Effect of Resins and DBSA on Asphaltene Precipitation from Petroleum Fluids

Lamia Goual and Abbas Firoozabadi
Reservoir Engineering Research Institute, Palo Alto, CA 94306

This work examines the effect of various resins and dodecyl benzene sulfonic acid (DBSA) amphiphile on asphaltene precipitation from different petroleum fluids. Various resins are added to three different petroleum fluids to measure precipitation with n-pentane. Results show that the dipole moment of resins (which is a measure of polarity) has a strong effect on precipitation. Resins with a high dipole moment are more effective than resins with a low dipole moment. The effectiveness is defined in terms of the increase in the onset point of precipitation. However, addition of resins to a petroleum fluid increases the amount of precipitated asphaltenes. This is the first report of such a behavior in the literature; the increase is less pronounced with the most polar resins. Addition of asphaltenes to a petroleum fluid results in a high amount of precipitation. As expected, the onset point of precipitation from asphaltene addition to a petroleum fluid is different from that of resins. When the DBSA amphiphile is mixed with the petroleum fluid at different concentrations, we observe a retrograde phenomenon. The amount of precipitated asphaltene increases first with increasing DBSA concentration. Beyond a certain concentration, there is a decrease in precipitation. At higher concentrations, DBSA proves to be very effective to move the onset point of precipitation. The data show the complex interactions between various species in petroleum fluids. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 470–479, 2004

Keywords: asphaltenes, resins, DBSA, interactions, precipitation, petroleum

Introduction

The description of the structure and properties of asphaltenes has been a challenge over the past several decades. More recently, a growing interest has developed toward the study of resins with the recognition of their effect on the stability of asphaltenes in petroleum fluids. The stabilizing effect is understood to be related to the association of resins with asphaltenes to form micelles (Swanson, 1942). It is believed that in a micelle, asphaltenes self-associate into an aggregate to form the core, and resins adsorb onto the core to form a steric shell (Firoozabadi, 1999).

A petroleum fluid can be divided into three parts: (1) oils (that is, saturates and aromatics), (2) resins, and (3) asphaltenes. This partition is very broad; every part of the petroleum fluid also consists of a wide range of molecules with varying structures and properties. Asphaltenes and resins are polar molecules, while the oils are either non- or mildly polar. In a previous work (Goual and Firoozabadi, 2002), the dipole moment (a measure of polarity) of asphaltenes, resins, and oils was investigated for eight petroleum fluids. The dipole moment was found to increase sharply from oils (0–1 D) to resins (2.4–3.2 D) to asphaltenes (3.3–6.9 D). Polar species with a high dipole moment (greater than 2 D) affect molecular interactions in the petroleum fluid and result in the formation of micelles. Therefore, because of their polar character, resins act as natural dispersants of asphaltenes. A viable option for the inhibition of asphaltene precipitation is the mixing of resins or some dispersants with the petroleum fluid in a batch process. Yet, field data show that in some cases the resins and dispersants not only do not inhibit precipitation, they may also promote it. The study of the effect of resins and chemical dispers-

---

Correspondence concerning this article should be addressed to A. Firoozabadi at af@rerinst.org.

ants on precipitation contributes significantly to the understanding of molecular interactions in petroleum fluids. Such interactions are believed to be key elements for proper modeling of asphaltene precipitation. Currently, most models fail to predict precipitation because they do not take into account the interactions involving polar molecules.

Generally, molecular interactions are classified into two types: (1) short-range, and (2) long-range interactions. Hydrogen bonding, charge transfer, and repulsion are short-range interactions, while van der Waals interactions are long-range (Ratajczak and Orville-Thomas, 1980). The difference between short- and long-range interactions is mainly in the bond distance between interacting molecules. Short-range interactions occur when the bond distance between molecules is smaller than the sum of the van der Waals radii, resulting in an overlap between the electron clouds and the formation of molecular complexes (Ratajczak and Orville-Thomas, 1980). Hydrogen bonding consists of the sharing of a proton between the proton acceptor of a molecule and the anion derived from the proton donor of another molecule; charge transfer consists of the transfer of electrons between an electron donor and electron acceptor of two molecules (Huyskens et al., 1991). The repulsion interaction is orientation dependent and occurs when the electronic orbital of two approaching molecules begin to overlap noticeably (Israelachvili, 1991). The main contributions to the van der Waals interactions are (1) electrostatic (orientation or dipole-dipole), (2) induction (debye or dipole-induced dipole), and (3) dispersion (London or induced dipole-induced dipole) interactions (Maitland et al., 1981). In electrostatic interactions, the rotating dipoles of two polar molecules interact by aligning into a favorable arrangement. Hydrogen bonding is no more than a particularly strong type of directional dipole–dipole interaction (Israelachvili, 1991). In induction interactions, the permanent dipole of a polar molecule distorts the electron charge distribution of a nonpolar molecule, and an induced dipole moment is created. In dispersion interactions, the instantaneous positions of the electrons around the nucleus protons of a molecule create a finite dipole moment, which in turn generates an electric field that polarizes a nearby molecule, inducing a dipole moment in it (Israelachvili, 1991).

