

## Asphaltene and Normal Paraffin Effect on Gas-Oil Interfacial Tension During CO<sub>2</sub> Injection into Asphaltenic Oil Reservoir

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### Abstract

Asphaltene precipitation in oil reservoirs has been involved with numerous problems. Therefore, it is required to understand the precipitation mechanisms in detail in order to diminish the associated difficulties. There are several ways to detect asphaltene precipitation. One of these methods is vanishing interfacial tension (VIT) method. In this method by plotting the equilibrium interfacial tension (IFT) versus pressure, the asphaltene precipitation conditions can be predicted. In this study, for more accurate evaluation of asphaltene precipitation in oil reservoirs by using IFT versus pressure plots, synthetic oil solutions made up of toluene and normal paraffins are used. Solutions with different compositions of toluene and normal paraffins such as n-decane and n-heptane with and without asphaltene (extracted from crude oil) are prepared. Then, the equilibrium IFT of the solutions in the proximity of CO<sub>2</sub> at different pressure conditions is measured. By plotting the IFT data versus pressure, the onset of asphaltene precipitation in presence of gas and the impact of different parameters on this phenomenon are investigated. Experimental results show that the presence of asphaltene in synthetic solutions changes the behavior of IFT data with pressure. For a solution of toluene and normal paraffin containing asphaltene, the IFT of the solution in presence of CO<sub>2</sub> decreases linearly with two different slopes at low and high pressure ranges. The results confirm that the presence of normal paraffin intensifies asphaltene precipitation. The experimental results show that the higher mass fraction of asphaltene is, the higher would be the intensity of the asphaltene precipitation for the attempted mass fractions.

**Keywords:** asphaltene precipitation, interfacial tension, minimum pressure of miscibility, carbon dioxide, normal paraffin.

## 1. Introduction

Nature of heavy organics in crude oil and their role in extraction, transfers and processing, has been well understood [1-3]. Comprehensive investigations at different area such as exploration, drilling, production, enhanced oil recovery and processing of low quality oil have been performing. Injection and re-injection of gas into oil reservoirs are cost-effective methods [4]. One of the major problems in these recovery processes is blockage of pores by asphaltene precipitation, which could significantly reduce oil recovery efficiency [5]. Combination of a miscible fluid with oil could significantly affect phase behavior. However, precipitation of heavy organic materials is a major drawback of phase change that could consequently affect production from oil reservoirs or oil flow rate through wells and pipelines [6]. Precipitation of heavy organic material usually yields pore blockage and wettability alteration of reservoir rock [7].

Asphaltene precipitation in porous media can also lead to a decrease of 20 percent effective permeability [8-9]. Due to damage to the formation, oil and gas production rate from the reservoir decreases [9]. When the reservoir pressure is close to the precipitation pressure, asphaltene precipitation in reservoir takes place; this creates a failure condition at the wellbore [10]. Asphaltene precipitation process and its consequences have been shown to be very complex [11-12].

Various methods has been used and proposed to detect asphaltene precipitation process. These methods include microscopic method [13], light absorption method [14], gravimetric method, electrical conductivity method [15], viscometer method, heat transfer measuring method and vanishing interfacial tension (VIT) method [16-17]. The vanishing interfacial tension (VIT) method is a new method that can accurately detect the starting point of asphaltene precipitation [18-19]. In this method, the equilibrium IFT data of oil and gas is plotted against pressure, and the trend of the resultant curve is interpreted to discover mechanisms,

the start point and intensity of asphaltene precipitation [20]. In this method, as soon as the precipitation starts, the trend of the IFT plot versus pressure changes sharply [21]. This method is quite accurate, and a small amount of sample is required for evaluation [22]. The optimum conditions of miscible gas injection can be determined using the rapid VIT method [22-23].

The VIT method has been developed and employed to measure the miscibility conditions of various crude oils with deferent gases. The following are some of the studies in this field. Nobakht et al. showed that equilibrium  $\text{CO}_2$  gas-oil IFT often reduces linearly with pressure to the pressure from which the IFT-pressure trend changes. This pressure is known as threshold pressure. They also observed that if the equilibrium pressure is higher than the threshold pressure, light oil components quickly get out from the oil droplet and turn into the gas phase. This physical phenomenon is known as the extraction of very light components [24].

Nobakht et al. also measured the solubility of  $\text{CO}_2$  at different equilibrium pressures and at 27 °C. They concluded that by extrapolating the first slope of the IFT data versus pressure down to the point at which IFT becomes zero, the minimum miscible pressure (MMP) can be estimated [25].

Wang et al. investigated the interaction of three Canadian crude oil (two light oil and a medium one) with  $\text{CO}_2$ , by using the VIT method. They found that the equilibrium IFT decreases linearly with the equilibrium pressure at three distinct pressure ranges. In the first interval, with increasing pressure, IFT reduces due to increasing solubility of  $\text{CO}_2$  in oil. In the second interval, IFT suddenly increases, then quickly decreases, and again becomes linear. They stated that the sudden increase in IFT was owing to asphaltene precipitation, and rapid separation of light compositions. They concluded that, in this range, the measured IFT is between relatively heavy compositions of crude oil and  $\text{CO}_2$ . At the last stage, different light components began to separate from oil. At this stage, the measurement of IFT is between the heaviest compositions of crude oil and  $\text{CO}_2$  gas [26].

