

## **A Novel Technique for Determination of the Onset of Alkane Induced Asphaltene Precipitation Using Accurate Density Measurements**

**Mahdi Kalantari Meybodi<sup>1</sup> and Jamshid Moghadasi<sup>2,\*</sup>**

<sup>1</sup> M.S. Student, Department of Petroleum Engineering, Petroleum University of Technology, Ahwaz, Iran

<sup>2</sup> Associate Professor, Department of Petroleum Engineering, Petroleum University of Technology, Ahwaz, Iran

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### **Abstract**

Onset of asphaltene precipitation is the key parameter in dealing with asphaltene problems because it is the starting point of the asphaltene separation from the solution. In this study, a new technique is provided based on the experimental observations for the determination of the onset of asphaltene precipitation using accurate density measurements of the crude oils upon titration with precipitating agents like n-alkanes. Moreover, density measurements have been conducted for three different crude oils diluted with different ratios of precipitating agents, i.e. n-pentane, n-hexane, and n-heptane. The experimental results confirmed that, as it was expected, the density showed a decreasing trend as the dilution ratio increased, except at one point, at which the density increased with raising dilution ratio; this corresponded to the onset of asphaltene precipitation. For all the crude oils used, a sample diluted with a non-precipitating solvent (toluene) was also used as a reference system, its densities were measured upon titration with toluene, and the results were used for comparison with the other systems diluted with precipitating solvents. The measured onsets of asphaltene precipitation using this technique were confirmed with the onsets obtained by using interfacial tension approach.

**Keywords:** Onset of Asphaltene Precipitation, Density, Asphaltene, Precipitant, Dilution

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### **1. Introduction**

Asphaltenes are the problematic matters in petroleum industry (Tharanivasan, 2012), and they are investigated in many studies; however, they are relatively unknown yet (Fossen et al., 2011). Asphaltene problems can occur in petroleum reservoir, production wells, surface facility, surface pipelines, and nearly everywhere crude oils exist (Escobedo et al., 1995). Unfortunately, remedial actions for the asphaltene problems are so expensive (Carlos Da Silva Ramos et al., 2001) that it is very important to predict and prevent the problems from occurring or treating them at the least cost; this needs to understand the mechanisms, the ways, and the situations that asphaltene problems occur.

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\* Corresponding Author:

Email: [j.moghadasi@put.ac.ir](mailto:j.moghadasi@put.ac.ir)

Asphaltenes are the heaviest part of the crude oil with large molecules and high molecular weights (Sztukowski et al., 2003). It is believed that they are nearly dissolved and partially suspended in the crude oil before separation from solution (Kawanaka et al., 1989; Sheu et al., 1992). In dealing with asphaltene problems, there are 5 different separation points, including onset of asphaltene precipitation (APO), onset of asphaltene/resin flocculation (ARFO), onset of asphaltene/resin deposition (ARDO), onset of asphaltene micellization (AMO), and onset of asphaltene coacervation (ACO) (Mousavi-Dehghani et al., 2004). Among these separation points, the onset of asphaltene flocculation and the onset of asphaltene precipitation are of more importance. In engineering investigations, the onset of asphaltene flocculation is more interesting because the asphaltene problems start to occur from this stage of asphaltene separation, whereas the onset of asphaltene precipitation is of more interest in research investigations because it is the starting point which makes it possible for the other onsets (like flocculation onset) and problems to occur. In more details, the onset of asphaltene precipitation determines the start point of the asphaltene precipitation stage, at which asphaltenes are segregated from the solution. In addition, there is a misunderstanding between the asphaltene precipitation and asphaltene flocculation/aggregation and their onsets in the literature; asphaltene precipitation is usually used instead of asphaltene flocculation/aggregation, whereas these concepts are completely different and they have completely different identification techniques (Mousavi-Dehghani et al., 2004). Quantitatively the onset of asphaltene flocculation/aggregation occurs later than the onset of asphaltene precipitation (Mousavi-Dehghani et al., 2004).

Precipitated asphaltenes are the asphaltenes come out of the solution, but they are not peptized by resins yet. In other words, in the precipitation stage, bare asphaltenes are developed in the solution. This process is called asphaltene precipitation and the start point of this process is called the onset of asphaltene precipitation. Numerous experiments have been conducted on the asphaltene precipitation and the amount of precipitated asphaltenes, but most of them have usually investigated the flocculation/aggregation of the asphaltene instead of precipitation because of the previously mentioned misunderstanding about the common use of asphaltene precipitation and flocculation (Buckley et al., 1998; Burke et al., 1990; Hammami et al., 1999; Hu et al., 2001; Tharanivasan, 2012).

As mentioned above, asphaltenes are usually considered to be dissolved and partially suspended in the crude oil and are stabilized in it by natural resins (Kawanaka et al., 1989). This stability can be disrupted if any parameters alter the resin-asphaltene interactions. It can happen due to the change in pressure, temperature, and the composition of the crude oil system (Tharanivasan, 2012). The reason is that generally crude oil is assumed to consist of different components with different solubilities, and the solubility interactions between these components determine the solubility or insolubility of each of these components (Abdelrahim, 2012). Changes in the pressure, temperature, and the composition of the crude oil induce the alteration in these solubilities and solubility interactions, and thus the asphaltenes may come out of the solution and become precipitated; this is the way that asphaltene precipitation happens. The onset of asphaltene precipitation and the amount of precipitated asphaltenes are dependent on the power of the solvent and the composition and properties of the crude oil (Mousavi-Dehghani et al., 2004).

