



An analysis of methods for determination of onsets of asphaltene phase separations

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Abstract

It is demonstrated that one may identify up to seven distinct phase transition points due to separations of heavy organics (saturates, resins and asphaltenes) from petroleum fluids. They include saturates-cloud point, saturates-pour point, asphaltene-precipitation onset (APO), asphaltene + resin-flocculation (colloid formation) onset (ARFO), asphaltene + resin-deposition onset (ARDO), asphaltene-micellization onset (AMO) and asphaltene-coacervation onset (ACO). The existing experimental methods for determination of the onsets of asphaltene phase separations/transitions are analyzed. It is demonstrated that these threshold-point measurement techniques are for various purposes, and they serve to measure onset of different phase separations due to changes in the conditions of a petroleum fluid under consideration.

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1. Introduction

Many problems could arise during production, processing, transportation and storage of petroleum fluids due to heavy organics (diamondoids, paraffins/waxes, resins and asphaltenes) separation. Therefore, it is crucial to know “when” and “how much” heavy organics will separate out of solution in the form of a heavier phase under a given set of operating conditions. Accurate determination of the threshold points of heavy organics separation from petroleum fluids is

required in order to characterize petroleum fluids, develop preventive measures for phase separation and possibly formulate theoretical models for phase separation prediction. Understanding the meaning of any experimental results of such analyses are the cornerstone of any characterization, predictive and preventive measures for heavy organics deposition from petroleum fluids.

Asphaltene particles are believed to exist in petroleum partly dissolved and partly in steric-colloid and/or micelle forms depending on the polarity of their oil medium and presence of other compounds in oil. In the last few years, the precipitation, flocculation and deposition of these molecules have been characterized and analyzed (Riazi, 1989; Kawanaka et al., 1989; Pan and Firoozabadi, 2000; Wu et al., 1998; Rassam-

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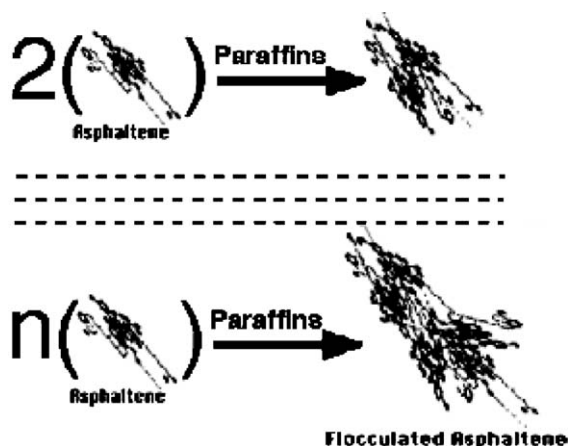


Fig. 1. Various stages of asphaltene flocculation due to excess amounts of paraffins in the solution.

dana et al., 1996; Branco et al., 2001). A steric-colloid is formed when a large non-soluble particle (asphaltene) is stabilized in the solution by adsorption of grafted polymers (resin) on its surface. The layer(s) of resin on large asphaltene particles will then repel each other if they are in a “good” solvent, and this overcomes the van der Waals attraction so that the asphaltene particles will not aggregate. A micelle consists of a reversible assembly of molecules such as surfactants (asphaltene) that assemble together in a solution. Micellization is a phenomenon originally observed due to the self-association process of the surface active materials in aqueous solutions. These surface active materials, known as surfactants, tend to self-assemble into different geometric (disks, spheres, cylinders) shapes and become suspended in the solution. This phenomenon occurs only when the surfactant concentration exceeds a threshold known as critical micelle concentration (CMC). Whether the asphaltene particles are dissolved in crude oil, in steric-colloid state or in micelle form, to a large extent, depends on the presence of other particles (paraffins, aromatics, resins, etc.) in the crude oil. The existence of various states of asphaltenes in crude oil has been extensively discussed in numerous other publications (Nellensteyn, 1983; Yen and Chilingarian, 1994; Laux and Rahimian, 1994; Mansoori, 1996, 1997; Vasquez and Mansoori, 2000).

Smaller-size asphaltene particles may be dissolved in petroleum fluid, whereas relatively large asphaltene

particles may precipitate out of the solution due to addition of a certain amount of a paraffin hydrocarbon. The onset of precipitation of asphaltenes in a crude oil can be accurately detected by measurement of the interfacial tension (IFT) as demonstrated by Vuong (1985) and Kim et al. (1990).

Upon introduction of additional paraffin hydrocarbons to the oil, asphaltene will flocculate out of the solution forming random aggregates as shown in Fig. 1.

