depends mainly on the volume fraction, mixing time and temperature, along with several minor effects, such as shear rate, shear stress stream and viscosity of oil.

تأثير زمن الخلط ودرجة الحرارة على ريولوجي مستحلب ماء/نפט

الخلاصة

تم دراسة تأثير درجة الحرارة على ريولوجيا السائل وكذلك زمن الخلط والكسر الحجمي. حيث تم إعداد مستحلبات في ثلاثة نسب حجميه (30-70%, 40-60% and 50-50% w/o) وعند زمن خلط متغير (5، 15، و30 دقيقة) باستخدام نوع واحد من النفط الخام (خام كركوك). بعد استقرار المستحلب w/o تم قياس خصائص المستحلبات. ان لزوجة المستحلبات المائية في النفط تعتمد أساسا على الكسر الحجمي المائي في النفط الخام، زمن الخلط ودرجة الحرارة، جنبا إلى جنب مع عدة عوامل ثانوية، مثل معدل القص وإجهاد القص ولزوجة النفط الخام.

INTRODUCTION

An emulsion is a mixture of two or more immiscible (un-blendable) liquids. Emulsions are part of a more general class of two-phase systems of matter called colloids. Although the terms colloid and emulsion are sometimes used interchangeably, emulsion tends to imply that both the dispersed and the continuous phase are liquid.^(1,2,3,&4) Water is also injected into the crude to remove salts or as steam to improve fractionation. An emulsion is a colloidal dispersion of one liquid (disperse phase) in another (continuous phase)⁽⁵⁾. Petroleum emulsions (typically water-in-oil) readily form with water in the highly turbulent nozzles and piping used for oil production. These emulsions can increase pumping and transportation expenses, corrosion of pipes, pumps, production equipment and distillation columns and the poisoning of downstream refinery catalysts. It is well recognized that emulsion stability arises from the formation of elastic interfacial film^(6, 7).

Emulsions of crude oil and water can be encountered at many stages during drilling, producing, transporting and processing of crude oils and in many locations such as in hydrocarbon reservoirs, well bores, surface facilities, transportation systems and refineries. A good knowledge of petroleum emulsions is necessary for controlling and improving processes at all stages. Many studies have been carried out in the last 40 years and have led to a better understanding of these complex systems^(4, 5).

Mixing immiscible liquids such as oil and water with a surface active agent will often yield an emulsion of oil droplets in water (oil-water) or water droplets in oil (water-oil) according to Bancroft's rule⁽⁶⁾.

In general, emulsions contain a polar and a non-polar liquid phase. The former is usually water or a solution of electrolytes, polymers or other chemicals in water, and it is termed the water (W) phase. The latter refers to liquids such as hydrocarbons, triglycerides and silicone fluids, among others, and it is commonly named the oil (O) phase. Molecules exhibiting both non-polar (hydro- or fluorocarbon chains, naphthenic or aromatic rings) and polar groups (structures with heteroatoms O, S and N) might be present as small fractions of these phases.

An emulsion can be classified according to different criteria, the most important being the morphology or spatial arrangement of the phases (Figure.A)^(4, 5, 9). The two most common types are emulsions of water dispersed in oil (W/O) and oil dispersed in water (O/W)⁽⁶⁾. For W/O emulsions, water is considered the dispersed or internal phase, and oil is the continuous or external phase, and conversely for the O/W type. More complex morphologies such as mixed emulsions in which more than one dispersed phase is present [(O₁ + O₂)/W or (W₁ + W₂)/O] and multiple emulsions, say W/O/W (in which a water phase is dispersed within the droplets of the oil phase, and the latter in another aqueous phase) and conversely O/W/O are also relevant in some cases^(6, 7, 8).

Finally, the process through which an emulsion is formed is called emulsification. Emulsification can be induced by the action of devices such as a turbine blender, an of measuring the emulsion viscosity is described. The accuracy and reproducibility of the results obtained in this work are discussed.

RHEOLOGY

Rheology in general is defined as the study of the flow deformation and flow of materials under influence of an applied shear stress. The rheological behavior of emulsions has been of great interest not only for fundamental scientific understanding but also for practical industrial applications^(5,6,7).

The rheological behavior of an emulsion can be either Newtonian or non-Newtonian depending upon its composition. At low to moderate values of dispersed phase concentration, emulsions generally exhibit Newtonian behavior. In the high concentration range, emulsions behave as shear-thinning fluids^(5, 6, 7).

Materials

The properties of crude oil used in this study are shown in table.1.

Table(1) Crude oil properties⁽¹⁷⁾

Charectrastion	Crude oil (Kirkuk)
API gravity at 15.6°C	35.8
Specific gravity at 15.6°C	0.845
Kinematic viscosity at 10°C	9.55
21.1°C	7.29
37.8°C	4.78
H ₂ S %wt	0.0012
Pour point °C	Below-26
Salt content ppm	50 max.
Asphaltene % wt	1.25
Vanadium ppm	20
Nickel ppm	9

EXPERIMENTAL WORK

The experimental setup and resources used in this work, together with the procedures of executing the (Brookfield DV-II + Rheometer) experiment and emulsion preparation are described.