It is mentioned that the only way for the determination of the onset of asphaltene precipitation is to measure the interfacial tension (IFT) of the crude oil against water through dilution (Kim, 1987; Mousavi-Dehghani et al., 2004; Voung, 1985). In the determination of the onset of asphaltene precipitation using IFT measurement technique, the IFT of the diluted crude oil against water will be constant with very small deviations up to a specific dilution ratio which corresponds to the onset of asphaltene precipitation, and after that, the IFT will change drastically with some irregularity. This

occurs because after the onset, the bare asphaltenes develop in the system, which can be adsorbed at the interface between the diluted crude oil and water (Mohammed et al., 1993; Mousavi-Dehghani et al., 2004; Sjöblom et al., 1992). Some other techniques like light transmission technique (Buenrostro-Gonzalez et al., 2004; Hammami et al., 1999; Yang et al., 1999) and visual techniques (Hotier et al., 1983) are also mentioned in the literature for determining the onset of asphaltene precipitation; however, it should be mentioned that these methods are standard methods for the determination of the onset of asphaltene flocculation/aggregation not the onset of asphaltene precipitation (Buenrostro-Gonzalez et al., 2004; Hammami et al., 1999; Hu et al., 2001).

The solution behavior of asphaltene in crude oil is investigated in some literatures; it has been shown that the asphaltene in crude oil solutions have a non-ideal behavior and the volumetric behavior of its solution is not ideal (Wang et al., 2001; Wu et al., 1998). Therefore, it is expected that by the density investigation of the crude oil through dilution with a precipitating agent, the asphaltene separation onset point, in which asphaltenes come out of the solution, can be identified.

In this study, a new experimental technique for the determination of the onset of asphaltene precipitation is developed based on the observations of the experimentally measured densities of diluted crude oil as a function of precipitant concentration upon titration.

## 2. Experimental work

### 2.1. Materials

All the precipitants, i.e. n-heptane, n-hexane, and n-pentane, and toluene used in this study were reagent grade (>99% pure) purchased from Merck; their measured densities at 28 °C and atmospheric pressure are given in **Error! Reference source not found.**

**Table 1**  
Densities of the precipitants and toluene at 28 °C and atmospheric pressure.

Diluent	n-Pentane	n-Hexane	n-Heptane	Toluene
Density (g/cm <sup>3</sup> )	0.61791	0.65204	0.67707	0.85950

Three dead crude oil samples used in this study were obtained from three different oil reservoirs in the south of Iran. The crudes were filtered first with Wattman 42 filter paper and were then kept in a dark place for about 2 months to reach relative equilibrium. The densities of the crude oil samples (after filtration) at 28 °C and atmospheric pressure along with their SARA analyses measured by DBR method (Kharrat et al., 2007) are given in **Error! Reference source not found.**

**Table 2**  
Densities of the crude oils at 28 °C and atmospheric pressure and their SARA analyses.

Crude oil sample	Sample 1	Sample 2	Sample 3
Density (g/cm <sup>3</sup> )	0.89955	0.92046	0.89862
Saturates (%)	56	51	48
Aromatics (%)	14	11	39
Resins (%)	26	27	8
Asphaltenes (%)	2.79	9.41	4.36

For the interfacial tension measurements against water, distilled water was used as the water phase.

## 2.2. Experimental apparatus

In the current work, DMA 5000 was used for accurate density measurements. DMA 5000 is a high quality oscillation type densitometer which measures the density according to the change in the period of oscillation of a built in U-tube due to the density of the filled sample. DMA 5000 could measure densities at temperatures up to 90 °C and pressures up to 1 MPa with an accuracy of  $1 \times 10^{-5}$  gr./cm<sup>3</sup>. The apparatus was previously calibrated at atmospheric pressure by using double-distillated water and air both at 40 °C and 60 °C according to the manual of the apparatus.

Pendant drop apparatus was also used for the interfacial tension measurements to determine the onset of precipitation based on the technique mentioned in the literature (Kim, 1987; Mousavi-Dehghani et al., 2004; Voung, 1985) for the confirmation of the results of the density measurement technique developed in this study. The pendant drop apparatus was similar to the one previously described elsewhere (Abdelrahim, 2012). The apparatus could measure IFT up to a temperature of 200 °C and a pressure of 40 MPa. The apparatus had a capillary tube used for drop formation of the sample in the cell filled with distillated water. The pendant drop apparatus was equipped with an imaging system including a high quality video camera, a monitor, and a personal computer. The imaging system was used for capturing the images of drops for IFT calculations using pendant drop technique. The images of the drops were analyzed by the axisymmetric drop shape analyses (ADSA) technique (Rotenberg et al., 1983) using a commercial software.

An Inco syringe pump 100DX was also used for drop formation. The pump could pump distillated water as accurately as 0.00001 cm<sup>3</sup>/min and was selected to make it possible to employ a very low flow rate for drop formation because, in pendant drop technique, the drop must be grown only due to buoyancy (gravity), and a very low pumping rate must be employed only to provide the sufficient fluid for drop growth not forcing it. The used pump could only displace distillated water, and for displacing other fluids like crude oils, a transfer vessel with a displaceable piston was used.

## 2.3. Experimental procedure

### a) Apparatus cleaning

Before conducting any measurements, all the wetted parts of densitometer, IFT cell, transfer vessel, and all connections must be completely cleaned because trace amounts of remained hydrocarbons could alter the results, especially the IFT results. For this reason, the system was flushed with toluene first, and the acetone was then used to remove the toluene from the system. Afterward, acetone was evaporated with pressurized air. Finally, the water was flushed through the system and the compressed nitrogen was used for water evaporation. This procedure was repeated before each measurement.

