

## CHAPTER IV

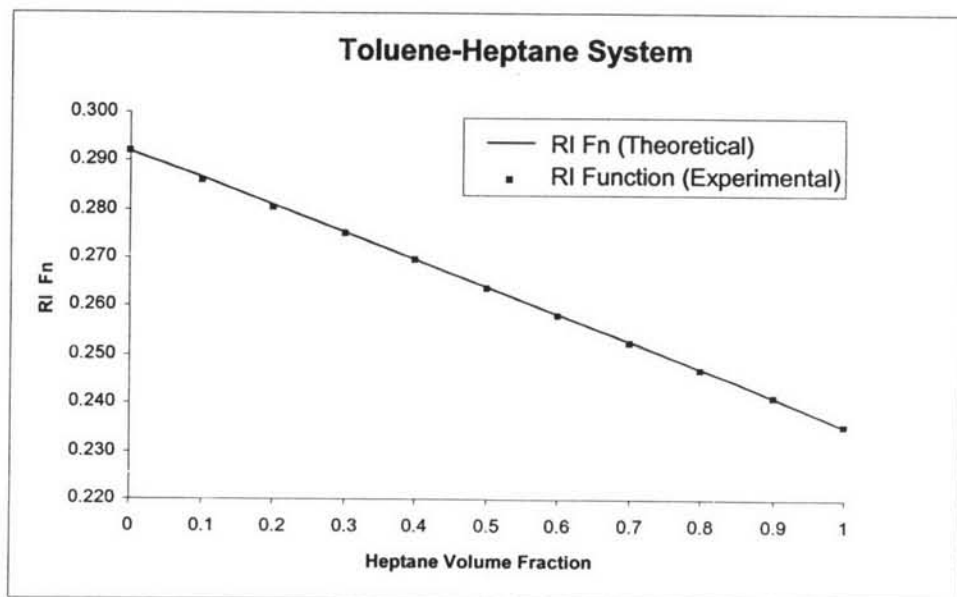
### RESULTS AND DISCUSSION

#### 4.1 Asphaltene Precipitation Onset by Refractive Index Measurement

As discussed in the previous chapter, the onset of asphaltene precipitation was detected from the deviation of the refractive index function from the linearity as precipitant was added to crude oil.

##### 4.1.1 Results for Model System

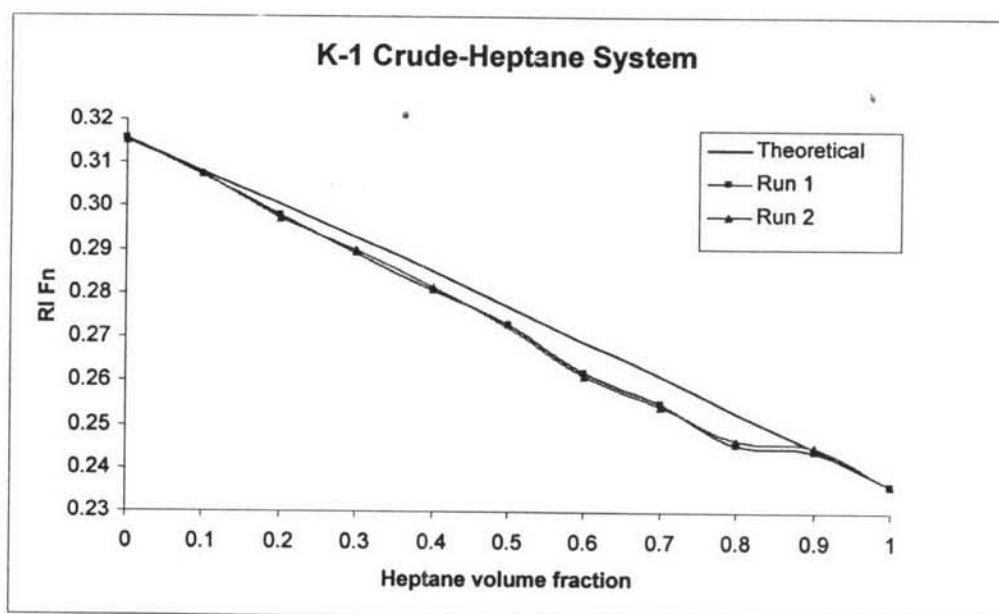
In order to establish confidence in the technique, a model system of toluene and heptane was studied. Figure 4.1 verifies the linear relationship between the refractive index function (RI Fn) and the volume fraction of the individual components of the mixture. RI Function is defined as  $RI Fn = ((n^2 - 1)/(n^2 + 2))$ , where  $n$  is the refractive index of the mixture.



**Figure 4.1** Refractive index function of toluene-heptane mixture as a function of heptane volume fraction.

#### 4.1.2 Results for Crude Oil

Similar titration experiments were carried out with K-1 crude oil and heptane. The results are shown in Figure 4.2.



**Figure 4.2** Refractive index function of K-1 crude-heptane mixture as a function of heptane volume fraction.

These results show that the refractive index function of the crude-heptane mixture deviates at heptane volume fraction of 0.1, the first addition of heptane. It has been discussed in section 2.3 that the deviation from linearity is due to the fact that when asphaltenes precipitate out, they do not contribute to the refractive index of the mixture. This indicates that for Figure 4.2, asphaltenes start to precipitate out at heptane volume fraction of 0.1.

From field observations of K-1 crude, it is known that asphaltenes do not start precipitating until the heptane volume fraction is about 0.5. Therefore, the results in Figure 4.2 do not match with field observations. Further investigations which were carried out to rectify this inconsistency are discussed below.