In this study the impact of parameters such as pressure, asphaltene content and oil composition on asphaltene precipitation is investigated through VIT method.

## 2. Experimental

Synthetic solutions are prepared by mixing different amounts of toluene, normal paraffins and asphaltene, which was extracted from an Iranian crude oil sample. The composition of this crude oil sample is shown in Table 1.

To extract asphaltene from crude oil, different standards are available. In this study,

the ASTM (D2007-80) was applied [17].

After extracting asphaltene from the crude oil sample, synthetic oil sample is prepared. Asphaltene is insoluble in the normal paraffins; however, it is soluble in toluene due to similar ring structure. To study the effect of synthetic oil composition on IFT, solutions with different volume percent of toluene and normal paraffins are used. For preparing the samples, the normal paraffins and toluene, with desired volume percents are mixed. Then, 5 wt% asphaltene is added and the prepared mixture is shaken for 6 hours by magnetic stirrer so that the whole asphaltene dissolves in the solution. Table 2 shows 18 oil solutions used in IFT tests.

Table 2. Compounds of solutions used as oil in IFT experiments

Component	CO <sub>2</sub>	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	iC <sub>4</sub>	nC <sub>4</sub>	iC <sub>5</sub>	nC <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>	C <sub>10</sub>	C <sub>11</sub>	C <sub>12</sub> <sup>+</sup>
Mole fraction	0.01	0.38	0.51	1.28	0.44	1.84	1.44	2.33	7.43	8.73	6.74	8.69	7.73	5.04	47.41

Table 1. Composition of the oil used for asphaltene extraction

Sample	Toluene (volume percent)	n-Heptane (volume percent)	n-Decane (volume percent)	Asphaltene (mass percent)
T-100-A	100	0	0	0
T-100-B	100	0	0	wt% of the solution 5
H-10-A	90	10	0	0
H-10-B	90	10	0	wt% of the solution 5
H-20-A	80	20	0	0
H-20-B	80	20	0	wt% of the solution 5
H-30-A	70	30	0	0
H-30-B	70	30	0	wt% of the solution 5
H-40-A	60	40	0	0
H-40-B	60	40	0	wt% of the solution 5
D-10-A	90	0	10	0
D-10-B	90	0	10	wt% of the solution 5
D-20-A	80	0	20	0
D-20-B	80	0	20	wt% of the solution 5
D-30-A	70	0	30	0
D-30-B	70	0	30	wt% of the solution 5
D-40-A	60	0	40	0
D-40-B	60	0	40	wt% of the solution 5

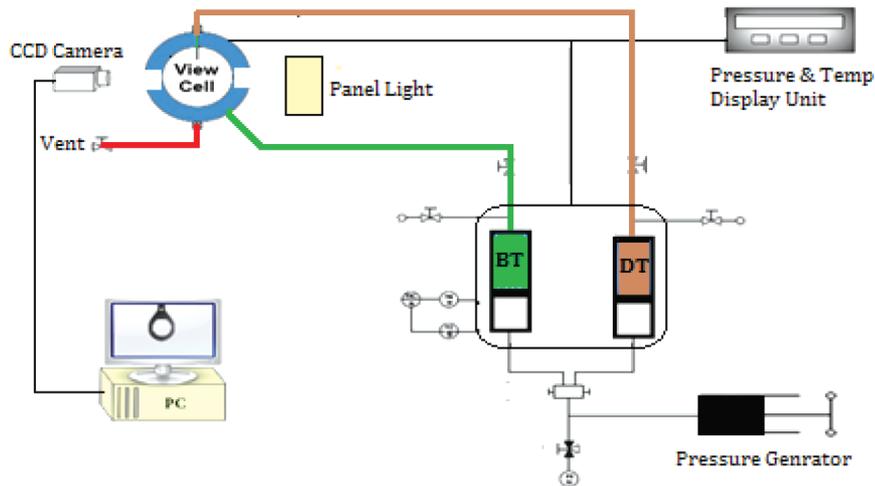


Figure 1. Schematic illustration of the experimental setup

$\text{CO}_2$  gas (with a purity of more than 99.99%) was prepared from a local company. The pendant drop method was applied to determine the IFT of gas-oil at reservoir conditions. Figure 1 shows the IFT measuring device, which includes a visible high pressure chamber.

The apparatus also includes a high pressure pump and a pressure gauge employed to measure the pressure in the system. The whole system is covered with a controllable thermal chamber. The IFT device is equipped with a high resolution camera, which is located at one side of the chamber, and a light source placed at the other side of the chamber. The camera is connected to a computer with drop shape analysis software to estimate the IFT of oil and gas based on the shape of the pendant drop.