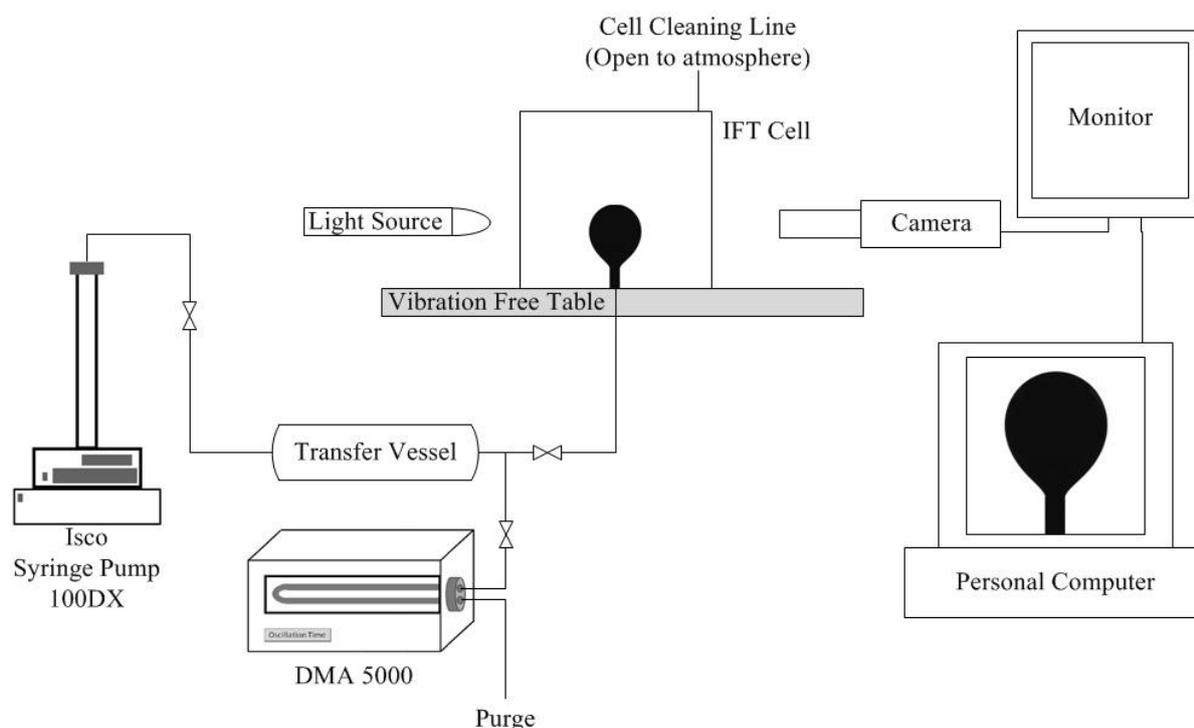
### b) Sample preparation

For each measurement, a 30 cm<sup>3</sup> mixture was needed which was prepared by mixing the proper weight of diluent (i.e. n-pentane, n-hexane, n-heptane, and toluene) and the crude oil in a closed container with a piece of aluminum foil during the mixing.

### c) Density and IFT measurement procedures

For density and IFT measurements, the setup shown in **Error! Reference source not found.** was utilized. This setup makes it possible to measure the density and IFT of the samples simultaneously,

which provides the confidence of the sameness of the samples used for density and IFT measurements. For conducting the measurement, the IFT cell was first filled with distilled water, and its temperature was set at 28°C by using an air chiller. Also, the same temperature was set on the DMA 5000. Then, the prepared mixture was transferred to the transfer vessel immediately after mixing. Next, the pump was started to pump the fluid while all the valves in **Error! Reference source not found.** were open. Pumping was continued until the used sample started to exit from the outlet of densitometer and the inlet valve of densitometer was then closed, and the pumping was continued for drop formation in IFT cell at a very low pumping rate ( $<0.01 \text{ cm}^3/\text{min}$ ). Afterward, the density was measured by selecting “start” on the DMA 5000 and directly reading the measurements. The IFT was also measured by analyzing the image of the drop taken just before the separation of the drop from the needle. It should be noted that this image was extracted from the video of the drop captured from the start of drop formation to the separation of the drop from the needle. The IFT and density were measured 3 times for each mixture, which confirmed that the accuracies of the density and IFT measurements were  $1 \times 10^{-4} \text{ g/cm}^3$  and  $0.2 \text{ mN/m}$  respectively. The averages of the 3 values of density and IFT measurements were used as the density and IFT value of each sample.



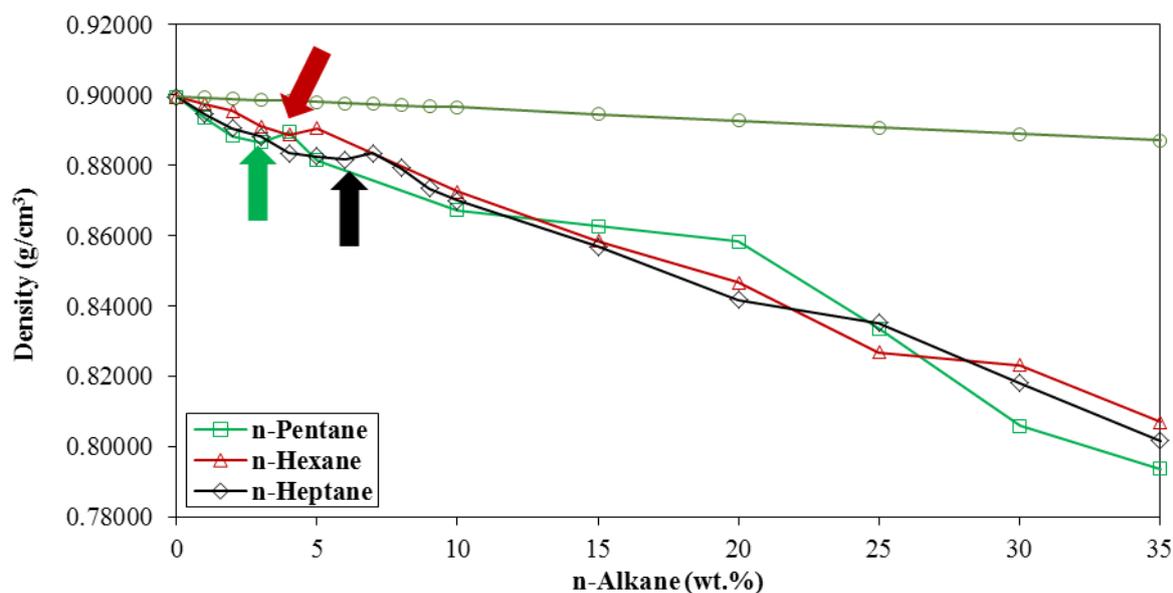
**Figure 1**  
Density and IFT measurement setup.