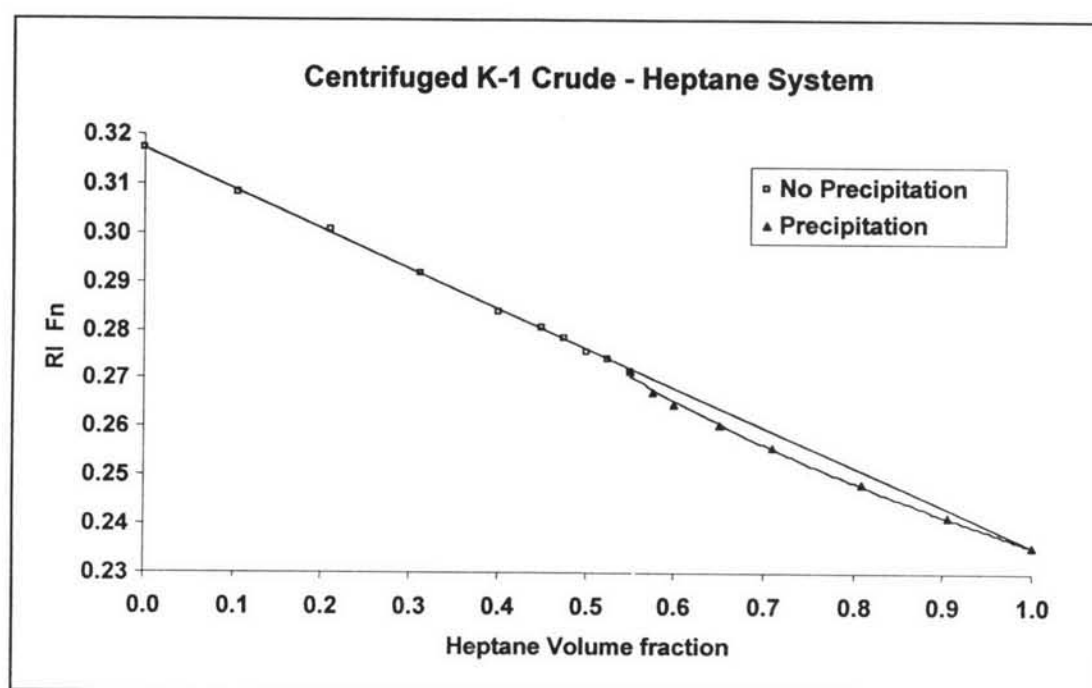
The crude oil sample was observed under the microscope to verify its homogeneity. Small droplets of water were observed in the sample which could affect the results in Figure 4.2.

#### 4.1.2.1 Water Content of K-1 Crude

The water present in the crude oil was removed by centrifugation at 2500 rpm (relative centrifugal field = 1300 g) for ten hours. Samples of uncentrifuged and centrifuged K-1 crude oil were sent to ConocoPhillips for water content analysis by COSA CA-100 Karl Fischer Moisture-meter. The moisture content of uncentrifuged K-1 crude was found to be 10.65 weight % and that of centrifuged K-1 was 0.53 weight %. This confirms that the centrifugation could successfully remove almost all the water in K-1 crude oil.

#### 4.1.2.2 Onset Experiments After Centrifugation

The results of titrating centrifuged K-1 crude oil with heptane are shown in Figure 4.3. The onset of asphaltene precipitation was observed to be at a heptane volume fraction of about 0.55.

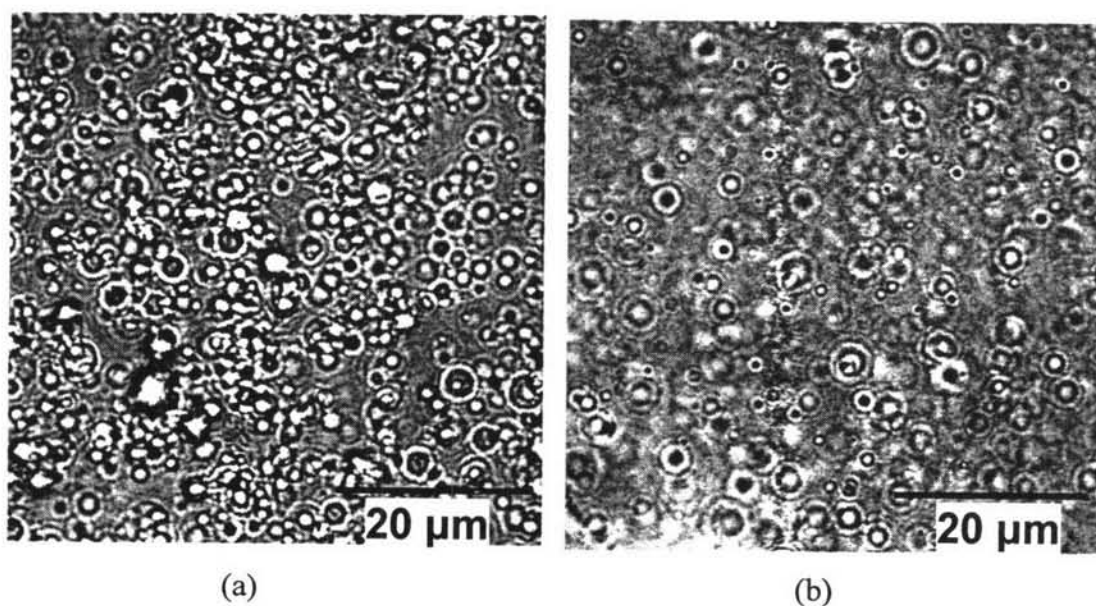


**Figure 4.3** Refractive index function of centrifuged K-1 crude-heptane mixture as a function of heptane volume fraction.

It can be concluded from this experiment that the presence of water in crude oils affects the determination of onset point for asphaltenes precipitation.