The IFT value is very sensitive to impurities; therefore, cleaning different parts of the device is very crucial; hence, before starting any test, cleaning of the inside parts of the device is performed by injecting toluene, then, acetone followed by rinsing with de-ionized water. To start a test, the oil phase is transferred into the droplet fluid storage tank (DT) using a piston and the gas phase is transferred into the bulk fluid storage tank (BT). Next, the temperature of visible chamber and reservoir tanks of bulk fluid and drop are set to a desired temperature. A pressure producer is used to inject the gas into the cell and to pressurize it at a desired value. A capillary tube is mounted at the top of the high pressure cell from which

the oil droplet is injected to the bulk gas. To achieve equilibrium conditions (i.e. constant temperature and pressure conditions) enough time should be given. Then the IFT between two fluids is recorded over time until reaching the thermodynamic equilibrium conditions. In order to reach to thermodynamic equilibrium at a shorter time, several drops (20-30 drops) of oil are injected into the chamber. The test is considered at the equilibrium condition when the IFT does not change with time significantly. All experiments were performed at constant temperature of 323.15 K. To estimate IFT, it is necessary to determine the density of two fluids at experimental temperature and pressure conditions. Therefore, the fluids density was measured at different pressures and temperatures using a hydrometer (Anton Parr device) with high accuracy (i.e., 0.00001 (g/ml) ). Density of  $\text{CO}_2$  gas at any pressure and temperature is taken from valid references [27].

### 3. Results and Discussion

#### 3.1 Impact of normal paraffin on asphaltene precipitation

Interfacial tension of toluene-n heptane solutions and  $\text{CO}_2$  gas was measured at different pressure conditions ranging from 3 to 7 MPa and the temperature of 323.15 K, and the results are shown in Figure 1. Since n-heptane is lighter than toluene (in terms of molecular weight), as more

heptanes is added to the mixture, molecular weight of the solution decreases. Thus, the IFT

between synthetic solution and CO<sub>2</sub> decreases by increasing the heptanes content.

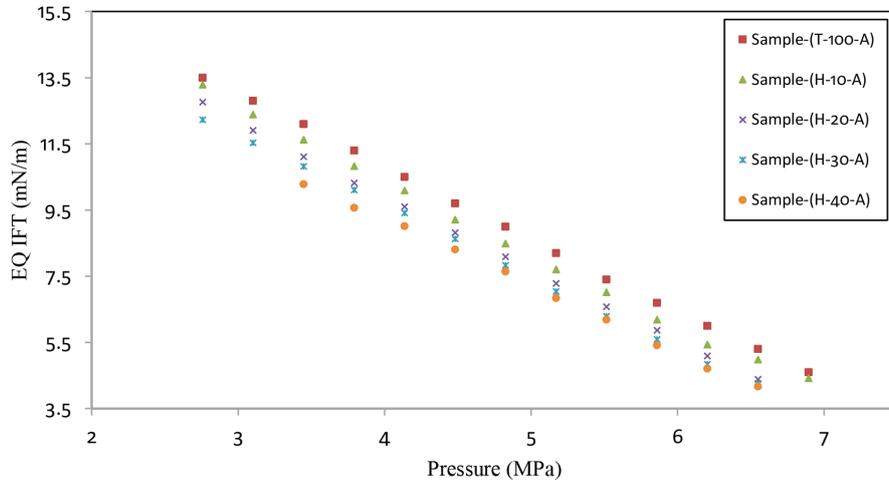


Figure 2. The equilibrium IFT versus pressure diagram of toluene-n heptane and CO<sub>2</sub> solutions at temperature 323.15 K

The linear data presented in Figure 2 shows that the difference between IFT data of various solutions reduces at high pressure conditions. That is at high pressures the impact of heptane content on IFT values reduces. The IFT of toluene-normal paraffins solutions containing 5

wt% asphaltene with CO<sub>2</sub> was measured in order to investigate the impact of asphaltene on IFT in the synthetic solutions. Figure 3 shows the IFT of toluene-n heptane-asphaltene and CO<sub>2</sub> at different pressures.

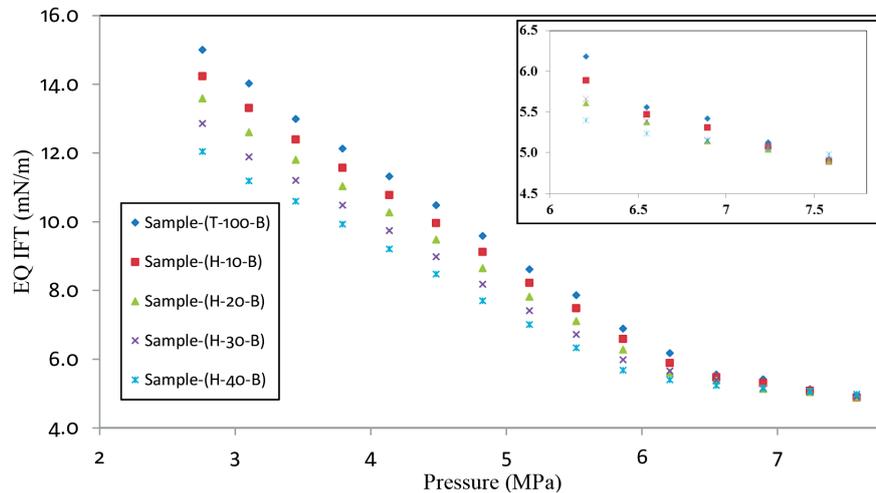


Figure 3. The equilibrium IFT versus pressure diagram of toluene-n heptane-asphaltene and CO<sub>2</sub> at 323.15K