### 3. Results and discussion

IFT and density measurements were first conducted for the dilutes samples of each crude oil with 0, 5, 10, 15, 20, 25, 30, and 35 wt.% of each n-alkane, i.e. n-pentane, n-hexane and n-heptane; this was carried out to find the probable region of asphaltene precipitation onset point. Then, the measurements were conducted for the diluted samples in the probable range of asphaltene precipitation onset by the dilution increment of 1 wt.%. After that, the densities of the samples diluted with toluene, which was the reference case because of the non-precipitating nature of toluene, were measured at all the dilution ratios used in previous measurements, and the results were utilized for comparison purposes. It should be noted that all the measurements were made at  $28 \pm 0.5 \text{ }^\circ\text{C}$  and atmospheric pressure.

**Error! Reference source not found.** shows the interfacial tension of Sample 1 during dilution with n-pentane, n-hexane and n-heptane. According to the method for the determination of asphaltene precipitation onset using IFT measurement (Kim, 1987; Mousavi-Dehghani et al., 2004; Voung, 1985), the weight percentage of the n-alkane to which the IFT of the sample is constant and deviates after that is the onset of asphaltene precipitation. **Error! Reference source not found.** shows that the onset of asphaltene precipitation occurs at 3, 4, and 7 wt.% for the titration of Sample 1 with n-pentane, n-hexane, and n-heptane respectively. Figure 2

IFT graphs of Sample 1 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).

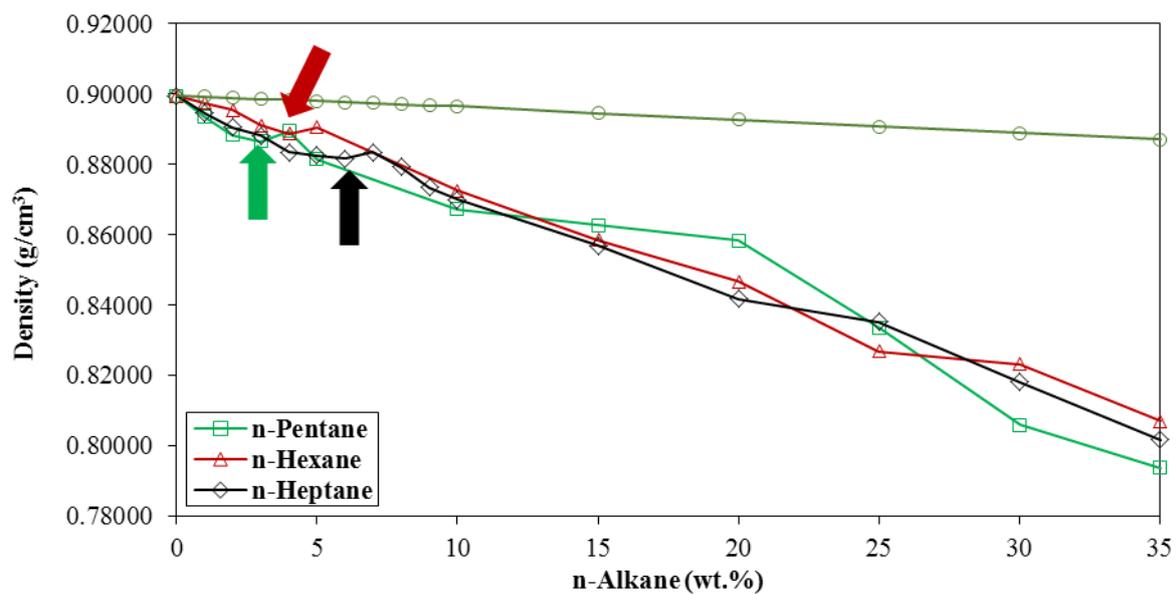


**Figure 3**

Density graphs of Sample 1 during dilution with 3 n-alkanes and toluene (onset of each case is shown by an arrow with the same color).

shows the densities of Sample 1 during dilution with the mentioned n-alkanes and toluene. Normally, we expected that the densities of the sample diluted with n-alkane and toluene would be decreased as the dilution ratio increased because the crude oil used was denser than the n-alkanes and toluene; however, as it is shown in Figure 2

IFT graphs of Sample 1 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).



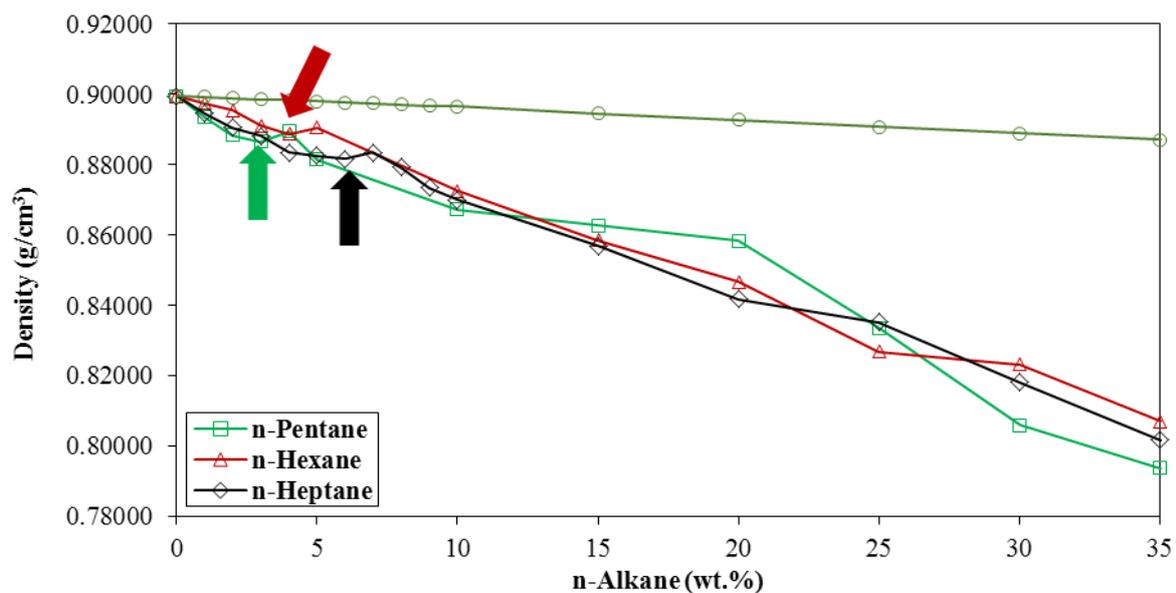
**Figure 3**

Density graphs of Sample 1 during dilution with 3 n-alkanes and toluene (onset of each case is shown by an arrow with the same color).