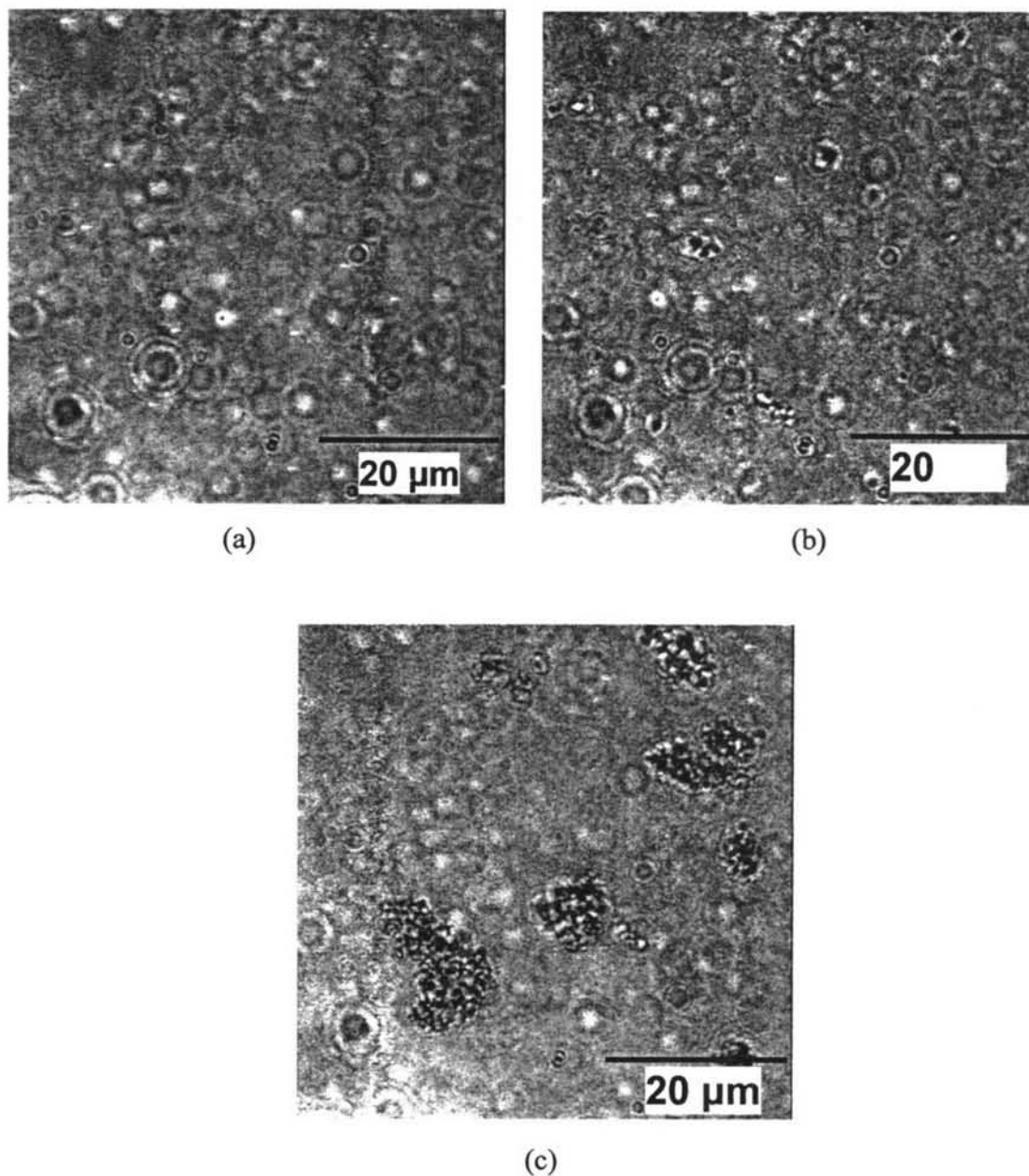
#### 4.2 Onset Study by Microscopy

Samples of the crude oil and its mixture with heptane were observed under an optical microscope to study their homogeneity. Figure 4.4 shows the difference between the crude oil before and after centrifugation. Prior to centrifugation, the crude oil was not homogeneous and large water droplets could be easily seen in it while the centrifuged crude oil consisted of very small amount of water droplets.



**Figure 4.4** Micrographs of K-1 crude oil : (a) Uncentrifuged crude [10.65 weight % water] (b) Centrifuged crude [0.53 weight % water] (magnification: 100x).

Figure 4.5 shows the crude oil - heptane mixtures with increasing amount of heptane. A mixture containing 52.5 volume % heptane did not show any signs of asphaltene precipitation. The mixture containing 55.0% heptane shows formation of very small asphaltene particles, indicating the onset of asphaltene precipitation. For the mixture containing 57.5 % heptane, asphaltene precipitation is evident.



**Figure 4.5** Crude oil - heptane mixtures with increasing amount of heptane (a) 52.5 volume % heptane (b) 55.0% heptane and (c) 57.5 % heptane (magnification: 100x).

These tests confirm the results for asphaltene precipitation onset obtained from the refractive index technique for the centrifuged crude oil as discussed in the previous section.