As shown in Figure 3, IFT decreases with two different trends at low and high pressure intervals. The IFT reduction at low pressure interval (i.e. 3-5.5 MPa) could be mainly due to higher mass transfer between the gas and oil phase as the system is more pressurized. As pressure increases, more CO<sub>2</sub> dissolves in the oil phase and hence the oil phase swells and gas-oil

IFT decreases. However, the rate of IFT reduction at high pressure range (i.e. 6-8 MPa) is smaller compared to that of the low pressure interval. At high pressure range, although dissolving CO<sub>2</sub> causes the reduction of IFT value, accumulation of asphaltene at the interface of the oil phase and CO<sub>2</sub> occurs, which results in increasing IFT. Increasing trend of IFT critically intensifies when

the surface coverage of the particles surpassed a threshold value (e.g., + 60 % surface coverage) [28-29]. However, the effect of CO<sub>2</sub> solubility on IFT is more intense than surface coverage. Therefore, at high pressure range the rate of IFT reduction is much smaller than that of the first interval.

From the experimental data shown in Figure 3, it can be also concluded that as the heptane content increases in the oil solution, more asphaltene accumulation and precipitation would take place. Tracking the trends of the plots indicates that upon raising the heptane content of the oil solution, the second trend starts at a lower pressure. This means that asphaltene starts to precipitate at lower pressures if heptane content of the test oil increases.

Table 3 shows the correlations obtained to relate IFT and pressure for each one of the oil solutions at two different pressure regions. The first column of the table specifies the tested sample. The second column shows the test pressure ranges and correlations relating IFT to pressure are given in the third column. The corresponding R<sup>2</sup> values for each of the proposed equations are reported in the fourth column, showing the goodness of fit. Minimum miscible pressure was estimated for each mixture by putting P equal to zero in the pertinent IFT-pressure correlation and is presented in the fifth column. The last column shows the percent increase of minimum miscible pressure calculated from the second interval equation compared to that of the first period.

Table 3. IFT and minimum miscible pressure of different mixtures of toluene-n heptane-asphaltene and CO<sub>2</sub> at temperature of 323.15 K

Sample	Pressure	IFT vs Pressure correlation	R <sup>2</sup>	MMP (MPa)	FCM / MCM
	P:	P:			
Sample-(T-100-B)	$2.75 \leq P \leq 6.55$	$IFT = -2.5096P + 21.73$	0.9984	8.66	1.76
	$6.55 \leq P \leq 7.58$	$IFT = -0.6410P + 9.79$	0.9844	15.27	
Sample-(H-10-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.4173P + 20.79$	0.9995	8.60	1.79
	$6.21 \leq P \leq 7.58$	$IFT = -0.6236P + 9.60$	0.9913	15.40	
Sample-(H-20-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.3018P + 19.79$	0.9993	8.59	1.91
	$6.21 \leq P \leq 7.58$	$IFT = -0.5511P + 9.03$	0.9548	16.38	
Sample-(H-30-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.1925P + 18.79$	0.9994	8.57	1.95
	$6.21 \leq P \leq 7.58$	$IFT = -0.5337P + 8.91$	0.9627	16.70	
Sample-(H-40-B)	$2.75 \leq P \leq 5.76$	$IFT = -2.0503P + 17.65$	0.9994	8.60	2.39
	$5.76 \leq P \leq 7.58$	$IFT = -0.3787P + 7.80$	0.9302	20.59	

As shown in Table 3, for each oil solution, the IFT plot versus pressure could be treated as two lines with two different slopes for low and high pressure ranges. The decrease of IFT with pressure in the first period could be related to the accumulation of asphaltene particles [23], and the decrease in the second period

would be caused by asphaltene precipitation at the interface [23]. The latter gentle slope would be due to asphaltene precipitation, and consequently altering the intermolecular forces at the interface of two phases. As Figure 3 and the corresponding equations in Table 3 show, slope of the first and the second lines become

gentler by increasing n-heptane content of the oil solution. For instance, for sample (T-100-B), which is free of n-heptane, decline slopes of the first and second period reduce from 2.5096 ((mN/m)/MPa) to 2.0503 ((mN/m)/MPa) and from 0.6410 ((mN/m) /MPa) to 0.3787 ((mN/m)/MPa), respectively, when the amount of n-heptane in the solution reaches to 40 percent. This change in the slopes could be an indication of this point that asphaltene precipitation in solutions containing n-heptane is more severe. According to the theory of vanishing interfacial tension (VIT), when IFT of two fluids becomes zero two fluids dissolve completely in each other. Based on the presented relationships in each of the pressure periods, there will be a certain pressure at which the IFT is zero. In the fourth column of Table 3, the minimum miscible pressure estimated from extrapolating the data of each period to zero IFT is given. As shown in this table, the minimum miscible pressure estimated from the first period is lower than that from the second period. This is because the minimum miscible pressure (MMP) estimated from the first period represents the multiple minimum miscible pressure (MCM) and the