Flocculation of asphaltene in paraffinic crude oils is known to be irreversible, having hysteresis when the conditions are returned to pre-flocculation point (Abedi et al., 1998; Acevedo et al., 1995; Birket, 1997; Fuhr et al., 1991). This is the major cause of unreparable arterial blockage damage to the flow of petroleum fluids. Due to their large size and their adsorption affinity to solid surfaces, flocculated asphaltenes can cause irreversible deposition which may not easily wash away. One of the effective remediation methods of heavy organic deposits is the use of strong aromatic/polar solvents that could dissolve the asphaltene deposits (Kim et al., 1990; Acevedo et al., 1995; Dubey and Waxman, 1995; Waxman et al., 1980; Sanchez and Mansoori, 1997). Asphaltene flocs (random aggregates) can form steric-colloids in the presence of excess amounts of resins and paraffin hydrocarbons (Swanson, 1942; Lichaa, 1977; Park and Mansoori, 1988; Mansoori et al., 1988; Mansoori, 1997) as shown in Fig. 2.

The onset of steric-colloid formation of asphaltenes in a crude oil can be accurately detected using viscometric techniques as demonstrated by Escobedo and Mansoori (1995).

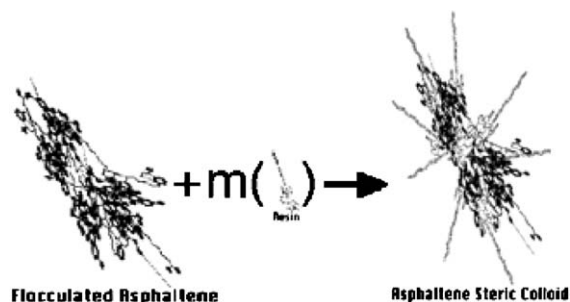


Fig. 2. Steric-colloid formation of asphaltene flocs (random aggregates) in the presence of excess amounts of resins and paraffin hydrocarbons.

Upon introduction of additional paraffin hydrocarbons, the asphaltene flocs will grow in size, and, as a result, larger and larger steric-colloids will be formed. Considering that there is always an upper size limit to the stability of a colloid in a medium the asphaltene steric-colloids will start to deposit at certain concentration of the added paraffin hydrocarbons. This limit, which can be observed by formation of deposited flocs of asphaltene+resin particles are known as the onset of asphaltene deposition. This onset point can be observed by a microscope, through changes in light transmissions and by measurement of electrical conductivity of the oil medium.

Various investigators have established the existence of asphaltene micelles when an excess of aromatic hydrocarbons is present in crude oil (Pfeiffer and Saal, 1940; Dickie and Yen, 1968; Galtsev et al., 1995; Mansoori, 1996; Priyanto et al., 2001). Several investigators have performed experimental measurements of critical micelle concentration for solutions of asphaltene in aromatics solvents (Sheu and Mullins, 1995; Andersen and Birdi, 1991; Rogacheva et al., 1980; Ravey et al., 1988; Priyanto et al., 2001). Furthermore, the phenomenon of self-association in asphaltene/toluene systems has been confirmed through measurements of surface tension (Rogacheva et al., 1980; Sheu and Mullins, 1995) and viscosity (Priyanto et al., 2001). It is shown (Sheu and Mullins, 1995) that at low concentrations, below the CMC, the asphaltenes in solution are in a molecular state, whereas, above the CMC, asphaltene micelle formation occurs in a manner similar to that in surfactant systems where surfactant monomers are much uniform in their structure and less polydisperse. With small concentration of asphaltene (less than 0.1–1.0 mg/g solvent), true solutions are formed (Rogacheva et al., 1980). Rogacheva et al. (1980) and Priyanto et al. (2001) have also reported experimental data for the phase diagram of asphaltene micelle formation when

asphaltene dissolved in toluene and methyl-benzene. They indicate that mixing a purified asphaltene with aromatic solvents results in formation of a true solution for asphaltene concentrations in the range 0–1 mg per gram of toluene. These experimental data indicate that further increase in asphaltene concentration, would start the asphaltene micelle formation. The aliphatic chain and the polynuclear aromatic core of an asphaltene molecule represent the solvent-hating and the solvent-loving portions, respectively, which may cause asphaltene micelle formation. They also indicate that an increase in the concentration of asphaltene in toluene will result in the formation of larger micelles, then of coacervates, and, finally, to the separation of asphaltene as a separate phase. The possibility of coacervation of asphaltene micelles were originally reported by Rogacheva et al. (1980). Priyanto et al. (2001) produced experimental data for the micelle coacervation point (MCP) of asphaltene through viscosity measurements.

Asphaltene molecules may have an average molecular diameter around 5 nm. The size distribution of asphaltene micelles may have an average size around 25 nm. Whereas micellar coacervates may have sizes greater than 25 nm. Espinat and Ravey (1993), with the use of scattering techniques, have shown that the best model to describe the morphology of asphaltene micelle in solution is a disk. However, several other experimental investigations have shown that asphaltenes could be of spherical-like, cylindrical-like or disk-like form (Yen and Chilingarian, 1994; Sheu and Mullins, 1995; Ravey et al., 1988; Espinat and Ravey, 1993). Several experimental investigations have indicated that asphaltene micelles could be of spherical-like, cylindrical-like or disk-like form (Espinat and Ravey, 1993; Yen and Chilingarian, 1994). All these investigations are indicative of the fact that asphaltene particles may self-associate, but not flocculate, and

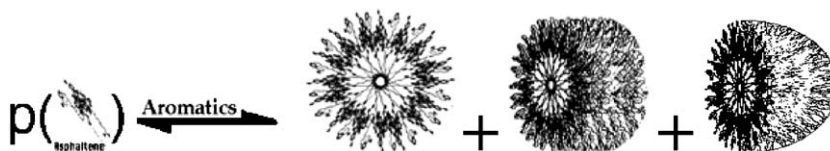


Fig. 3. Micellization (self-association) of asphaltene due to increase in aromaticity (polarity) of its medium.