Water-in-crude oil emulsions were prepared by dispersing brine (3.5 wt. % NaCl) in crude oil. No additives were used to stabilize the emulsions. Here the viscosities were measured with a Brookfield DV-II+ rheometer. For bulk fluid viscosity measurements, a spindle (type SC-27, viscosity range = 1.3 - 30,000 mPa.s) is immersed in a cylindrical cell containing approximately 10 mL of sample, and it is further set to rotate at a given angular velocity.

The principle of operation of this unit is to drive a spindle which is immersed in the test fluid. The viscous shear streams of the fluid against the spindle are measured by the spring deflection. This spring as a shear force deflection is measured with a rotary transducer. The measuring range of the unit (in centipoises) is determined by the rotational speed of the spindle, the size and shape of the spindle, the container the spindle is rotating in i.e. by the clearance between the spindle and its contained and the full scale torque of the calibrated spring.

Before any measurement was made, the rheometer was checked with a calibration fluid (Brookfield Standard Fluid, 516 cp at 25°C). The rheometer was thoroughly cleaned between measurements of different emulsion samples. The setup described in (Figure.B) was used for emulsion preparation. A schematic diagram for the spindle and sample holder that were used to measure the emulsions' viscosities in this experiment are shown in (Figures C).

Variables, such as viscometer and spindle type, sample container size, sample temperature, bulk fluids used and the emulsion sample preparation technique, all contribute to affect the accuracy of viscosity measurements. To prevent errors, those variables were kept constant during each set of measurement. Brookfield Viscometers are designed to be accurate to within $\pm 1\%$ of the full-scale range of the spindle/speed combination in use.

It is also worth mentioning that during emulsion preparation, the glass tubes' cleanliness and the mixer position were found to have significant effects on the reproducibility of the results. For these reasons, the normal cleaning with toluene and acetone was performed. During the initial experiments, the mixer was placed in the center of the sample and operated directly at the desired speed of 2000 rpm (by mixing range) for 5, 15 and 30 minutes.

RESULTS AND DISCUSSIONS

Mixing Time Effects

It is to be noted from Figures 1, 2 & 3 that the apparent change in the curves different depending temperatures starting from the first point at 5 minutes up to 30 minutes, causing increased time of mixing to increase the interference between the particles of the emulsion, which leads to increased viscosity with increasing time of mixing, as in the forms mentioned above. Also to be noted is the difference between the curves in Figured

(1) for the curves in Figure (2) and (3) as the first point of each curve in Figure (1) is located in the range (100 to 400) while in Figure (2) (200 to 800) In Figure (3) (250 to 1200). This difference is caused by the proportion of water in oil emulsion.

The influence of mixing time can be clearly observed, so the higher viscosity increased when mixing time increased because high cohesion between the oil and water particles. The change in viscosity level with the mixing time at different temperatures. At the lowest temperature 15°C higher viscosity is seen than for other temperatures respectively 20°C, 30°C and 40°C can be shown in figures.1, 2, & 3. The viscosity of water-in-oil emulsion increases with increasing the water cut before reaching what is called inversion point, beyond which the continuous phase changes to water. During the experimental work, the highest stable emulsion that can be observed (without seeing any separation) was about 50% water cut.

Effect of Temperature and Shear Rate

Figures(4, 5 and 6) show almost stable disposition with the marked difference in the level curves with different temperatures and change in level of viscosity rise slightly with increasing mixing time existence varying slightly in some curves such as the curve in Figure (5) at 15°C and 20°C as well as Figure (6) at a temperature of 15°C and 20°C due to the stability of viscosity with shear rate at temperature increase where curves at a temperature of 40°C more stability than other grades as seen in Figures (7, 8, 9, 10, 11 and 12).

It should be mentioned that this data reported in all Figures (4 to 12) were not taken at same shear rates due to the limitation of viscometer used and the wide range of shear rate. Instead, the viscosity at highest shear rate at each temperature is taken because the Brookfield Viscometers are designed to be more accurate at highest torque. For low temperatures, the viscosity varies with shear rate, indicating that the emulsions behave as non-Newtonian fluids. At lower temperatures, the presence of paraffinic crystals formed may provoke the non-Newtonian behavior.

CONCLUSIONS

From an analysis of the experimental data obtained for the rheology of the crude oil studied and its emulsions at different temperatures and dispersed phase volume fractions, at 50% water cut, emulsion viscosity increase from about 200 cp at 40°C to above 1800 cp at 15°C.

Viscosity of emulsions increases by almost two orders of magnitude with higher water cut. The highest stable emulsion viscosity was observed at 50% water cut. The rise curve was also predicted in Figure (12) at curve 15°C to be about 50% where the highest viscosity was also observed.