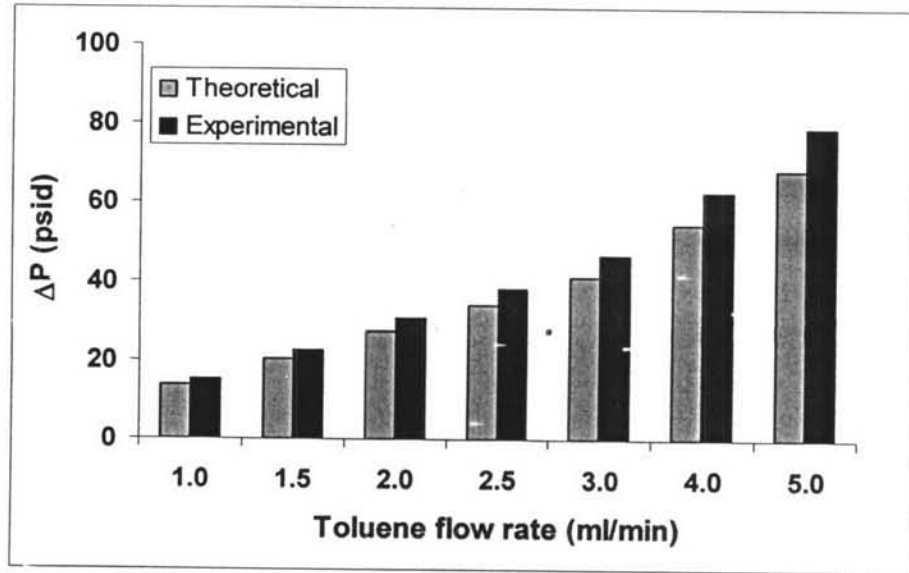
### 4.3 Design and Testing of Equipment for Asphaltene Deposition

The experimental setup for investigating asphaltene deposition was designed and assembled as discussed in the previous chapter. It was important to test the accuracy of the designed experimental setup before actual deposition experiments could be carried out.

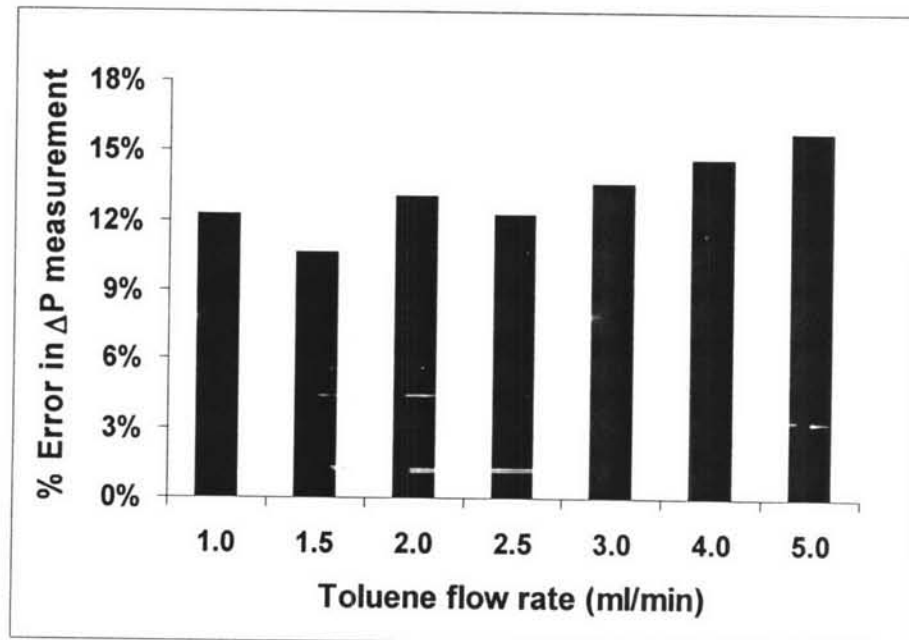
Tests were performed by flowing toluene through the system and measuring the pressure drop across the capillary. The objective was to compare the experimentally measured pressure drop values to the values predicted by the Hagen-Poiseuille equation:

$$\Delta P = \frac{8\eta}{\pi r^4} LQ \quad (4.1)$$

Figure 4.6 shows the results of these tests. The experimental values were found to be greater than theoretical values for all flow rates of toluene. The magnitude of the error between the theoretical and experimental values for the pressure measurement is shown in Figure 4.7. It is important to understand the reason why the pressure readings are high, because this error could yield misleading results, suggesting deposition of asphaltenes in actual experiments when none is actually occurring.



**Figure 4.6** Theoretical and experimental values of pressure drop across the capillary for different flow rates of toluene.



**Figure 4.7** Error between theoretical and experimental values of pressure drop for different flow rates of toluene.

### 4.3.1 Investigation of Factors That Could Cause Error in Pressure-Drop Measurement

The accuracy of the pressure transducers and data acquisition software has been established as discussed in the experimental section. Other possible factors and tests conducted to determine the cause of the error are discussed here.

#### *4.3.1.1 Flow Rate*

The flow rate of the pump was measured by noting the time required to pump a specified volume of fluid and was found to have an error of +/- 1.0 %. This was repeated for different flow rates with similar results, indicating that the error in pressure measurement could not be attributed to an error in flow rates.