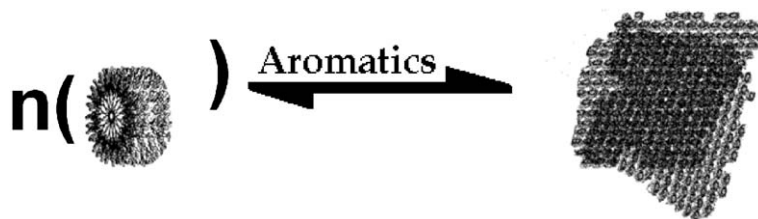


Fig. 4. Coacervation (self-association) of asphaltene micelles due to increase of micelle concentration in an aromatic (polar) medium.

form micelles in the presence aromatic hydrocarbons (or other polar solvents) as shown in Fig. 3. An example of asphaltene micelle coacervation is depicted in Fig. 4.

Sanchez and Mansoori (1998) developed a theoretical model to explain and quantify the phenomenon of asphaltene micellization and coacervation.

It should be noted from the above discussion that there may exist up to five distinct phase transitions during asphaltene separations from a petroleum fluids. These are:

1. Asphaltene-precipitation onset (APO)
2. Asphaltene + resin-flocculation onset (ARFO)
3. Asphaltene + resin-deposition onset (ARDO)
4. Asphaltene-micellization onset (AMO)
5. Asphaltene-coacervation onset (ACO)

APO, ARFO and ARDO are defined to be the points at which the asphaltene begins to precipitate, flocculate and deposit, respectively, due to addition of paraffin hydrocarbons to a petroleum fluid. AMO and ACO are defined to be the points at which the asphaltene begins to micellize and coacervate, respectively, due to addition of aromatic hydrocarbons to a petroleum fluid. Proper estimation of APO, ARFO and ARDO are of practical importance in a number of petroleum-related processes. In the following sections, experimental methods for the detection of the above onset points are further discussed.

2. Determination of asphaltene-precipitation onset

The only method known so far for determination of asphaltene-precipitation onset is based upon measurement of the IFT between oil and water phases. In this technique, the onset of asphaltene precipitated from

petroleum fluids can be closely related to a sudden change in IFT of the oil/water system.

To demonstrate this technique, the IFT between water and various crude oils mixed with *n*-heptane were measured by the DuNouy ring method. All measurements were made at 25 °C. Similar phenomena regarding the variations of surface tensions and IFTs of a variety of crude oils and blends were observed (Kim et al., 1990).

To demonstrate measurement of the APO, results of analysis of three different crude oils (Brookhaven, DK-107 and Sohio) are reported here. In Table 1, the weight percentages of asphaltene contents and molecular weight of these three crude oils are listed. It can be noted that DK-107(LST) crude has negligible weight percentages of asphaltenes.

Fig. 5 shows the variation of surface tension and IFTs of Brookhaven oil mixed with *n*-heptane versus the percentage in weight of *n*-heptane in the mixture. According to this figure, the influence of asphaltene precipitation on the IFT of the water and oil is dramatic after the onset of asphaltene precipitation is reached. Fig. 5 also displays the instability of IFT after the onset of asphaltene precipitation has occurred.

Fig. 6 shows the variation of IFT for a light oil (DK-107), which contains very small amount of asphaltene and has no onset of precipitation due to the presence of sufficient amount of appropriate resin in it, versus the weight percentage of *n*-heptane added to the oil. IFT of DK-107 oil + *n*-heptane mixture with

Table 1
Asphaltene content of crude oils

Oil	Molecular weight (g/mol)	Asphaltene (wt.%)
Brookhaven	186.4	6.8
DK-107(LST)	NA	0.8
Sohio	278.0	4.2

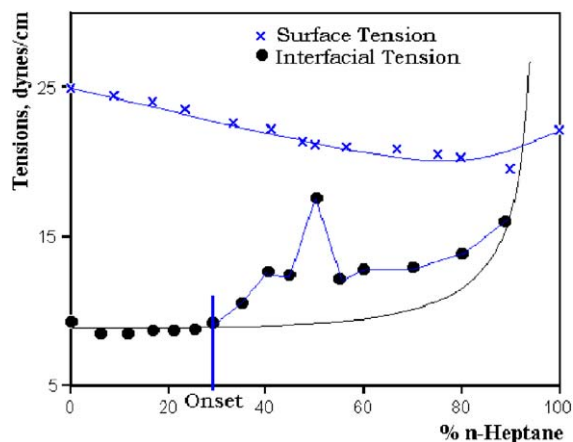


Fig. 5. Onset of asphaltene precipitation for Brookhaven oil due to addition of various weight percentages of *n*-heptane.