minimum miscible pressure estimated from the second period represents first contact miscible pressure conditions (FCM) [30]. The MMP at MCM conditions is not significantly affected by heptane content of the oil solution, whereas the MMP at FCM conditions is drastically affected by heptane content. The last column shows the ratio of the MMP estimated based on the data of the second period (high pressure range) to that based on the data of the first period (low pressure range). This column shows that this ratio increases as the heptane content increases. This could be due to asphaltene precipitation, which mainly increases the FCM pressure condition up to two times. The level of change in MMP shows the need for accurate prediction of asphaltene precipitation pressure.

Figure 4 shows the IFT versus pressure of toluene - n decane solutions in the proximity of CO<sub>2</sub> gas. Molecular weight of n-decane is closer to molecular weight of toluene compared to that of n-heptane. Therefore, the IFT values at a constant pressure are closer to each other for different solutions of n-decane and toluene in comparison with different solutions of n-heptane and toluene.

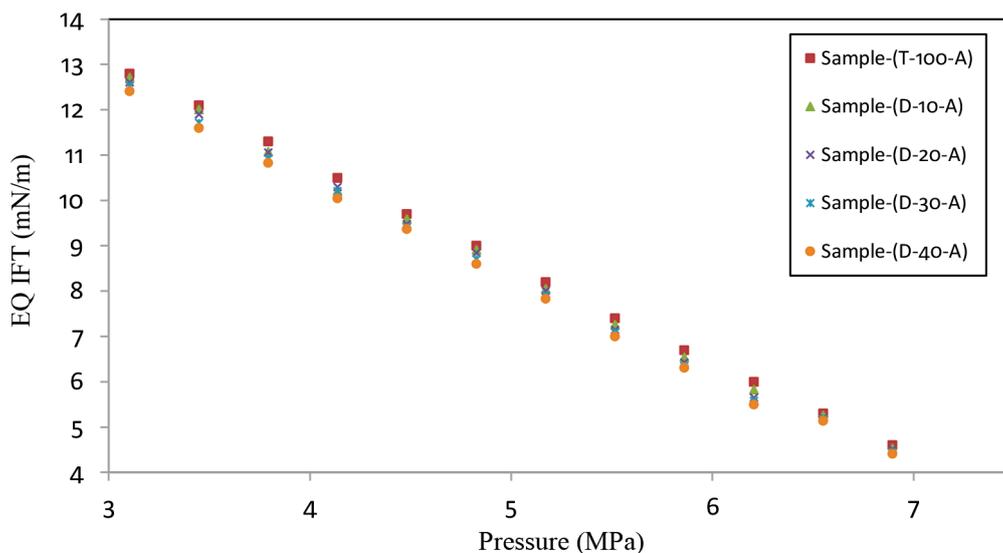


Figure 4. The equilibrium IFT versus pressure diagram of toluene-n decane solutions and CO<sub>2</sub> at temperature of 323.15 K

Figure 5 also shows that IFT values reduce linearly with pressure for different oil solutions and CO<sub>2</sub> systems.

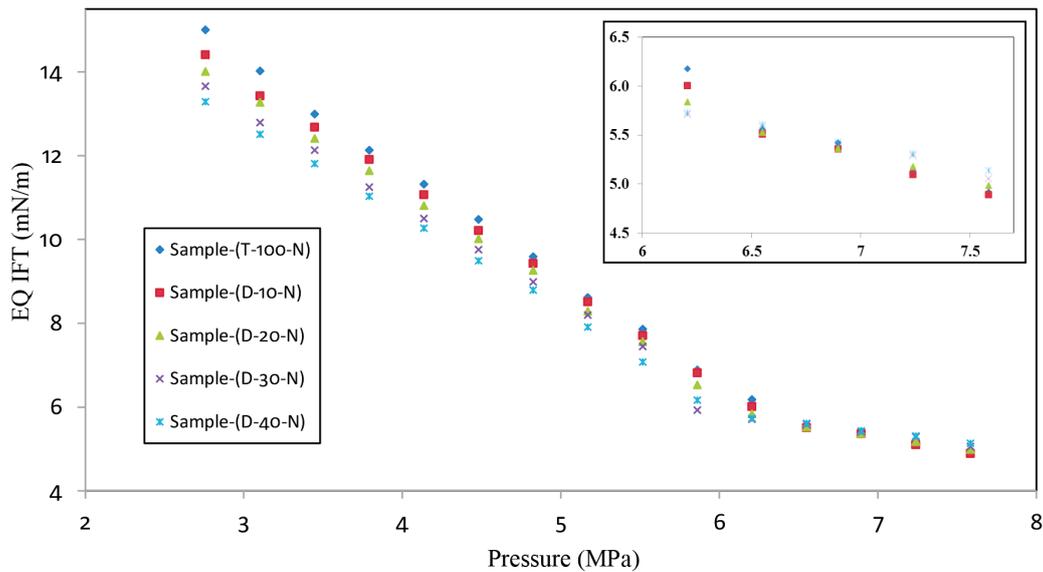


Figure 5. The equilibrium IFT versus pressure diagram of toluene-n decane-asphaltene solutions and CO<sub>2</sub> at 323.15 K