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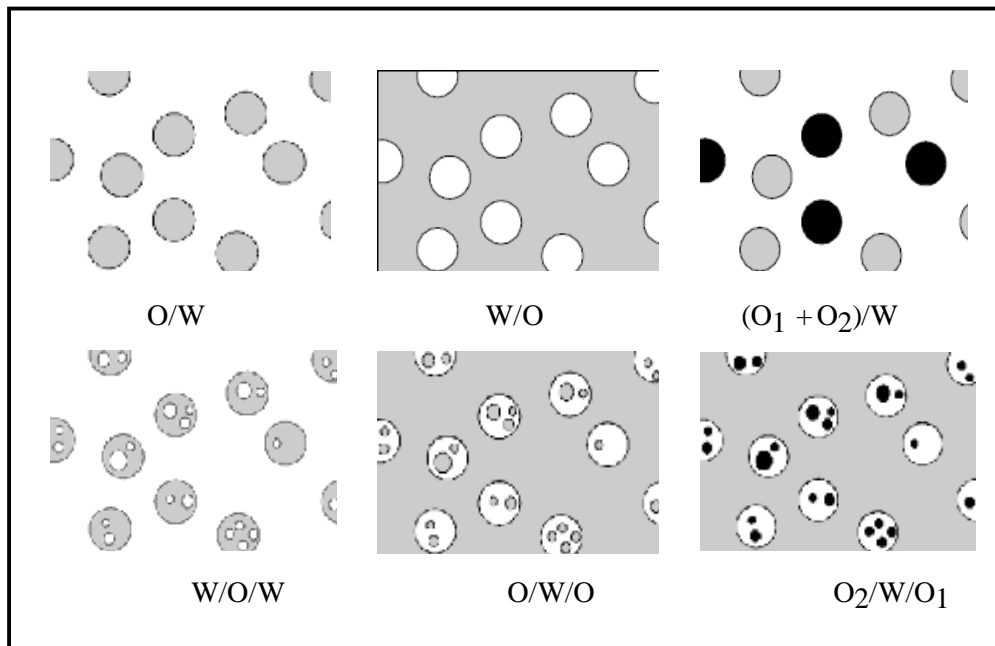


Figure (A) Common emulsion morphologies

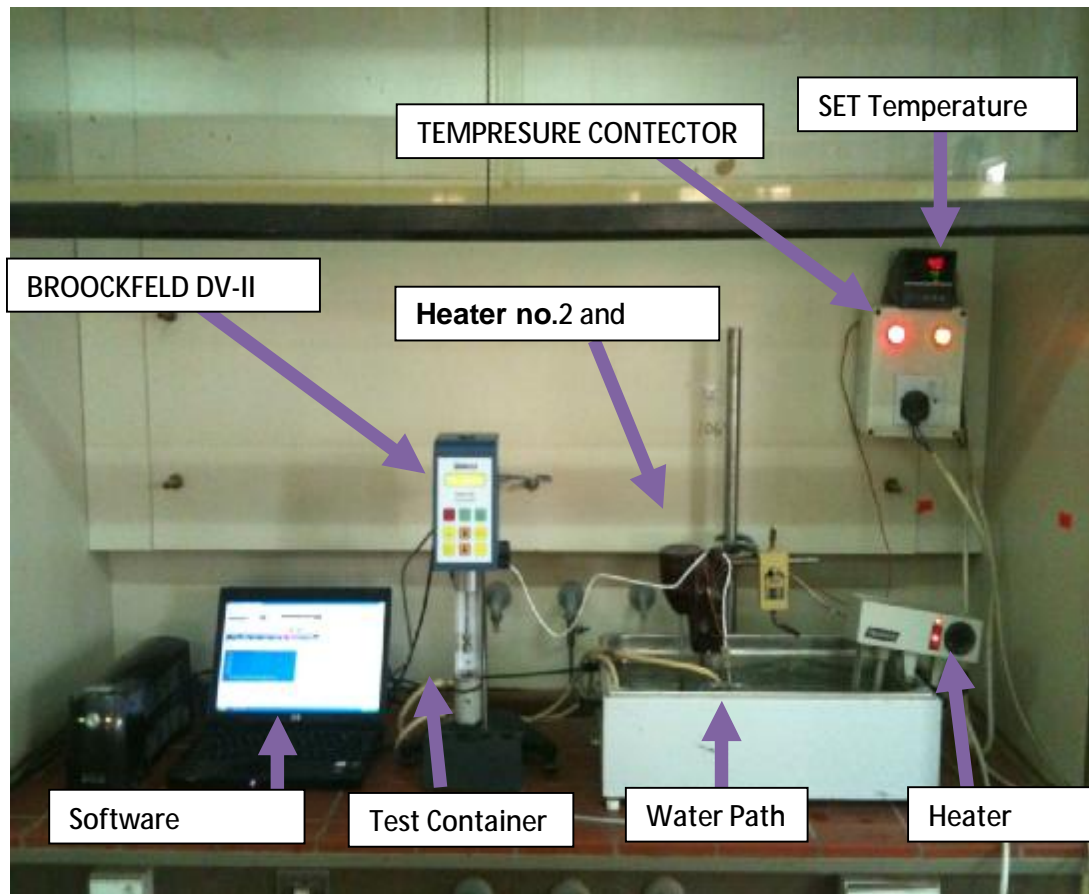
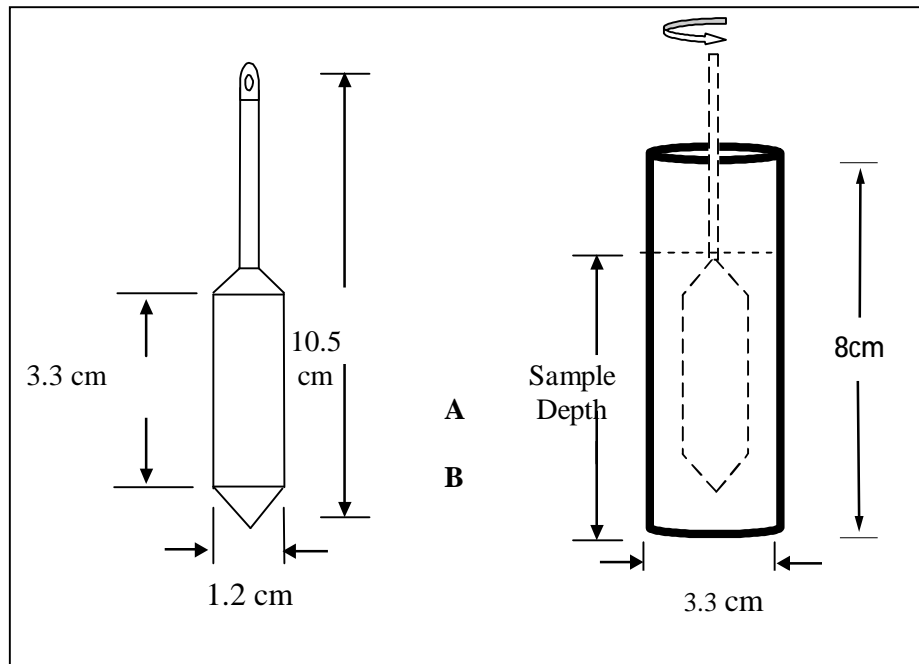