increase in the percentage of *n*-heptene in oil has a rather simple behavior as compared to that of Brookhaven oil which is asphaltenic, attaining steady low IFT of about 21 dyn/cm. Fig. 7 shows a similar trend as can be seen in Fig. 5 for an oil named 'Sohio'. Note in this figure the onsets of precipitation due to additions of *n*-pentane and *n*-heptane to Sohio Oil.

Comparing Fig. 6 with Fig. 5 indicates that the interface between the mixture of Brookhaven oil + *n*-heptane/water is a thermodynamically unstable system after the onset is reached. Several mechanisms may explain the instability of IFT between Brookhaven oil + *n*-heptane/water. Asphaltene precipitation seems

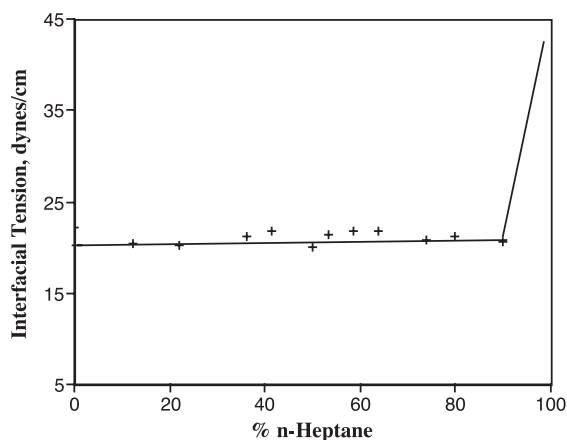


Fig. 6. Titration of DK-107(LST) oil with *n*-heptane which exhibits no asphaltene precipitation.

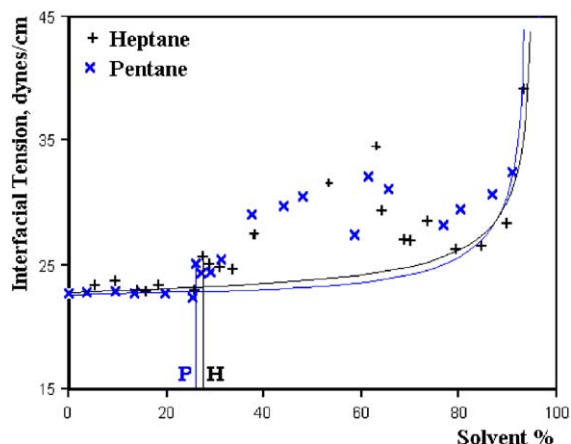


Fig. 7. Measurement of asphaltene-precipitation onset for Sohio Oil using two different asphaltene precipitating solvents.

to be the primary cause of the instability of oil/water IFTs. A number of researchers have examined the surface active materials that are concentrated at the oil/water interface. It was shown in the film-formation experiments that higher concentration of film-forming components (mainly asphaltenes) precipitated at the oil/water interface at lower temperatures (Hjelmeland and Larrondo, 1986). Due to high molecular weight and polarity, many of the asphaltenes precipitated will migrate to the interface between oil and water, resulting in the formation of an interfacial film. The observed IFT instability can then be attributed to the adhesion or deposition of surface active material at the interface between oil/*n*-heptane and water. It is well known that the interface between oil and water involving surface active material considered unstable, because of the small-scale interfacial turbulence created by the transfer of surface active materials.

3. Determination of asphaltene+resin-flocculation, asphaltene-micellization and asphaltene-coacervation onsets

In general, suspended particles affect the flow characteristics of the host fluid resulting in an increased viscosity. The problem of relating viscosities of colloidal suspensions to the properties of the dispersed particles has been the subject of numerous experimental and theoretical considerations (Einstein, 1956; Sherman, 1964; Goldsmith and Mason, 1964;

Graham, 1981; Gillespie, 1983). Einstein (1956) concluded that the effect of dispersed particles on the viscosity of a suspension depends only on the total volume that they occupy and is independent of their size. However, this is valid only for highly dilute suspensions of rigid, spherical, unisize and non-interacting particles. Rutgers (1962) and Sherman (1964) found that at moderate concentrations, the disturbances in the regions of flow around the particles are sizable, and they become more important for non-spherical and/or deformable particles. Although these findings are applicable to moderately concentrated suspensions, and account, to some extent, for non-rigidness; they consider only particle–solvent interactions but not particle–particle interactions (i.e., aggregation). For the case in which particles interact to form aggregates of different sizes and shapes, Gillespie (1983) studied the effect of particle aggre-

gation and particle size distribution on the viscosity of Newtonian suspensions arriving at the conclusion that it resulted in an increase in the relative viscosity of the suspension. Numerous experimental works have revealed the colloidal nature of certain asphaltene fractions of a crude oil peptized by resins (Chillinger and Yen, 1978). Kawanaka et al. (1989) consider the asphaltenes to exist in crude oil as both dissolved and suspended particles. Dispersed asphaltenes are sterically stabilized by neutral resins, they are electrically charged (Lichaa and Herrera, 1975) and they have a diameter of 30–40 Å (Ray et al., 1957).