Figure 5 shows the IFT versus pressure of different toluene-n decane solutions with 5 wt% of asphaltene at temperature 323.15 K. Similar to the data of n-heptane solutions, these data can be divided into two groups, each with different slope. The trend of the experimental data specifies that asphaltene precipitation occurs at lower pressure, if the amount of n-decane in the

oil solution increases.

Table 4 shows the equations fitted to the experimental data of IFT versus pressure for each of the oil solutions at two different pressure periods. The minimum miscible pressure estimated for each solution, and their percent increase in each period have been also reported in Table 4.

Table 4. IFT and minimum miscible pressure of mixtures of toluene-n decane-asphaltene and CO<sub>2</sub> at temperature of 323.15 K

Sample	Pressure $P = (\text{MPa})$	IFT vs Pressure correlation		$R^2$	MMP (MPa)	FCM / MCM
		$IFT: \left(\frac{\text{mN}}{\text{m}}\right)$	$P = (\text{MPa})$			
Sample-(T-100-B)	$2.75 \leq P \leq 6.55$	$IFT = -2.5096P + 21.73$		0.9984	8.66	1.76
	$6.55 \leq P \leq 7.58$	$IFT = -0.6410P + 9.79$		0.9844	15.27	
Sample-(D-10-B)	$2.75 \leq P \leq 6.55$	$IFT = -2.4205P + 21.05$		0.9997	8.70	1.79
	$6.55 \leq P \leq 7.58$	$IFT = -0.6149P + 9.56$		0.9904	15.55	
Sample-(D-20-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.3893P + 20.68$		0.9993	8.65	1.84
	$6.21 \leq P \leq 7.58$	$IFT = -0.5946P + 9.48$		0.9859	15.94	
Sample-(D-30-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.3578P + 20.23$		0.9934	8.58	1.97
	$6.21 \leq P \leq 7.58$	$IFT = -0.5641P + 9.51$		0.9873	16.87	
Sample-(D-40-B)	$2.75 \leq P \leq 6.21$	$IFT = -2.2694P + 19.615$		0.9990	8.64	2.26
	$6.21 \leq P \leq 7.58$	$IFT = -0.5462P + 9.24$		0.9960	19.57	

According to Table 4, as the amount of n-decane increases in the oil solution, asphaltene precipitation starts to occur at a lower pressure. Similar to heptane solutions, FCM pressure increases more than MCM pressure as n-decane in the oil solution increases.

### 3.2. Impact of asphaltene content on precipitation

As stated before, the change and rate of change of the IFT slopes specify the onset and strength of asphaltene precipitation. Figure 6 shows the impact of asphaltene mass fraction in the synthesized solutions on the change of IFT slope at different pressure regions and consequently the intensity of asphaltene precipitation.

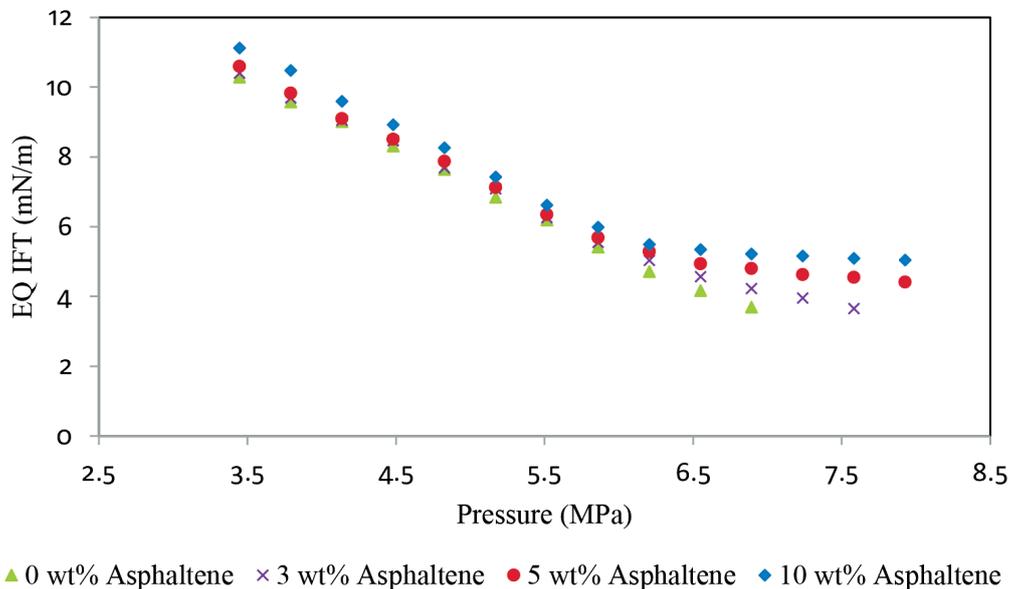


Figure 6. The equilibrium IFT versus pressure for CO<sub>2</sub> and oil solutions with different asphaltene content at temperature 323.15 K