Figure (B) Schematic diagrams for the emulsion viscosity measurements



Figure(C) Schematic diagrams for the SC-27 spindle (A) and (B) sample

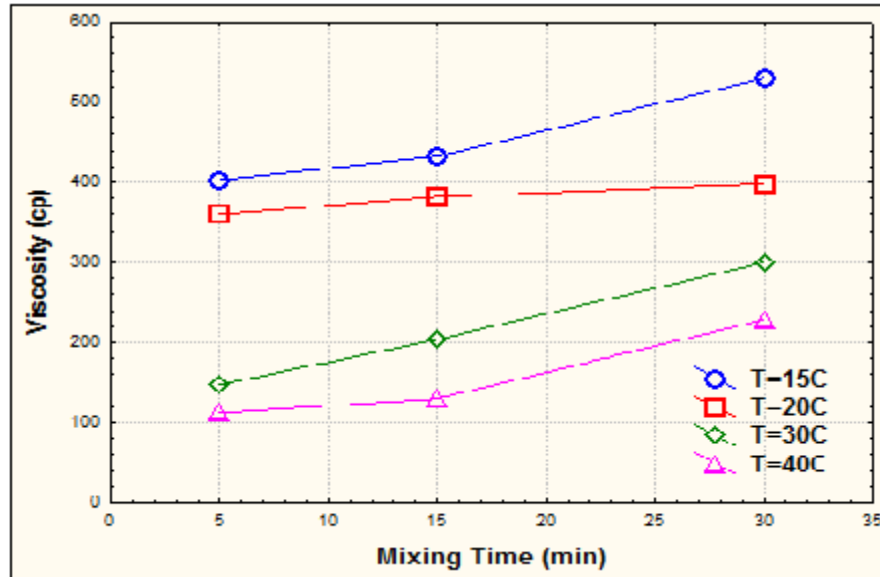


Figure (1) Effect mixing time vs viscosity at (70%Oil, 30%water) & different temperatures