When two asphaltene particles collide, aggregation could start. Upon growth of the aggregates, at a critical size limit, resin molecules will start to be adsorbed on the surface of asphaltene aggregate. Therefore, we may expect that at a particular solvent concentration the peptization process will be initiated.

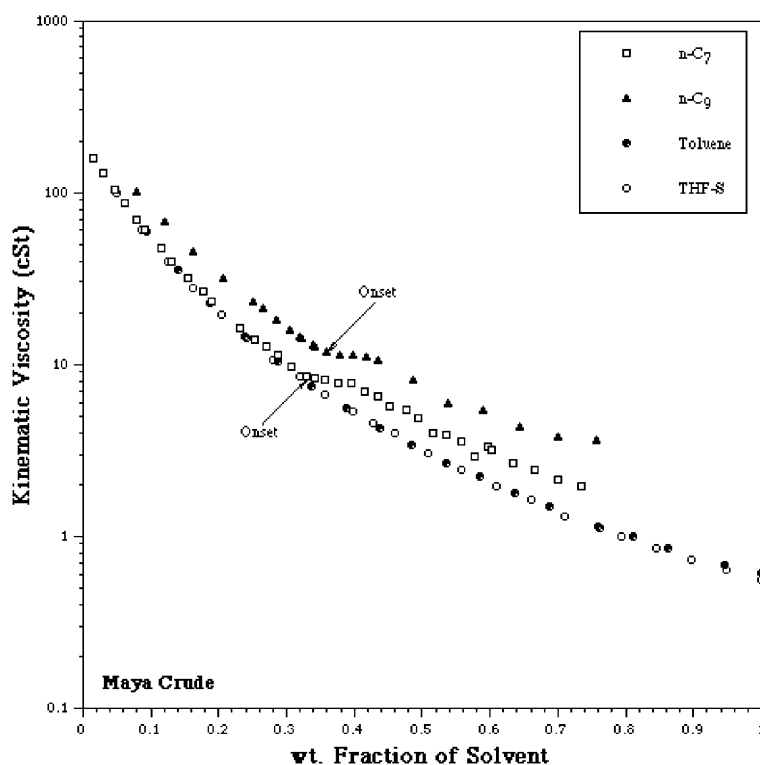


Fig. 8. Kinematic viscosity versus weight fraction of solvent in solutions of Maya crude with various solvents. ARFO was located at 32.9 wt.% (39.87 vol.%) for *n*-heptane and at 35.8 wt.% (41.8 vol.%) for *n*-nonane. The location of this point is enhanced by comparison with the toluene and THF-S curves. The THF-S is a 64.333 vol.% solution of THF in toluene. This solution has approximately the same kinematic viscosity as that of *n*-heptane.

This point is defined as asphaltene + resin flocculation onset or steric-colloid formation. The amount of solvent needed to arrive at this onset depends on the type of crude oil being analyzed, and the nature of the resin content (Leontaritis and Mansoori, 1989; Park and Mansoori, 1988; Vasquez and Mansoori, 2000). From the above facts and experimental observations, it seems possible that through accurate measurements of viscosity of crude oil upon titration with a precipitating agent ARFO can be determined. Therefore, in order to locate ARFO, we must analyze the trends of suspension viscosities as a function of precipitating solvent concentration.

To demonstrate the application of the viscosity as a means to measure ARFO, crude oils were diluted in various ratios with precipitating agents (i.e., *n*-pentane, *n*-heptane, etc.) at room temperature (Escobedo and Mansoori, 1995, 1997). Enough time was allowed for the mixture to reach thermal equilibrium and chemical stability before any measurement was made. The viscosity was measured using glass capillary

viscometers (Cannon-Fenske Opaque viscometer) suitable for dark fluids such as crude oils. In order to compare the results obtained from viscosity measurements, every sample was simultaneously analyzed using a microscope for visual detection of ARDO. It should be pointed out that ARDO occurs at a higher concentration of the flocculating agent than ARFO.