, this trend is nearly obeyed for increasing dilution ratio except at one point for each n-alkane at which the density of the diluted sample increases with increasing the dilution ratio. These points are nearly in the region of the onset of asphaltene precipitation and are determined from the IFT graphs.

According to Figure 2

IFT graphs of Sample 1 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).

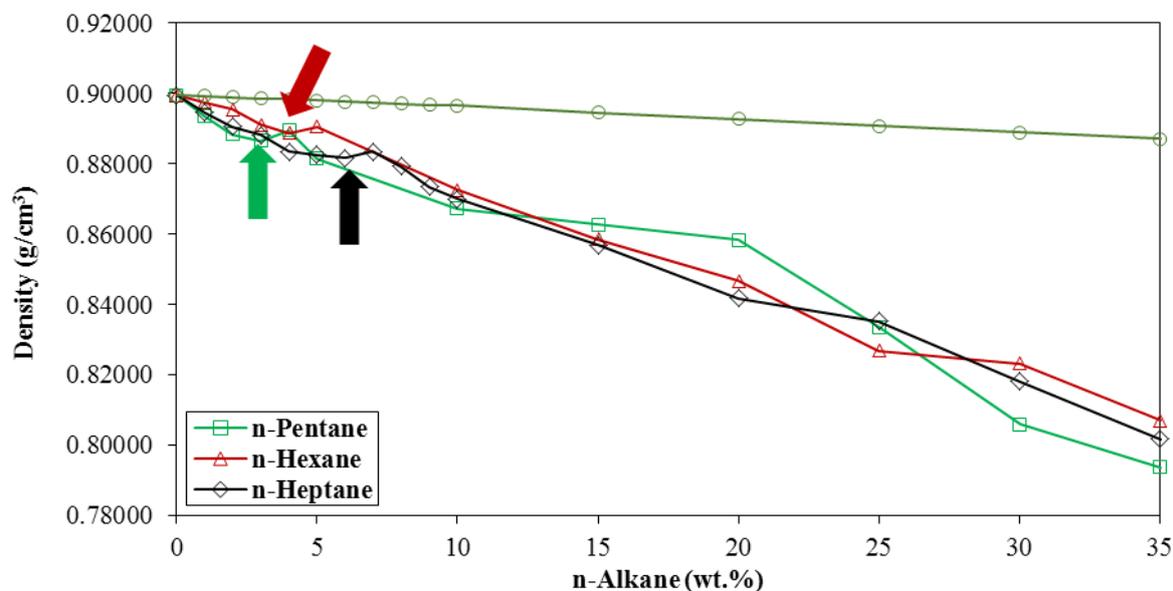


**Figure 3**

Density graphs of Sample 1 during dilution with 3 n-alkanes and toluene (onset of each case is shown by an arrow with the same color).

, the onsets of asphaltene precipitation identified using density graphs at 3, 4, and 6 wt.% of n-alkane during the dilution of Sample 1 with n-pentane, n-hexane, and n-heptane respectively are very close to the ones determined from the IFT graphs. As it is shown in Figure 2

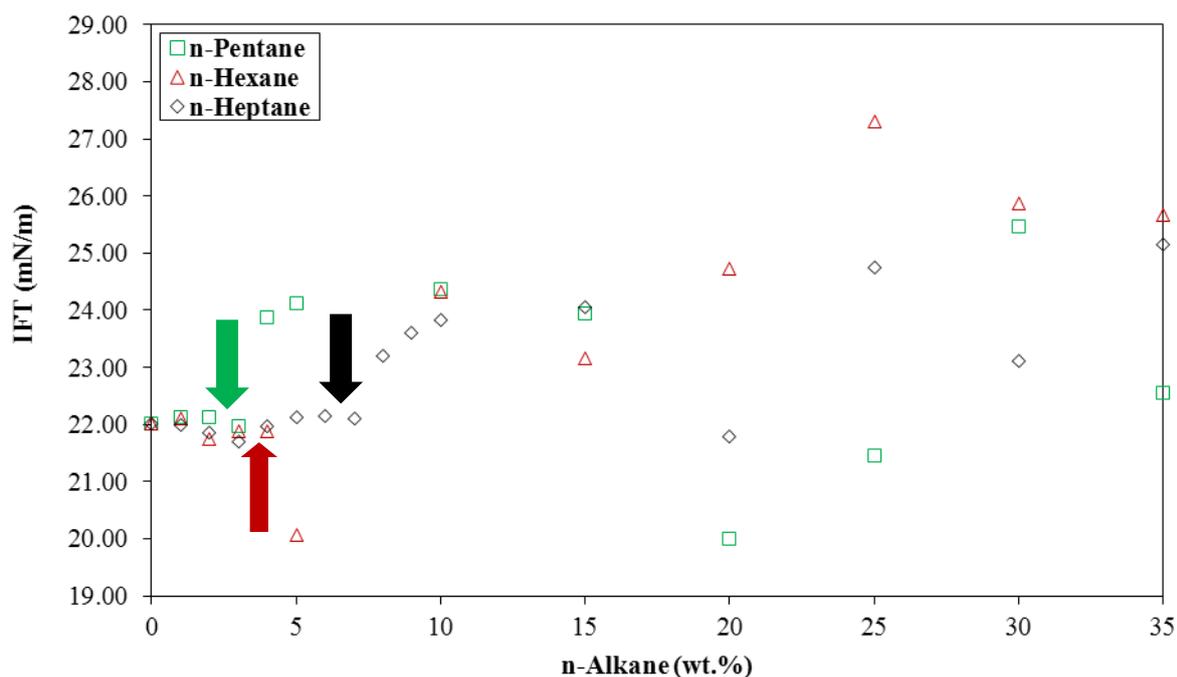
IFT graphs of Sample 1 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).