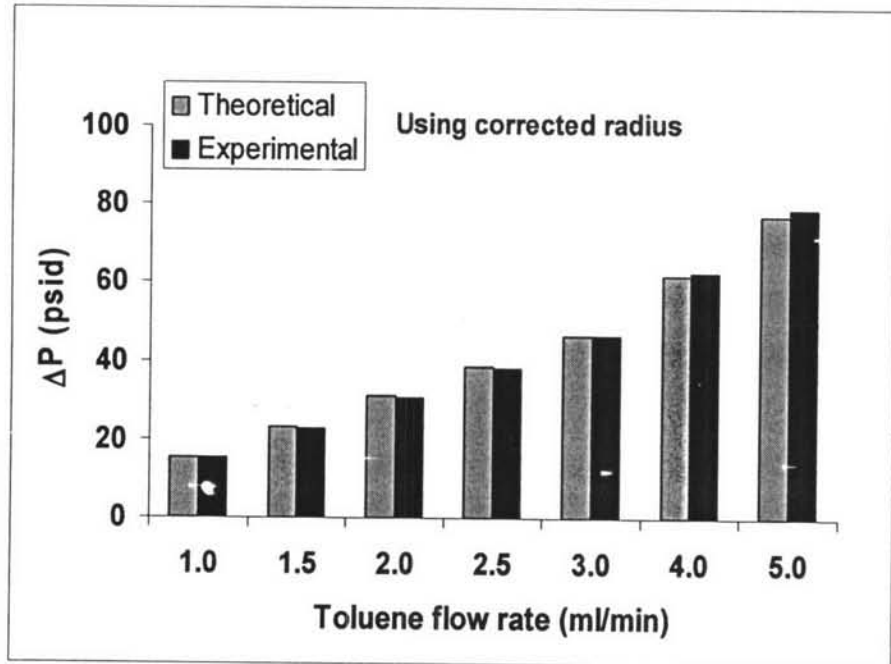
#### *4.3.1.2 Viscosity*

The actual viscosity of toluene sample at room temperature may not have been equal to its theoretical viscosity, possibly due to contamination, leading to an error in pressure drop values. The tests were repeated with new samples of toluene. Similar tests were conducted with heptane as well. All of these tests showed similar trends as seen in Figures 4.6 and 4.7, indicating that the viscosity of samples was not contributing to the error in the pressure measurement.

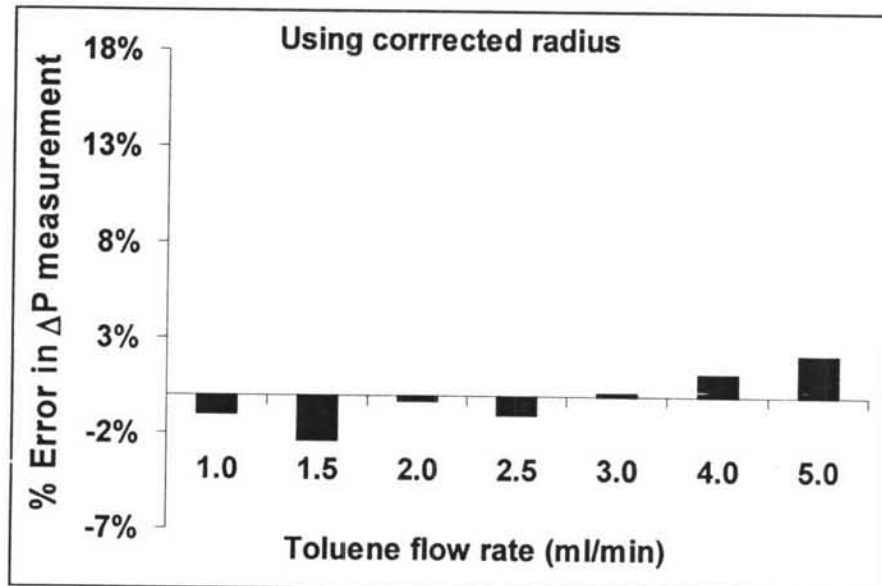
#### *4.3.1.3 Radius of Capillary*

The radius of the capillary tube is another factor that could lead to a higher pressure drop. The radius reported by the manufacturer was 0.254 mm. This value was used to calculate the theoretical pressure drop in Figure 4.6. Using the experimental data from Figure 4.6 to fit the Hagen-Poiseuille equation, the corrected radius was found to be 0.246mm. This radius measurement is within 3.2% of the radius claimed by the manufacturer, which is within the tolerance limits of +/- 5.0% specified by the manufacturer. Figures 4.8 and 4.9 show that with the new radius, the error in pressure-drop measurement was significantly reduced, to less than 2%. Therefore, the corrected radius was used in all subsequent calculations.





**Figure 4.8** Theoretical and experimental values of pressure drop across the capillary for different flow rates of toluene, using corrected radius for the calculations.