Fig. 8 shows the results obtained for the Maya crude, which has a density of 0.9164 g/cm³ at 25 °C and an asphaltene content of 12.31 wt.%. Two different flocculants (i.e., *n*-heptane and *n*-nonane) were used for the detection of ARFO in order to test the validity of the proposed technique. In addition, for comparison purposes, another run was made using toluene as solvent due to the fact that it does not cause asphaltene aggregation and flocculation. A fourth set of data is reported using a 64.33 vol.% solution of THF in toluene (THF-S). This solution was prepared to have the same kinematic viscosity as that of *n*-heptane knowing that it does not cause asphaltene aggregation and flocculation either. By inspection of

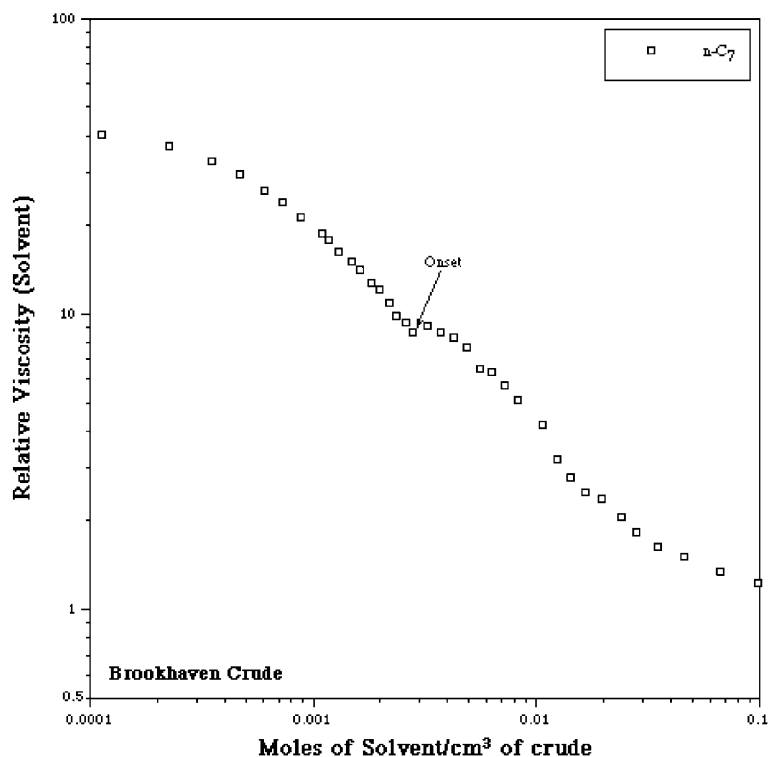


Fig. 9. Relative viscosity (with respect to pure solvent) versus moles of solvent per cubic centiliter of Brookhaven crude oil. ARFO for this crude oil was located at 0.00281 mol *n*-heptane/cc crude oil (29.32 vol.% *n*-heptane).

Table 2

Onset of asphaltene deposition and flocculation data based on the visual method and the viscometric methods, respectively

Sample	ARFO (viscometry)	ARDO (visual)
<i>Brookhaven crude</i>		
<i>nC7</i>	29.32	32.26
<i>Maya crude</i>		
<i>nC5</i>	35.95	37.96
<i>nC7</i>	39.87	41.15
<i>nC9</i>	41.80	43.88
<i>Isthmus crude</i>		
<i>nC7</i>	41.17	44.0
<i>Crude oil I</i>		
<i>nC7</i>	28.58	29.63
<i>Crude oil II</i>		
<i>nC7</i>	34.43	35.48

The reported onset is given as volume percent precipitant in the *n*-alkane–crude oil mixture (Escobedo and Mansoori, 1995).

viscosity versus *n*-C7 and *n*-C9 dilution curves on Fig. 8, one can see that the viscosity of the suspension shows a smooth decrease upon addition of flocculant. However, a strong deviation at the ARFO is noted.

Fig. 9 shows the results obtained for the Brookhaven oil which has a density of 0.883 g/cm³ at 25 °C and has an average asphaltene content of 6.5 wt.%. In this figure, the data are presented in a somewhat different fashion as compared to Fig. 8. This change in modality was made in order to enhance the graphical visualization of the onset of asphaltene flocculation. In this figure, the term relative viscosity refers to:

$$\eta_r = \frac{\text{viscosity of the suspension (asphaltene - crude oil - solvent)}}{\text{viscosity of the pure solvent}}$$

The overall results for a number of crude oil samples analyzed are summarized in Table 2 in which the data for the visual detection of the onset of asphaltene deposition which is discussed in the next section are included. The reported onsets on this table are given as volume percent of *n*-alkane in the mixture.

The viscosity technique can be also used for detection of the micellization and coacervation onsets of asphaltene in polar solvents (Priyanto et al., 2001). This method is based on observations of the trend in the relative viscosity variations with increase in the

concentration of purified asphaltene in a polar solvent. The points of inflection on plots of relative viscosity versus concentration of asphaltene in a polar solvent at various temperatures, corresponding to the CMC and MCPs. In such a measurement, one can also produce both lower and upper limits to micellization (CMC and micelle saturation points) as well as lower and upper limits to micelle coacervation (MCP and phase separation), which was shown difficult to measure by other techniques.