**Figure 3**

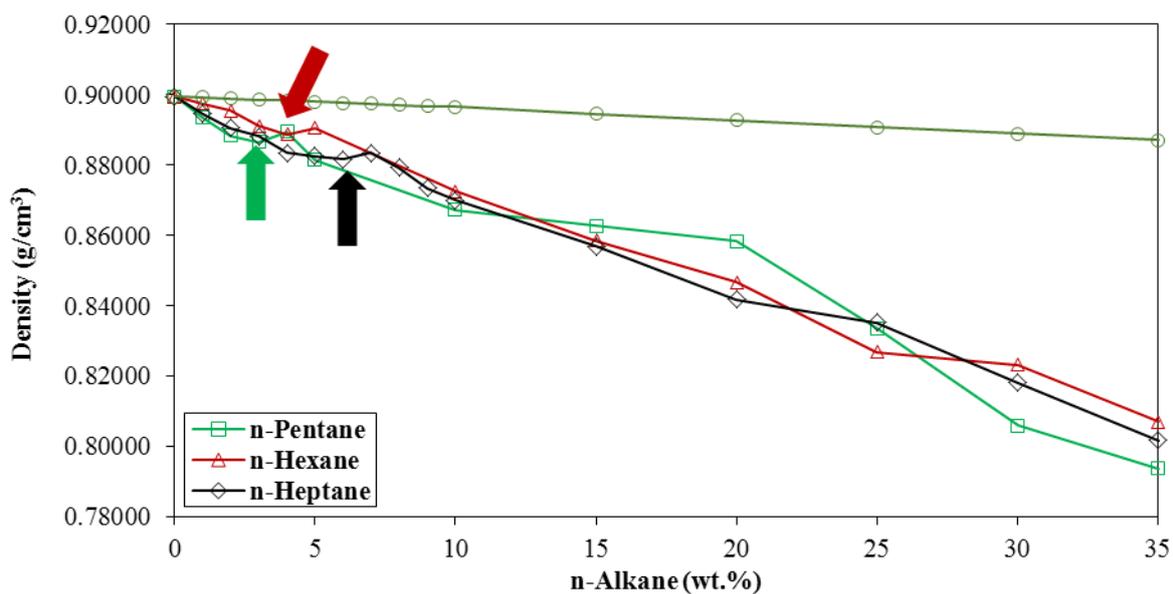
Density graphs of Sample 1 during dilution with 3 n-alkanes and toluene (onset of each case is shown by an arrow with the same color).

, the expected decreasing trend is obeyed during the dilution of Sample 1 with toluene, which confirms that the out trend (and nearly trend change) occurring in the densities of diluted Sample 1 during titration with n-alkanes is related to the asphaltene precipitation happening due to the n-alkanes precipitating nature. This out trend is not identified in the sample diluted with toluene because of the non-precipitating nature of toluene.



**Figure 2**

IFT graphs of Sample 1 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).

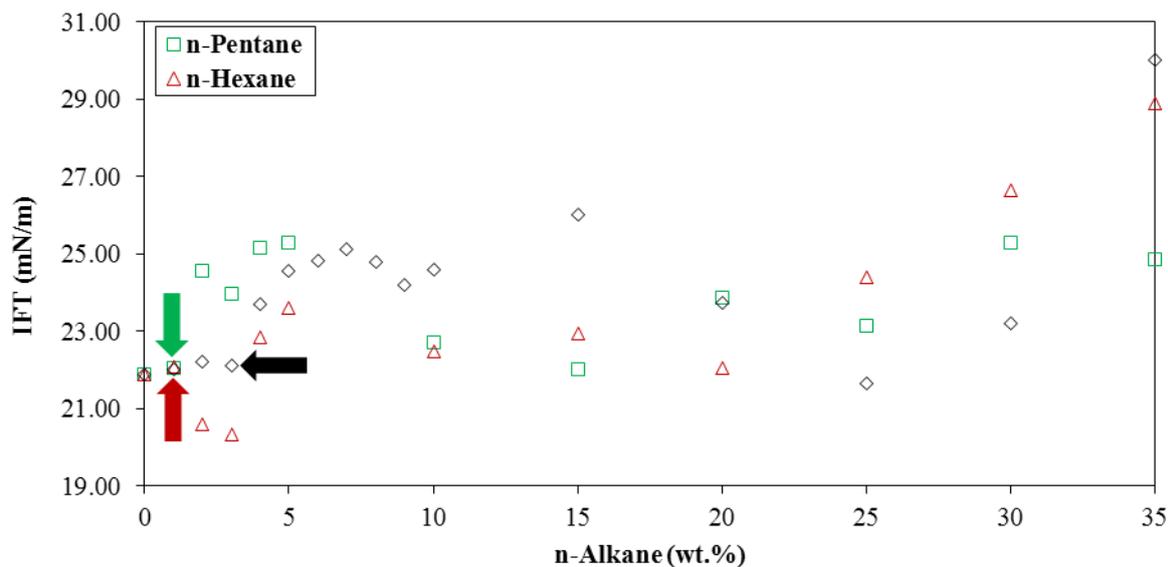


**Figure 3**

Density graphs of Sample 1 during dilution with 3 n-alkanes and toluene (onset of each case is shown by an arrow with the same color).