Figure 6 also illustrates the variation of IFT versus pressure for different mass fractions of asphaltene in the solution along with CO<sub>2</sub> gas. At low pressures i.e. the first region, IFT decreases as pressure increases with a sharp slope, though, the trend is nearly similar for all four tested solutions. However, at high pressures, because of asphaltene precipitation, the rate of IFT reduction declines for all three solutions containing asphaltene (3, 5, 10 wt%). Nevertheless, for solution with 10 wt% asphaltene the slope of second region is the smallest compared to

those of other two solutions because of more asphaltene precipitation. Intense precipitation of large asphaltene molecules in this solution at the interface of CO<sub>2</sub> gas and oil has led to disruption of intermolecular forces and IFT increase. Percentage change in the slope of the second region than in the first region is an appropriate criterion for assessment of the rate of asphaltene precipitation. Figure 7 shows the percent of change in the slope of the second region than the slope of the first region for four solutions with different asphaltene percent.

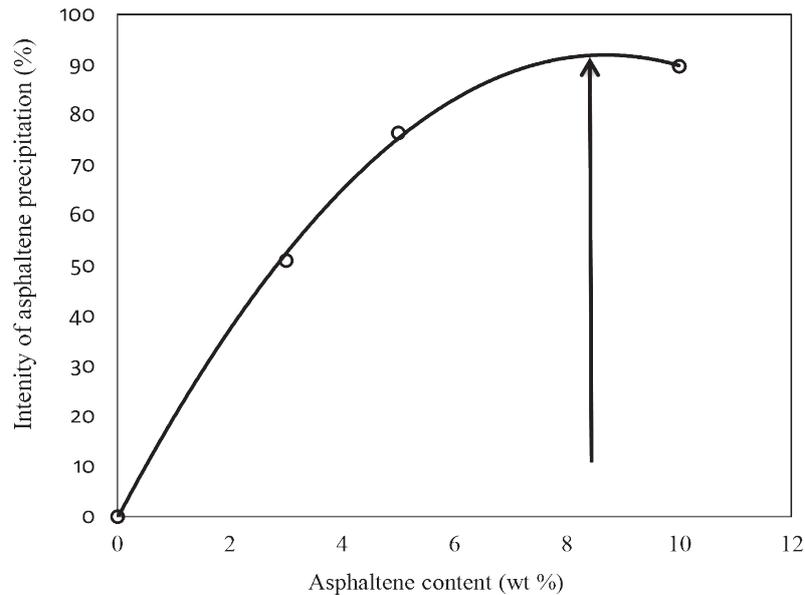


Figure 7. Intensity of asphaltene precipitation for four solutions with different asphaltene content

According to figure 7, increasing asphaltene particles increases asphaltene aggregation at the surface. In the second region (e.g., + 60 % surface coverage) the asphaltene particles aggregation increases the IFT, on the other hand, the  $\text{CO}_2$  solubility decreases the IFT. Therefore, the percent change in the slope of the second region in comparison with the first region increases with increasing asphaltene content. The maximum asphaltene precipitation is for 8-9% asphaltene solutions, according to the second polynomial function. This means that the suspended particles do not tend to be at the fluids interface after surpassing a certain concentration. Therefore, the increase of IFT extent, which is because of asphaltene precipitation at fluids interface, decreases and asphaltene precipitation extent decreases accordingly.

### 3.3. Validating the experimental data

The reproducibility of the experimental results presented here was examined by repeating the IFT test three times at each pressure and temperature conditions. The amount of the standard deviation between the data was observed to be less than 0.1 (mN/m). In this study, average of three data was used as the IFT corresponding to the desired pressure and temperature conditions. To compare the measured data from the experiments of this study with those from the previous studies, the IFT of n-heptane and  $\text{CO}_2$  versus pressure were measured at temperatures of 333.15 and 323.15 K. The estimated minimum miscible pressure (using vanishing interfacial tension in this study) is compared with the values estimated from the similar systems in other studies [22, 31]. The results are shown in Table 5.