To demonstrate this technique, we like to refer to a number of experiments which were run at various temperatures by Priyanto et al. (2001). The micellization and coacervation phase diagrams of Arabian Medium Heavy Resid (AMHR) and Pentane-Insoluble Bitumen Fraction (PIBF) asphaltenes in 1-methyl naphthalene solvent were produced in the temperature ranges of 0–160 and 0–180 °C, respectively, with increments of 10 °C. Experimental observations (Fig. 10) reveal a decrease in the viscosity of asphaltene in 1-methyl naphthalene dilution as temperature increase and an increase in the viscosity of dilution as asphaltene concentration increase. Because of the self-association of asphaltene particles and asphaltene micelles sudden increases of viscosity of solution with increase of asphaltene concentration occur (Fig. 10), which were accurately detected and measured.

As can be seen in Fig. 10, variation of relative viscosity versus concentration for this mixture is not monotonic at all and several sharp changes of slope are observed. In order to make a better recognition of these changes of slope, the data of Fig. 10 are divided into two zoomed out sections (0–1 and 1–10 mg/g of

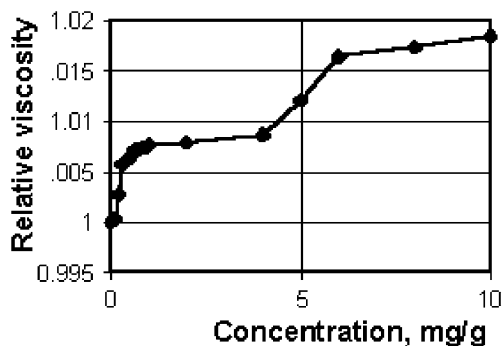


Fig. 10. The effect of concentration on the relative viscosity of pentane insoluble-asphaltene in 1-methyl naphthalene at 90 °C.

asphaltene in solvent) and Fig. 11(a) and (b) is reported.

According to Fig. 11(a), two distinct points of change of slope for the relative viscosity versus concentration of asphaltene in solvent are recognized in the 0–1 mg/g concentration range. The lower-concentration change of slope point represents the critical micellization concentration (CMC) of asphaltene and the other (higher concentration) change of slope point represents the completion of micellization (or micellization saturation) point. According to Fig. 11(b) also, two distinct points of change of slope for the relative viscosity versus concentration of asphaltene in solvent are recognized in the 1–10 mg/g concentration range. The lower-concentration change of slope point corresponds to the MCPs of asphaltene and the other (higher concentration) change of slope point represents the coacervate separation point. By repeating the relative viscosity measurement at various other temperatures in the range of 0–160 °C, and various

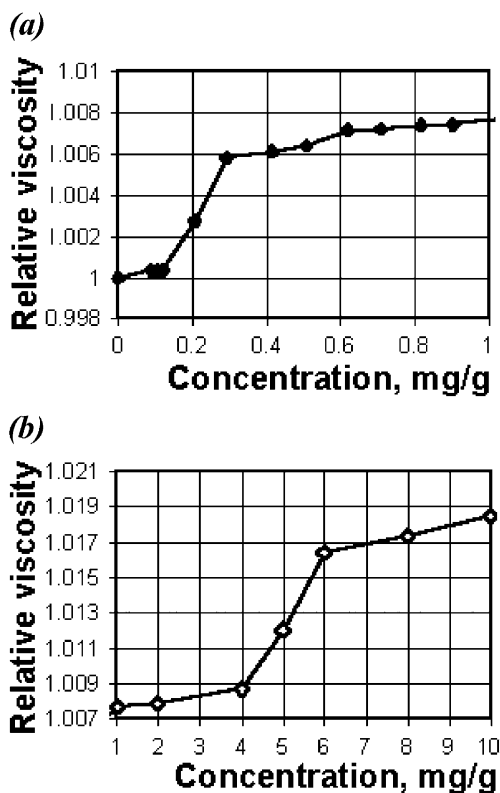


Fig. 11. The same data as in Fig. 10 but in expanded scales.

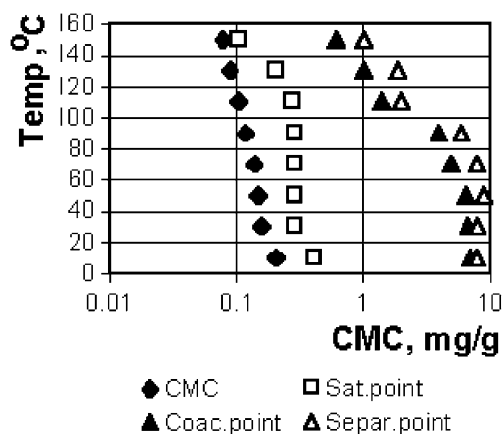


Fig. 12. The effect of temperature on the CMC, saturation point, MCP and separation point of pentane insoluble-asphaltene from bitumen in 1-methyl naphthalene.

concentrations of asphaltenes in polar solvents, similar figures, as Fig. 11, were obtained which could provided the necessary data to construct the micellization, saturation, coacervation and phase separation diagrams of asphaltene in polar solvents as reported in Figs. 12 and 13.