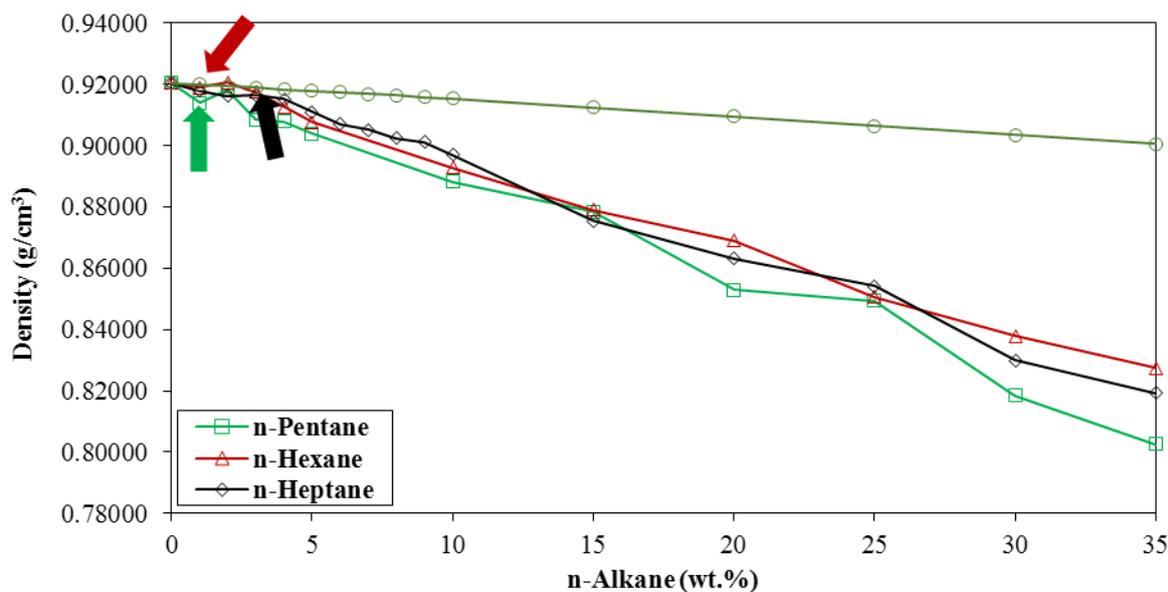
**Error! Reference source not found.** shows the IFT of Sample 2 during dilution with the mentioned n-alkanes. This figure shows that the onsets of asphaltene precipitation of Sample 2 during dilution with n-pentane, n-hexane and n-heptane occurred at 1, 1, and 3 wt.% respectively. **Error! Reference source not found.** shows the density graphs for Sample 2 diluted with different n-alkanes and toluene.

The behavior was similar to the one discussed for Sample 1. According to **Error! Reference source not found.**, the onsets of asphaltene precipitation occurred at 1, 1, and 2 wt.% of n-alkanes for Sample 2 diluted with n-pentane, n-hexane, and n-heptane respectively; the onsets are close to the ones determined by IFT graphs. **Error! Reference source not found.** also states that the reference system, i.e. the sample diluted with toluene, did not experience any out trend during dilution just like what was seen for Sample 1.



**Figure 4**

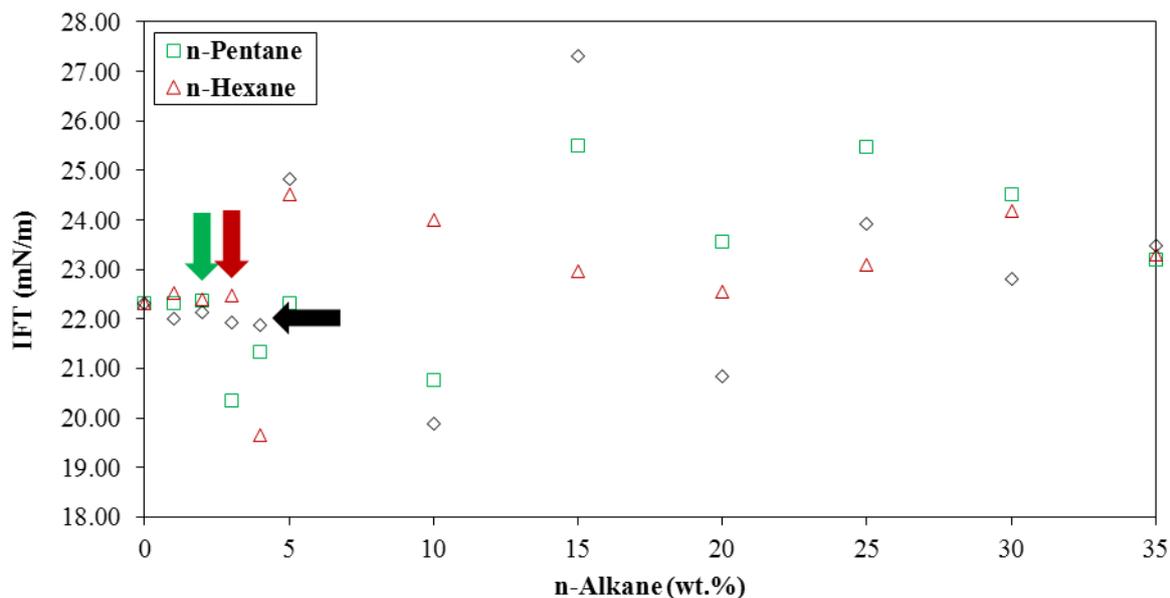
IFT charts of Sample 2 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).