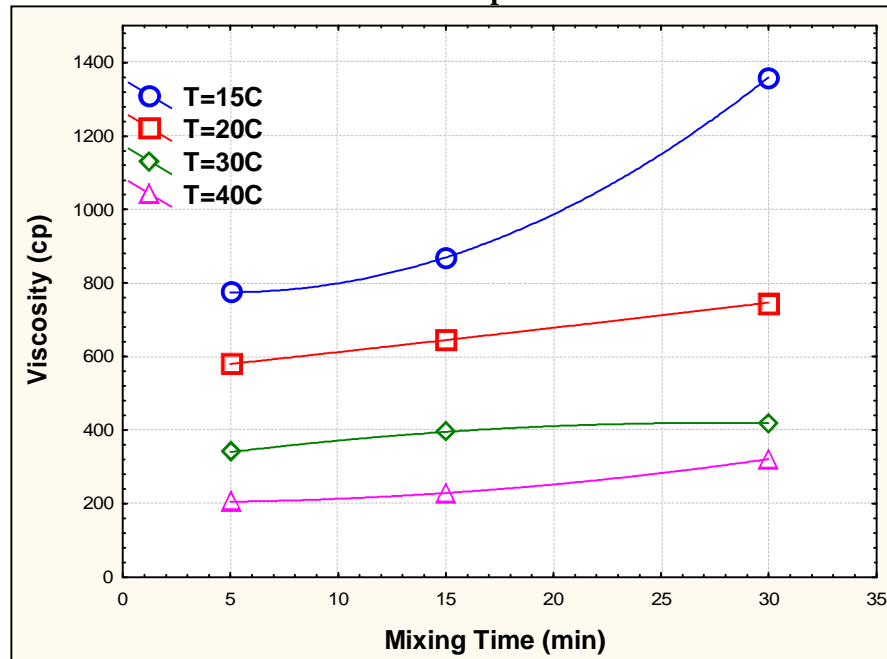


Figure (2) Effect mixing time vs viscosity at (60%Oil, 40%water) & different temperatures

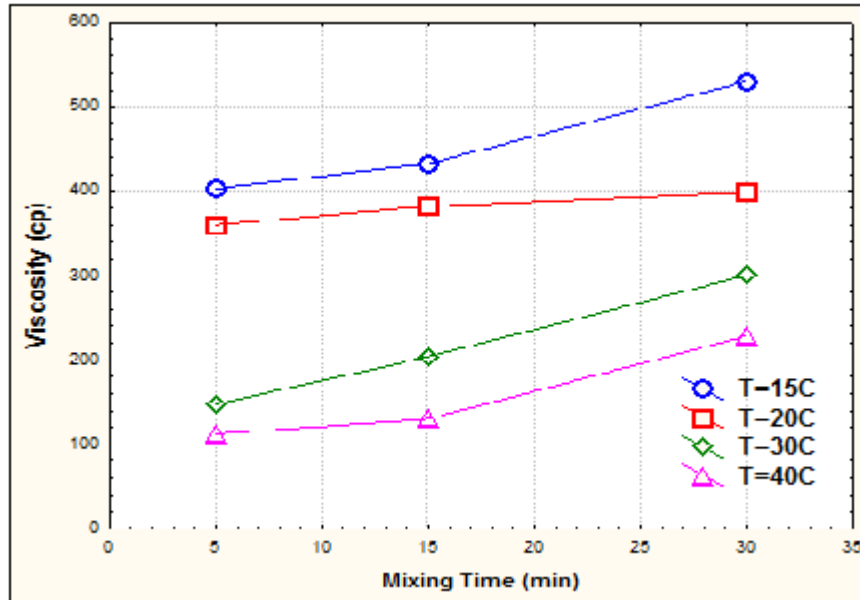


Figure (3) Effect mixing time vs. viscosity at (50%Oil, 50%water) & different temperatures

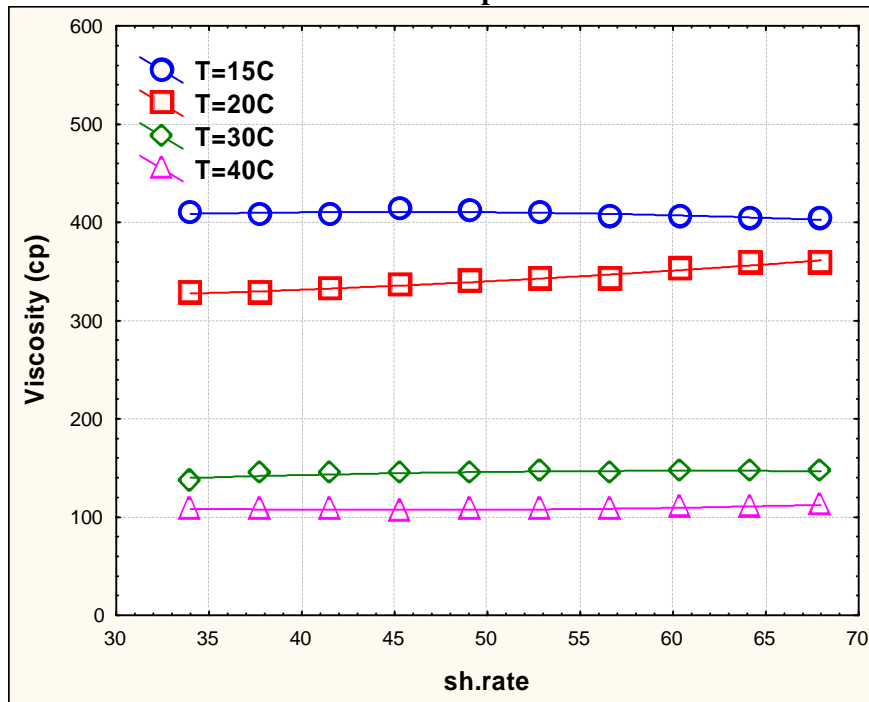


Figure (4) Effect Sh.rate vs. viscosity at (70%Oil, 30%water)