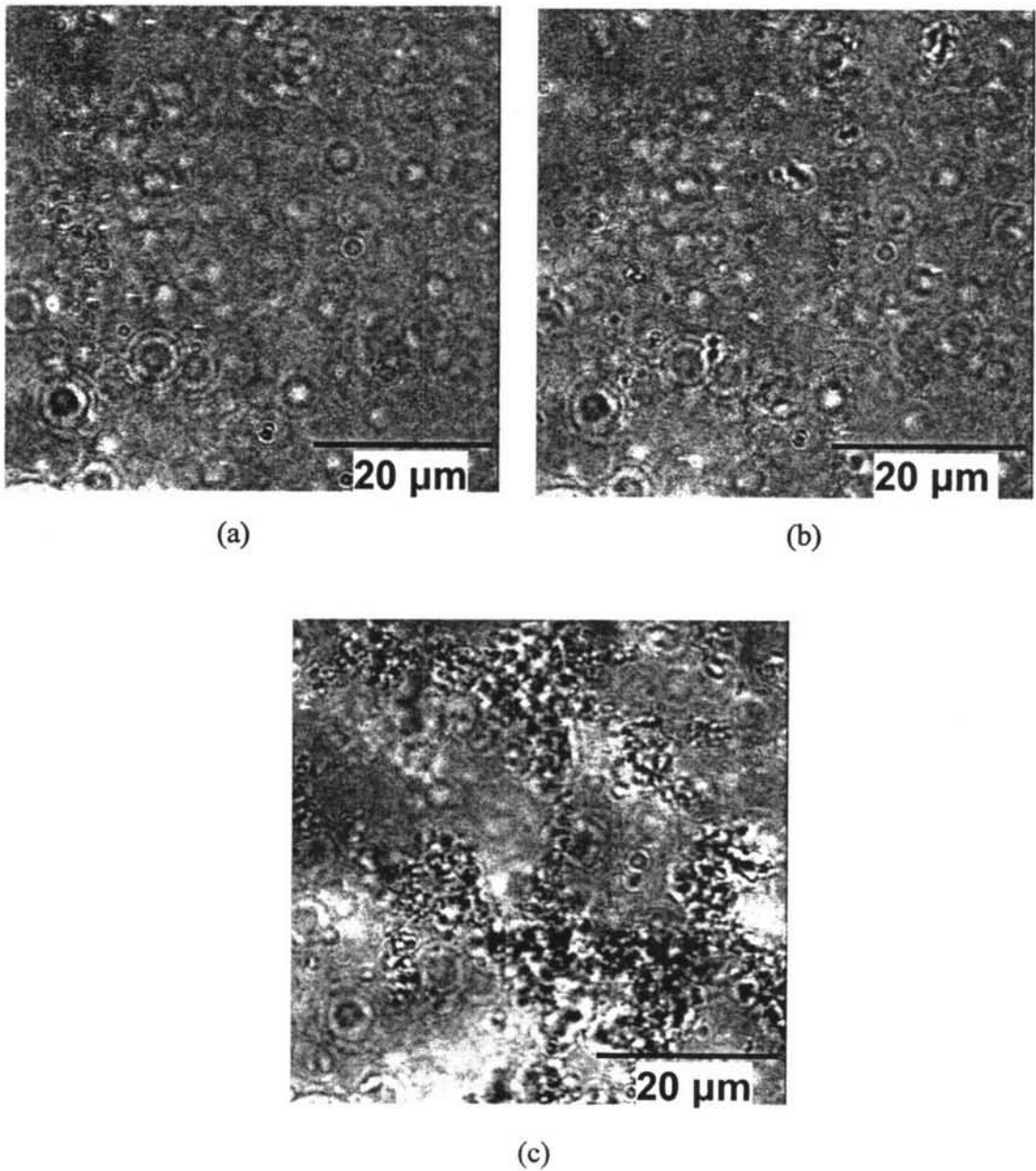


**Figure 4.9** Error between theoretical and experimental values of pressure drop for different flow rates of toluene, using corrected radius for the calculations.

#### 4.4 Improvements Made in the Deposition Apparatus

As discussed in section 2.5, in the experiments conducted by Wang *et al.* (2004), asphaltenes may already precipitate out in the connecting tubing before entering the capillary. In order to eliminate the precipitation of asphaltenes before entering the capillary, the ultrasonic bath was replaced by a mixing-tee with a 10-micron frit. The mixing-tee was connected directly to the capillary tubing, minimizing the residence time between mixing and the entrance to the capillary to less than 2.5 seconds.

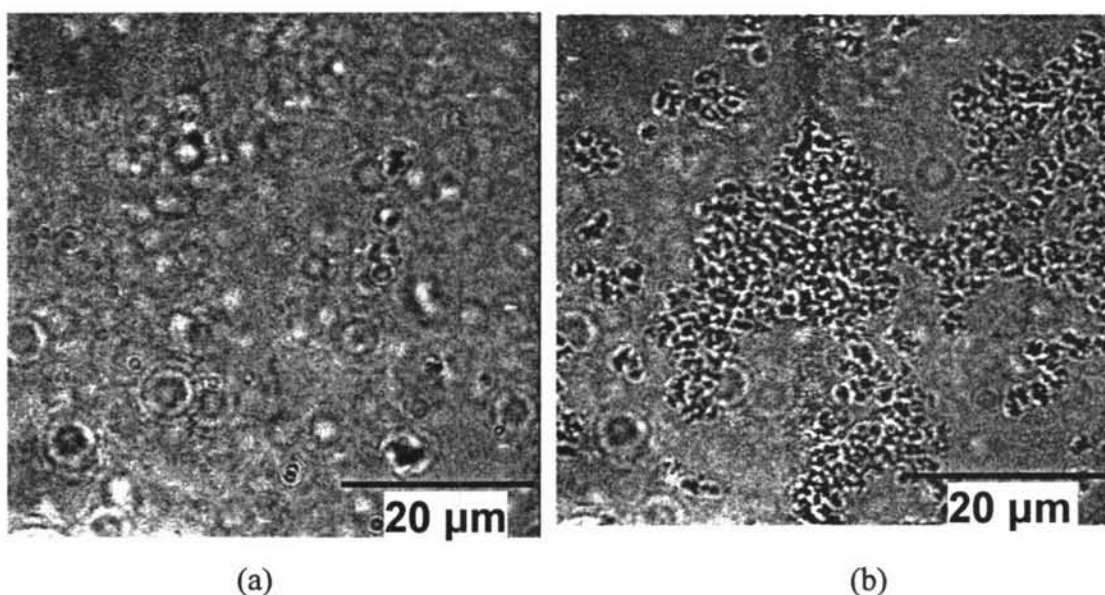
To test the degree of mixing, crude oil was mixed with heptane using the mixing-tee and the crude-heptane mixtures with different compositions were observed under the microscope. Figure 4.10 shows the crude oil - heptane mixtures with increasing amount of heptane. The mixture containing 55.0% heptane shows onset of asphaltene precipitation, which is in agreement with onset determination using refractive index technique (section 4.1) and onset determination by microscope technique (section 4.2). Hence it can be concluded that the mixing caused by the mixing-tee is acceptable.



**Figure 4.10** Testing the effectiveness of the mixing-tee: Crude oil - heptane mixtures with increasing amount of heptane (a) 52.5 volume % heptane (b) 55.0% heptane and (c) 57.5 % heptane (magnification: 100x).