**Figure 5**

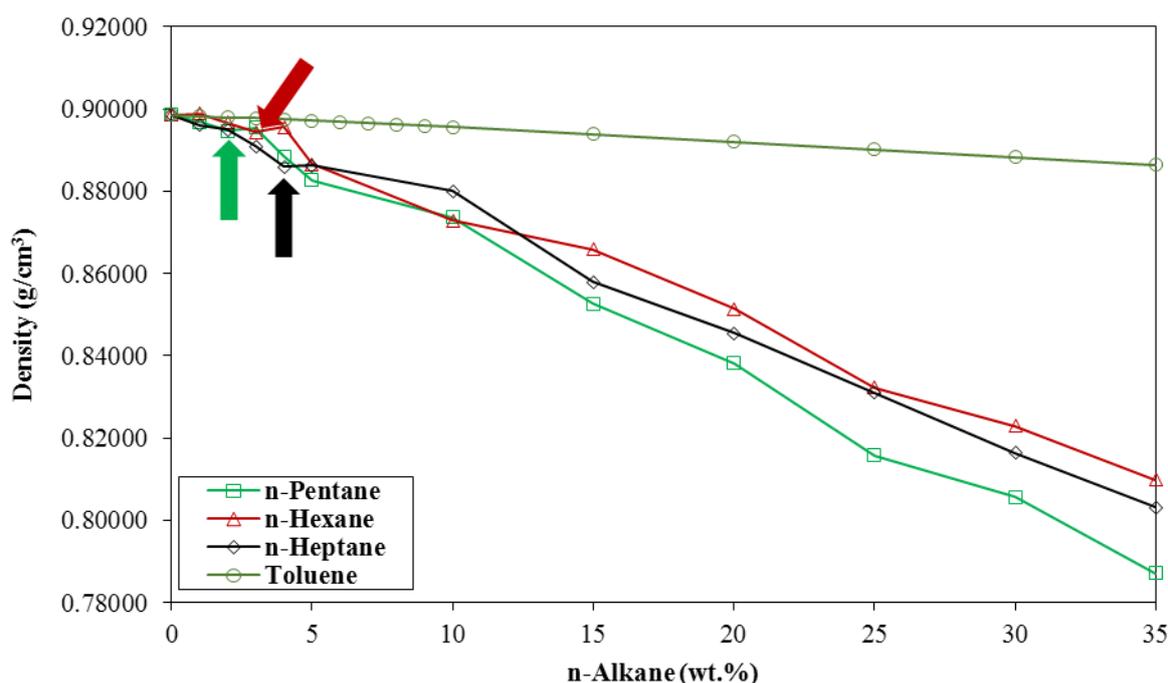
Density charts of Sample 2 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).

**Error! Reference source not found.** shows the IFT of Sample 3 during dilution with the mentioned precipitants. This figure shows that the onsets of asphaltene precipitation occurred at 2, 3, and 4 wt.% for Sample 3 diluted with n-pentane, n-hexane, and n-heptane respectively. **Error! Reference source not found.** shows the densities of Sample 3 diluted with the precipitants and toluene. It shows that the onsets of the asphaltene precipitation of Sample 3 occurs at 2, 3, and 4 wt.% of precipitant when it is diluted with n-pentane, n-hexane, and n-heptane respectively; the onsets are the same as the ones determined by IFT charts. For this crude oil, it is also seen that the sample diluted with toluene, which was used as the reference system, does not exhibit any out trend in density chart.



**Figure 6**

IFT charts of Sample 3 during dilution with 3 n-alkanes (onset of each case is shown by an arrow with the same color).



**Figure 7**

Density charts of Sample 3 during dilution with 3 n-Alkanes (onset of each case is shown by an arrow with the same color).

As it occurred for some diluted crude oils with precipitants (Sample 1 diluted with n-heptane and Sample 2 diluted with n-heptane), the onsets of asphaltene precipitation determined from the density graphs are relatively lower than the ones determined by IFT graphs. This is because of the fact that as the system reaches the onset of asphaltene precipitation, the concentration of bare asphaltenes precipitating is so low and so little amount of these precipitated asphaltenes may be adsorbed on the interface in a short time that IFT does not change remarkably at the onset. However, as the precipitation continues, more bare precipitated asphaltenes are provided in the diluted sample and more asphaltenes can be adsorbed on the interface in a short time, thereby causing rapid deviation in IFT graph. In the density measurement, the whole sample is placed in the densitometer sample chamber and each change in the bulk of the fluid influencing the density of the sample can be detected just as it occurs. In other words, in the IFT measurement technique, a mass transfer is required before the onset can be detected, but in the density measurement method, mass transfer is not required and the onset can be detected as it occurs. Therefore, the onset of asphaltene precipitation determined by the novel method of the current work can be relatively lower and more responsible than the ones determined by IFT graph.

The density measurement method is easier than the IFT measurement method; the latter is time consuming and needs high attention to produce accurate and responsible results. The density measurement is a particularly suitable method for the onset of asphaltene precipitation determination in high pressure and high temperature conditions, where the applicability of IFT method is difficult and more problematic.

The authors recommend that this method should be used with the crude oils with high asphaltene content because in the crude oils having a low asphaltene content (less than 1 wt.%) the density change may be negligible and cannot be detected.

#### 4. Conclusions

In this study, a novel technique is developed for the determination of the onset of asphaltene precipitation of crude oils with a considerable amount of asphaltene content (higher than 1 wt.%). The fact that the density of the diluted crude oil changes as asphaltene separation occurs is used in developing the new technique. According to this fact and the experimental observations, the onset of the asphaltene precipitation can be determined by the observed deviation in the chart of measured densities as a function of dilution ratio upon the dilution of crude oil with a precipitant. This technique is very useful because interfacial tension measurement technique for the determination of the onset of asphaltene precipitation is relatively difficult to use, is time consuming, and needs high attention to produce accurate results; however, the new method can be conducted more easily and rapidly. This method is especially very useful for the determination of the onset of asphaltene precipitation in high pressure and high temperature conditions, where the interfacial tension measurements are more problematic.

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#### Nomenclature

ACO	: Asphaltene coacervation onset
AMO	: Asphaltene micellization onset
APO	: Asphaltene precipitation onset
ARDO	: Asphaltene resin deposition onset
ARFO	: Asphaltene resin flocculation onset
DBR	: DBR technology center, Schlumberger, Canada
IFT	: Interfacial tension
wt.%	: Weight percent

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