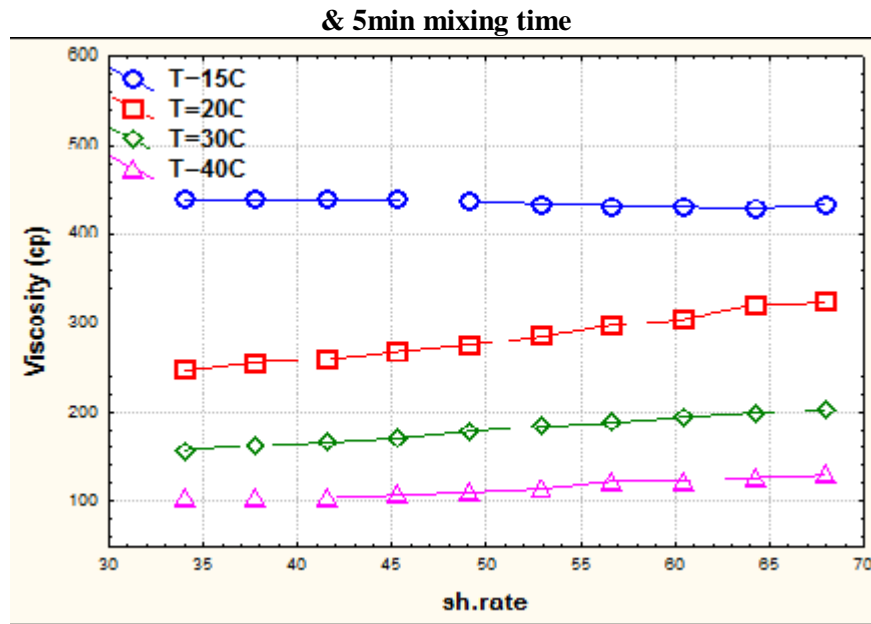


Figure (5) Effect Sh.rate vs. viscosity at (70%Oil, 30%water) & 15min mixing time

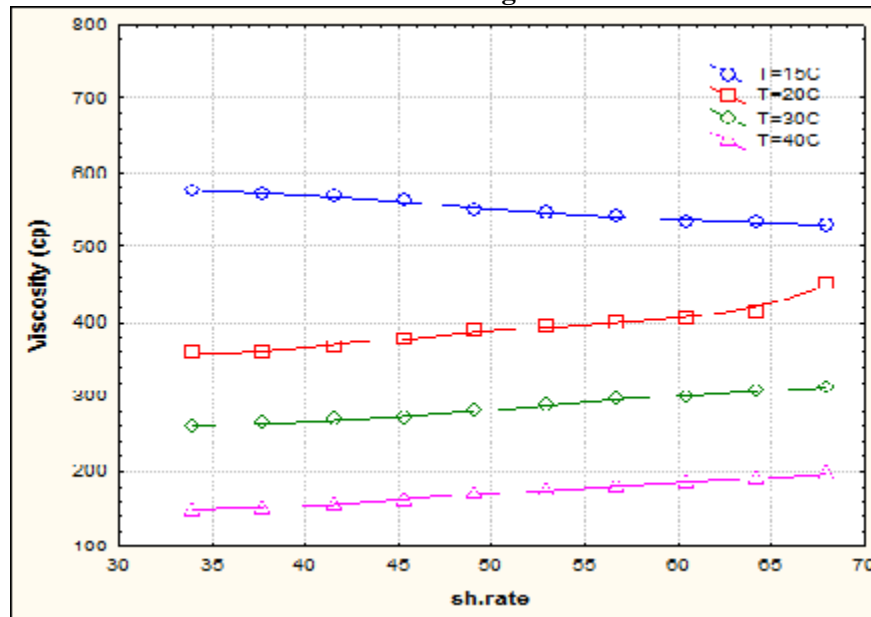


Figure (6) Effect Sh.rate vs. viscosity at (70%Oil, 30%water)