In order to test the hypothesis that the precipitation of asphaltenes before entering the capillary can be avoided by using the mixing-tee just upstream of the capillary, a mixture containing 60 volume % heptane and 40 volume % crude oil was made using the mixing tee and was pumped into the capillary. Samples were taken at

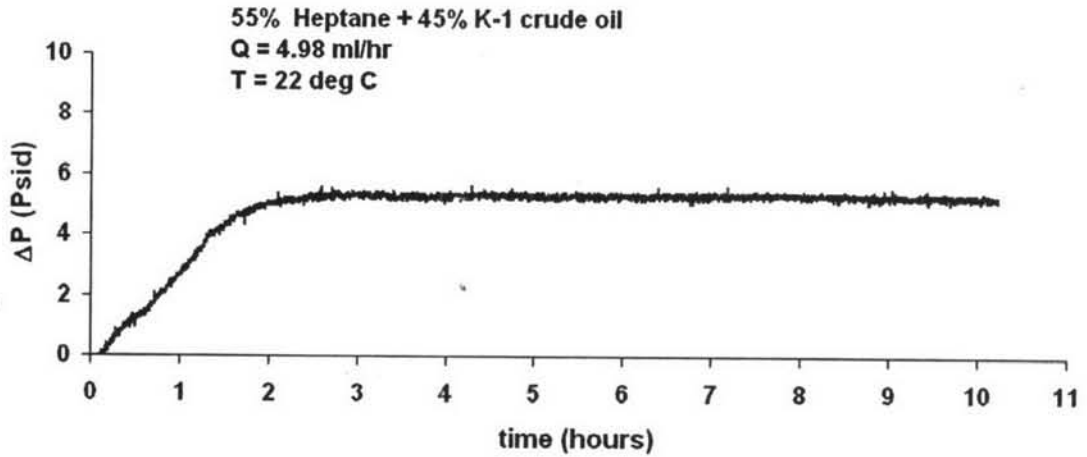
two points: before entering the capillary and at the capillary exit. Figure 4.11 shows the micrographs of both samples. The micrographs show that the mixture had very little asphaltenes precipitated before entering the capillary and at the capillary exit, a much larger amount of asphaltenes had been precipitated. This result proves that the reduced residence time obtained by using the mixing-tee helps in minimizing the asphaltene precipitation until the crude-heptane mixture enters the capillary.



**Figure 4.11** 40 % Crude - 60 % heptane mixture made using the mixing tee. (a) mixture before entering the capillary and (b) mixture after exiting the capillary (magnification: 100x).

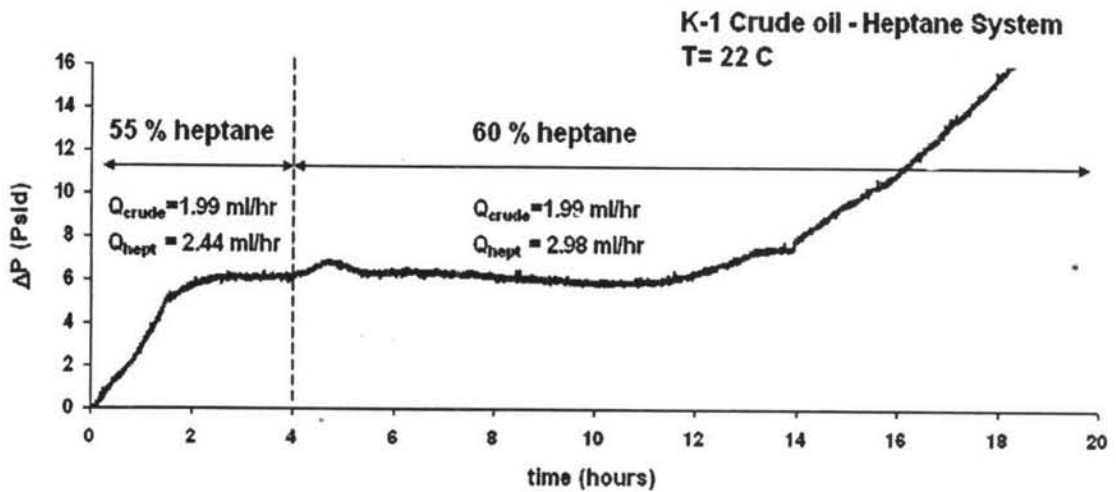
#### 4.5 Asphaltene Deposition Experiments

The next step after designing and troubleshooting the equipment was to carry out actual asphaltene deposition tests with crude oil. Figure 4.12 shows the results of pumping a mixture of crude oil K-1 and heptane, containing 55 volume % of heptane. Over a period of 10 hours, there was almost no increase in pressure, suggesting that the mixture did not cause any deposition at 55 volume % heptane.

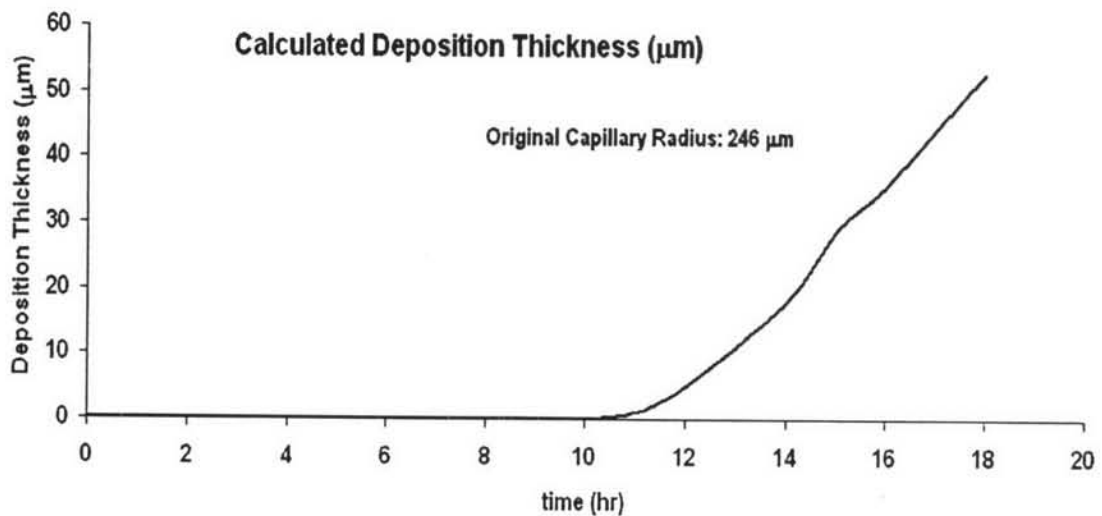


**Figure 4.12** Differential pressure readings for a mixture of crude oil K-1 and heptane, containing 55 % volume of heptane.