Fig. 12 shows the measured data for phase diagram of PIBF asphaltene dissolved in 1-methyl naphthalene, which includes the CMC, saturation point, MCP and separation point for the temperature range of 0–160 °C with 20 °C increment. Accord-

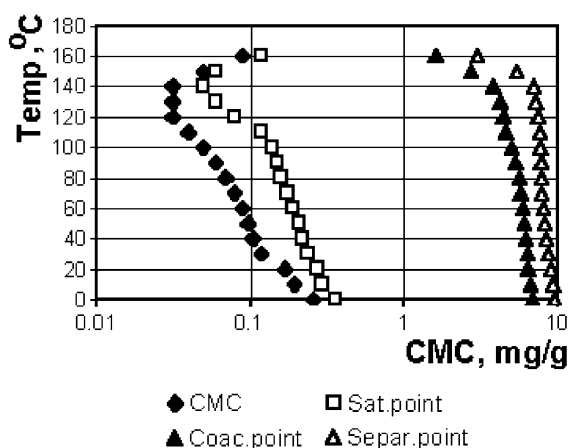


Fig. 13. The effect of temperature on the CMC, saturation point, coacervation point and separation point of AMHR asphaltene in 1-methyl naphthalene.

ing to this figure, the CMC, saturation point, MCP and separation point get closer to one another as temperature increases. Fig. 13 shows the measured data obtained for the phase diagram of AMHR asphaltene which has concentrations of 0.01–10.0 mg/g in 1-methyl naphthalene at the temperatures range of 0–180 °C. This data also includes the CMC, saturation point, MCP and separation point. According to this figure also, the CMC, saturation point, MCP and separation point get closer to one another as temperature increases.

4. Determination of asphaltene+resin-deposition onset

To determine the ARDO, petroleum fluids can be diluted in various ratios with liquid solvent in order to detect at which ratio the deposition takes place. The onset of asphaltene deposition are determined due to the introduction of solvent into crude oil at room temperature (25 °C) and at atmospheric pressure.

Hirschberg et al. (1984) could observe onset of deposition through microscope magnification. Table 3 gives the onset of asphaltene deposition at normal conditions measured following the suggested visual method (Kim, 1987; Kim et al., 1990).

The fact that ARDO is bigger than ARFO, and ARFO is bigger than APO, is consistent with the theory. In other words, considering that onset of precipitation occurs ahead of onset of flocculation and onset of flocculation occurs ahead of onset of deposition, the above results for the deposition tests of Brookhaven crude with *n*-heptane at normal conditions are obtained.

Table 3
Asphaltene + resin-deposition onset by visual method

Solvent	Brookhaven oil (cc/1 g crude oil)	DK-107 (LST) (cc/1 g crude oil)
<i>n</i> -Heptane	0.7 (32.2%)	1.5 (50.46%)
<i>n</i> -Hexane	0.7 (32.3%)	1.6 (51.01%)
<i>n</i> -Pentane	0.9 (36.0%)	1.7 (51.56%)

Note that for Brookhaven oil, when titrated with *n*-heptane at normal condition, the following onset data are obtained: APO=28.0% (IFT method), according to Fig. 5.

ARFO=29.3% (viscometric method), according to Fig. 9.

ARDO=32.2% (visual method), according to this table.

The visual method seems difficult to administer unless the oil is transparent enough for microscopic observation of asphaltene flocs deposition. Light oils that contain a very small amount of asphaltene, such as DK-107 (LST), can be accurately analyzed for the onset of asphaltene deposition with reasonable accuracy. However, a heavy crude, such as Brookhaven oil, is quite dark so that light cannot penetrate through it. As a result, it is hard to get a clear reading of its onset of deposition. One way to overcome some of the difficulties posed by this method is by careful preparation of thin films to be analyzed under a microscope.

5. Discussion

A number of other methods are proposed for determining the onsets of asphaltene phase separations/transitions (see, for example, Reichert et al., 1986; Fotland et al., 1993; Fuhr et al., 1991; Burke et al., 1990; Buckley, 1996). In general, methods for determining the onsets of asphaltene may be classified according to the procedure utilized to detect the onsets. In the following, we discuss about a couple of these methods.

Measurements of electrical conductivity (Fotland et al., 1993) as a function of precipitating agent have been proposed for the detection of the onset of asphaltene deposition. By adding precipitating solvent to oil, the mobility of conducting species increases to a maximum at which the onset of asphaltene deposition occurs. Their results show that deposition of asphaltenes are strongly related to the charge transport mechanism.

The Light Transmission (Fuhr et al., 1991) method is based on the detection of changes in transmitted light intensity as a function of deposited floc concentration in the crude oil mixture.

Gravimetric analysis (Burke et al., 1990) also allows for the detection of the onset and amount of asphaltene deposition. This technique is commonly used together with visual methods to verify results obtained by measurements of the electrical conductivity and light transmission.

It should be pointed out that the conditions of some oils (like heavy oils and dead oils) is such that one or more of their onset points have already passed.

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