& 30min mixing time

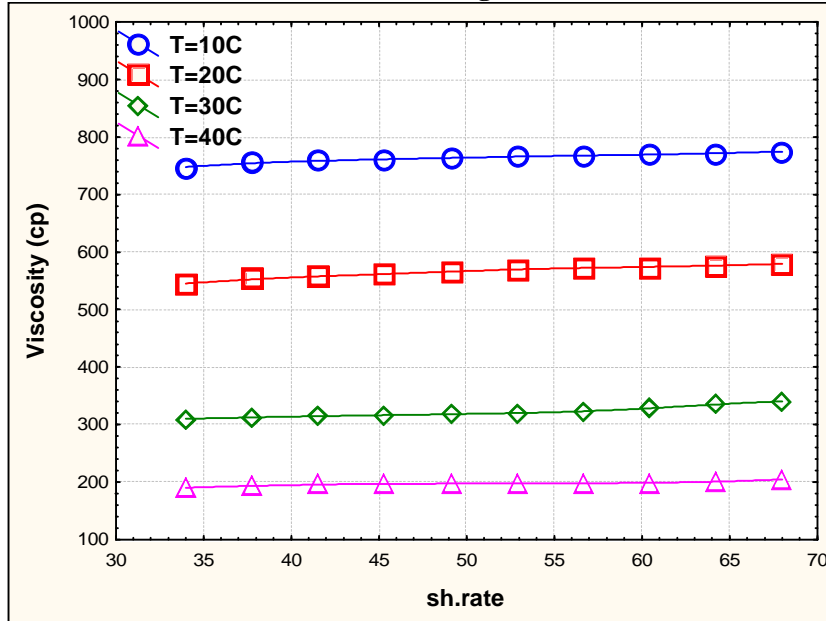
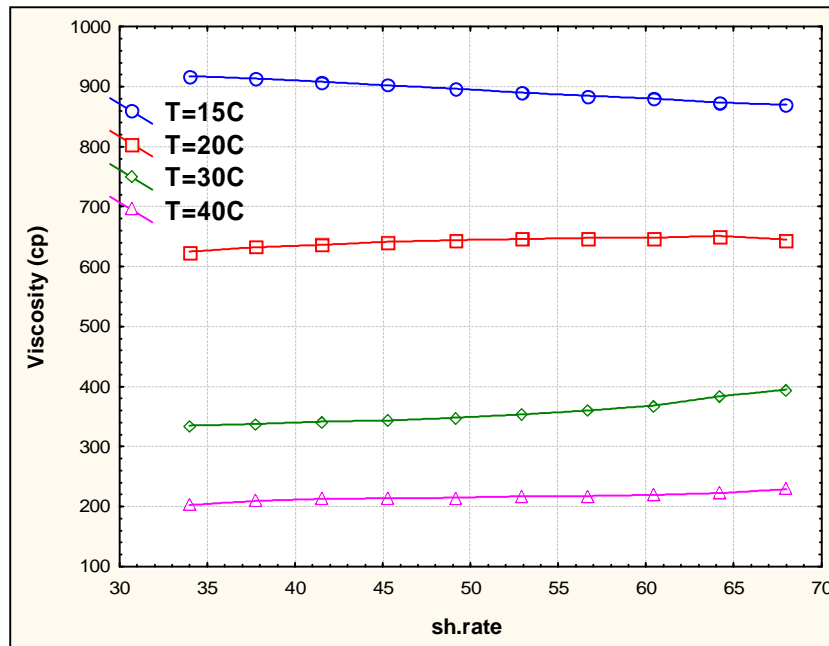


Figure (7) Effect Sh.rate vs. viscosity at (60%Oil, 40%water) & 5min mixing time



Figurer (8) Effect Sh.rate vs. viscosity at (60%Oil, 40% water) & 15min mixing time

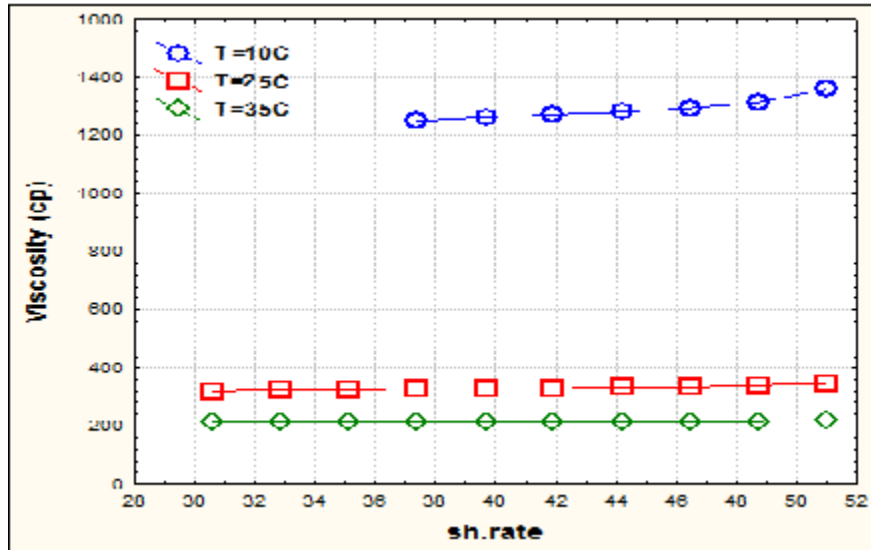


Figure (9) Effect Sh.rate vs. viscosity at (60%Oil, 40%water) & 30min mixing time