Table 5. The experimental results of this study versus the literature data

	T = 323.15 K			T = 333.15 K		
	Experimental Result	Ref [22]	Percent Difference	Experimental Result	Ref [31]	Percent Difference
Decline Slope ( $10^9 \text{ m}^3$ )	1.90	2	% -5	1.63	1.64	-0.60%
Estimated MMP (MPa)	8.40	8.5	% -1.2	8.93	9.00	-0.77%

## 4. Conclusions

Based on the results of this study, the following conclusions can be drawn:

- IFT data of toluene-normal paraffins solutions, containing asphaltene and  $\text{CO}_2$ , versus pressure shows two different slopes. The data in the first interval represents the conditions at which the solubility of  $\text{CO}_2$  gas in the oil solution takes place, while the second slope represents the asphaltene precipitation conditions at the interface of two phases (i.e. oil and gas). With increase in the normal paraffin content in the solution both slopes decrease, however, the decrease of the second slope is more pronounced. The asphaltene particles cover the interface of two fluids more rapidly by increasing the n-paraffin content of the oil phase, consequently:

- i) n-paraffins act as the asphaltene particles instability compounds, therefore, increasing normal paraffins means transferring more asphaltene to the fluids interface and hence increasing IFT. On the other side,  $\text{CO}_2$  solubility decreases IFT. The overall effect is that these two opposite factor make the slope of interfacial tension versus pressure plot to change at a lower pressure, showing that the asphaltene precipitates earlier.

- ii) Increasing n-paraffin means putting more asphaltene particles at the fluid surface. Thus, at a specific pressure for second region, by increasing n-paraffin, the size of asphaltene particles at surface grows. Accordingly, the IFT gets larger. On the other hand, rising pressure makes  $\text{CO}_2$  more soluble in the oil. This event decreases the IFT. Consequently, these two inconsistent phenomena cause lower slope for IFT plot and more n-heptane inside the oil drop.

Therefore, normal paraffin in the oil solution containing asphaltene improves and accelerates asphaltene precipitation.

- In oil solution- $\text{CO}_2$  systems, both trends of IFT data versus pressure have zero real roots. Based on the theory of vanishing interfacial tension (VIT), the pressure root would represent the MMP. The root that is estimated from the data at low pressure conditions (i.e. the first slope)

is equal to MCM pressure and the root of the data at high pressure conditions (i.e. the second slope) is equal to FCM. Due to the asphaltene precipitation, the difference between these two parameters becomes larger when the amount of normal paraffins in the solution increases.

- The amount of asphaltene precipitation depends on asphaltene concentration in the solution. By increasing asphaltene concentration until a certain amount, the particles will move toward gas-liquid interface. Presence of particles at the interface disturbs intermolecular forces and increases IFT. Also, dissolving  $\text{CO}_2$  in oil causes IFT to decrease. On the whole, these two different factors decrease the IFT. Therefore, presence of asphaltene at interface increases by increasing asphaltene concentration in solutions until a certain amount and it leads to decrease of IFT. However, presence of particle has a negligible effect after surpassing a certain amount of asphaltene concentration.

## 5. Acknowledgments

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## تاثیر نرمال پارافین ها و رسوبات آسفالتینی بر کشش بین سطحی نفت / گاز، حین تزریق گاز دی اکسید کربن به مخازن نفتی آسفالتینی

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### چکیده

رسوب آسفالتین در مخازن همواره مشکلات متعددی را به همراه داشته است. بنابراین شناخت دقیق مکانیزم رسوب لازمه مقابله با آن می باشد. روش های متعددی جهت شناسایی رسوب آسفالتین وجود دارد. یکی از این روش ها، روش ناپدید شدن کشش بین سطحی می باشد. در این روش با ترسیم نمودار کشش بین سطحی تعادلی بر حسب فشار، مکانیزم رسوب تشریح داده می شود. در این مطالعه به منظور بررسی دقیق تر رسوب آسفالتین در مخازن نفتی با استفاده از نمودارهای کشش بین سطحی بر حسب فشار، از محلول های سینتیتیک متشکل از تولوئن و نرمال پارافین ها استفاده می شود. به این منظور، محلول های با ترکیب درصد متفاوت از تولوئن و نرمال پارافین هایی همچون نرمال دکان و نرمال هپتان یک بار در حضور آسفالتین استخراج شده از نفت خام و یک بار در عدم حضور آن ساخته می شود. سپس کشش بین سطحی تعادلی آن محلول ها با گاز دی اکسید کربن در فشارهای مختلف اندازه گیری می شود. با ترسیم نمودارهای کشش بین سطحی بر حسب فشار، نقطه شروع رسوب آسفالتین و پارامترهای مختلف موثر، مورد بررسی قرار می گیرد. با توجه به نتایج آزمایش ها، حضور آسفالتین در محلول های سینتیتیک باعث تغییر در مقادیر و روند نمودار کشش بین سطحی بر حسب فشار می شود. بدین صورت که افزوده شدن آسفالتین به یک محلول از تولوئن و نرمال پارافین باعث می شود کشش بین سطحی محلول و گاز دی اکسید کربن بر حسب فشار در دو بازه ی مختلف با دو شیب مختلف افت می کند. نتایج تایید می کند که افزایش نرمال پارافین ها باعث تشدید رسوب آسفالتین می شود و همچنین با افزایش میزان رسوبات آسفالتنی موجود در محلول ها، شدت رسوب آن ها نیز افزایش می یابد.

واژگان کلیدی: رسوب آسفالتین، استخراج آسفالتین، کشش بین سطحی، کمترین فشار امتزاجی، تزریق گاز، نرمال پارافین