Figure 4.13 shows the results for a mixture containing 60 volume % heptane. The system was brought to a stabilized state using 55% heptane. Then, the flow of heptane was increased to raise the heptane amount in the mixture to 60 volume %. After a period of about 10 hours, the differential pressure started to increase, suggesting a decrease in the effective radius due to asphaltene deposition. Figure 4.14 shows the deposition thickness calculated using the data in Figure 4.13. It can be seen that after 18 hours, asphaltenes reduced the radius by approximately 20%.

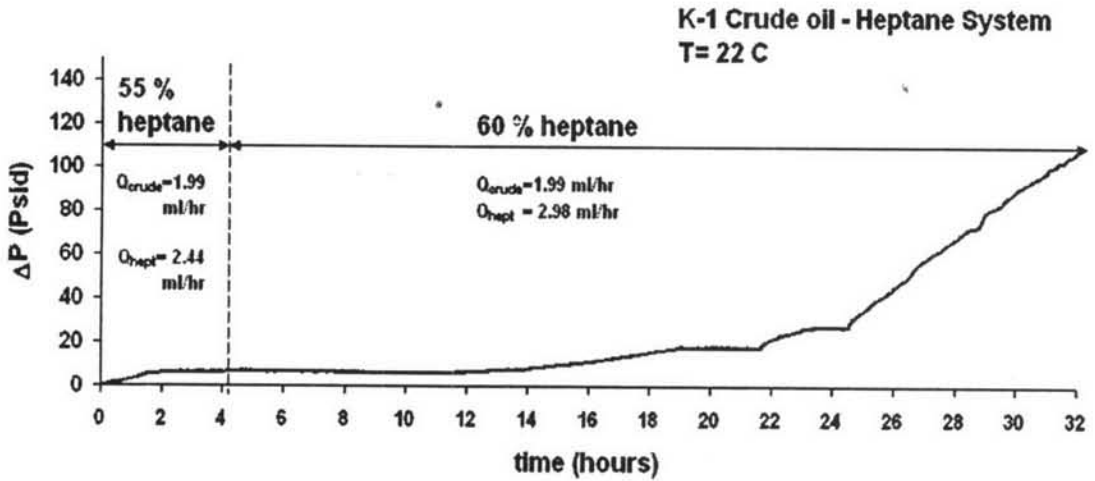


**Figure 4.13** Differential pressure readings for a mixture of crude oil K-1 and heptane, containing 60 % volume heptane.

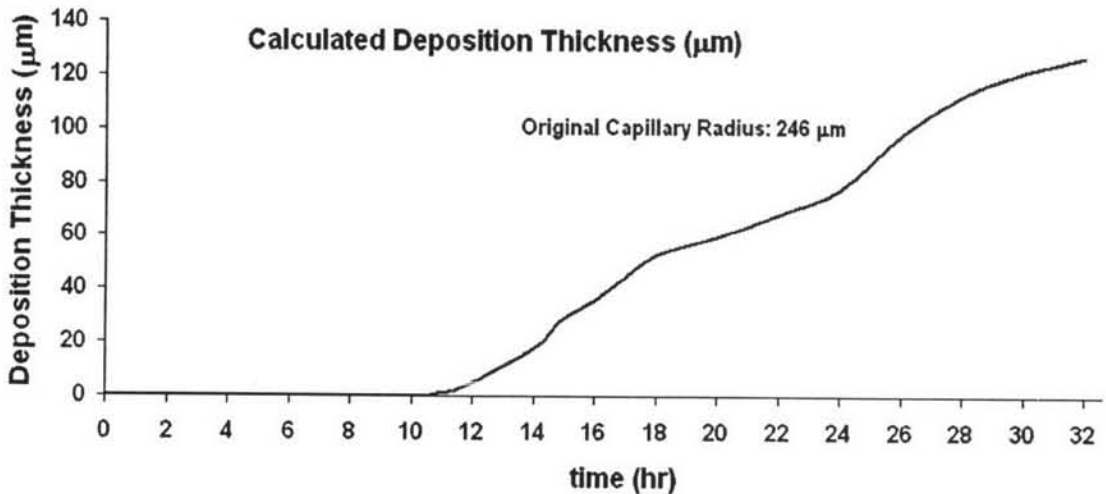


**Figure 4.14** Deposition thickness calculated by using the increase in differential pressure when pumping a mixture of crude oil K-1 and heptane, containing 60 % volume heptane.

Figures 4.15 and 4.16 show the data for the same experiment on an expanded time scale of 32 hours during which the radius of the capillary was almost reduced by half.



**Figure 4.15** Differential pressure readings for a mixture of crude oil K-1 and heptane, containing 60 % volume heptane (Expanded time-scale).



**Figure 4.16** Deposition thickness calculated by using the increase in differential pressure when pumping a mixture of crude oil K-1 and heptane, containing 60 % volume heptane. (Expanded time-scale).