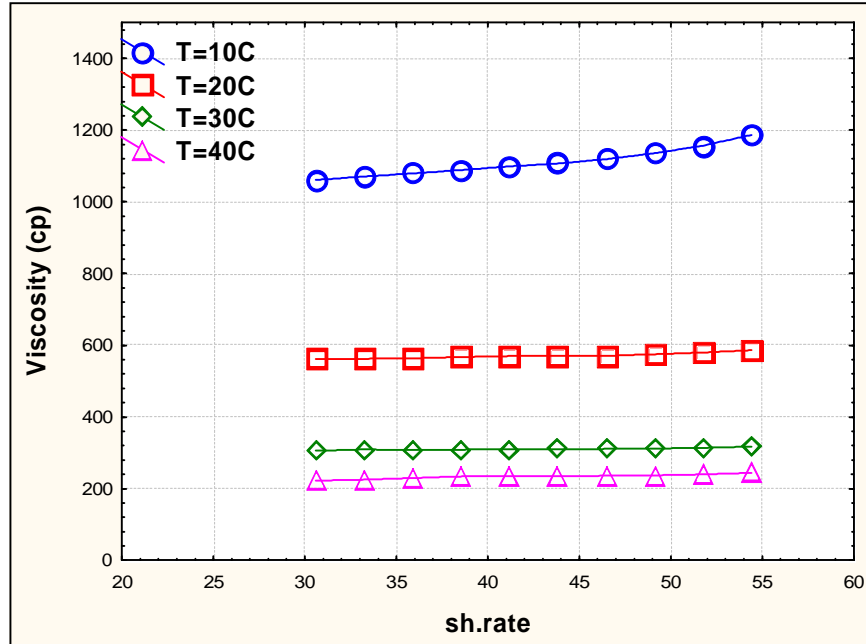


Figure (10) Effect Sh.rate vs. viscosity at (50%Oil, 50%water) & 5min mixing time

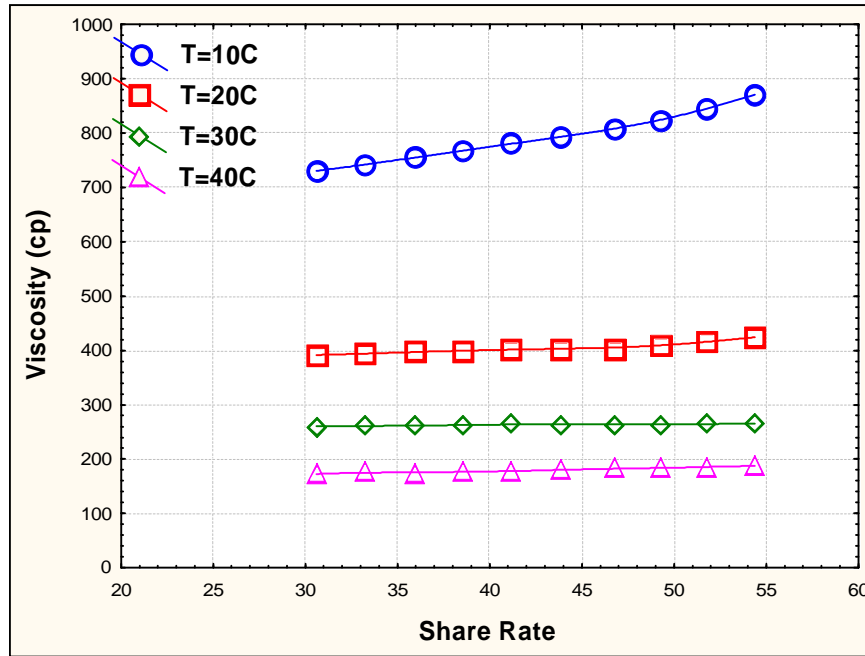


Figure (11) Effect Sh.rate vs. viscosity at (50% Oil, 50% water) & 15min mixing time

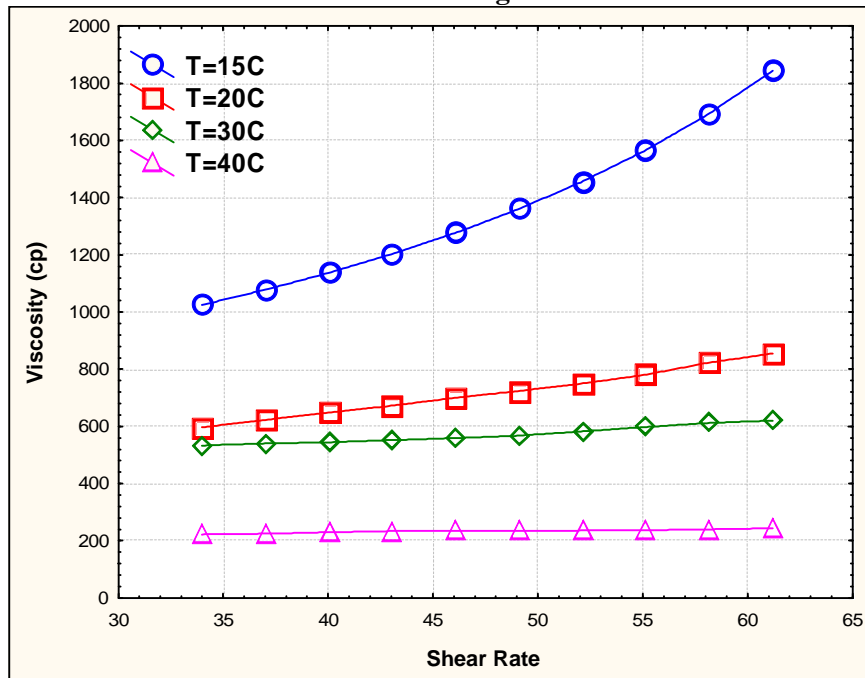


Figure (12) Effect Sh.rate vs. viscosity at (50% Oil, 50% water) & 30min mixing