It is believed that dispersion interactions affect asphaltene flocculation (Buckley et al., 1998; Rogel, 2000). Electrostatic and induction interactions, on the other hand, help stabilize the asphaltenes in the petroleum fluid (Moschopedis and Speight, 1976; Bardon et al., 1996; Li et al., 1997). Murgich (2002) presented a comprehensive analysis on the intermolecular forces in aggregates of asphaltenes and resins, and stated that the main contributions involved are the electrostatic, repulsion, and dispersion interactions. In order to understand the mechanism of asphaltene precipitation, it is very important to analyze the effect of resins on asphaltenes and to define the main interactions involved.

Very few studies have delved into the effect of resins on asphaltene precipitation. These studies center around the effect of resins on the onset point of precipitation. In addition, the effect of resins on asphaltene precipitation is usually assessed after asphaltenes have been precipitated from petroleum fluids and solubilized in aromatic solvents. Murzakov et al. (1981) investigated the micellar stability of asphaltenes in benzene solutions by means of gravimetric sedimentation analysis and found that the addition of resins (2–8 wt. %) to the solution decreased the amount of asphaltene precipitated by n-C_7. Lian et al. (1994) performed n-C_5 precipitation tests from asphaltene/toluene solutions and also found that addition of resins to the solution decreased the amount of asphaltene precipitated. Hammami et al. (1998) measured the onset point of asphaltene precipitation at ambient temperature and high pressure (690 kPa) and found that addition of resins with high content of basic functions to the petroleum fluid increased significantly the onset point of asphaltene precipitation by n-C_5. Recently, Carnahan et al. (1999) reported that resins from Boscan petroleum fluid could increase considerably the onset point of asphaltene precipitation from Hamaca petroleum fluid, suggesting that resins from Boscan petroleum fluid are more effective than resins from Hamaca petroleum fluid. However, the reasons underlying this phenomenon were not discussed.

Structural investigations of the resin fractions have not been carried out to the same extent as those of asphaltene fractions. Because asphaltenes and resins are two contiguous classes of components separated from a continuum of molecules, they may have a similar structure. However, the difference in size, aromaticity, polarity, and physical appearance confer different properties to asphaltenes and resins (Speight, 1999). Spectroscopic investigations indicate the presence of hydroxyl groups, as well as ester, acid, and carbonyl functions in the resin fractions (Speight, 1999). It has been postulated that resins contain long paraffinic chains with naphtenic rings and polar functions (Wu et al., 1998; Firoozabadi, 1999). This might confer to resins some of the properties of surfactants. By definition, a surfactant is a substance that lowers the surface tension of the medium in which it is dissolved (Hiemenz, 1986). Amphiphiles are the surfactants with molecules consisting of two parts: a polar head and a nonpolar long-chain hydrocarbon tail, each part having an affinity for different phases (Hiemenz, 1986). There have been several studies on the effect of amphiphiles on asphaltene precipitation. Chang and Fogler (1994) analyzed the effect of the structure of amphiphiles such as *p*-nonylphenol (NP) and dodecyl benzene sulfonic acid (DBSA) on asphaltene stabilization. They found that the polarity of the head and the length of the tail affect the effectiveness of the amphiphile and selected DBSA as the most effective stabilizer for asphaltenes. The effect of DBSA on asphaltene precipitation has been reported to be successful in some studies (Permukarome et al., 1997; Rogel et al., 2001; Al-Sahhaf et al., 2002) and not so successful by others (Clarke and Pruden, 1998). Recently, Al-Sahhaf et al. (2002) investigated the effect of resins and various amphiphiles on the onset point of asphaltene precipitation. They confirmed the observations of Chang and Fogler and reported the effectiveness of dodecyl resorcinol (DB) and DBSA amphiphiles. The same authors also reported that larger amounts of resins are required to produce the same effect on the onset point as low concentrations of amphiphiles.

In a previous work (Goual and Firoozabadi, 2002), eight petroleum fluids were separated into asphaltenes, resins, and oils. Asphaltenes were precipitated by n-C_5 according to a modified Syncrude analytical method. The choice of n-C_5 is preferred to n-C_7 because the latter would leave the n-C_5–n-C_7 fraction of asphaltenes soluble with resins. The resins were separated using two different methods: (1) propane precipitation, and (2) ASTM D2007 adsorption method on attapulgus clay with different n-C_5/toluene ratios to elute oils. The dipole

Table 1. Petroleum Fluids

Petroleum Fluid	Density at 20°C (g/cc)	API Gravity at 20°C	Asphaltenes wt. %	Resins wt. %	R/A
U	0.8550	34	2.5	8.6	3.4
TK	0.8520	35	1.3	7.5	5.6
C	0.8588	33	2.3	6.5	2.8

moment was used as a criterion for the determination of resins in petroleum fluids. Results showed that propane precipitation separates only part of the resins (the most polar portion). The adsorption method gives the true amount of resins, provided no toluene is used to elute oils. Material balance calculations reveal that the total amount of losses, including the resins irreversibly adsorbed on the clay, is less than 1 wt. %. Because the clay may cause chemical modification of the resin constituents, we have compared the resins adsorbed on clay and on silica gel and found that the resins recovered have the same properties. A full description of the separation procedure is provided in our previous publication (Goual and Firoozabadi, 2002).

The main objective of this work is to examine the effect of resins with different concentrations and dipole moments on asphaltene precipitation from three petroleum fluids using n-C_5 as a precipitant. Due to the complexity of interactions between asphaltenes and resins in a petroleum fluid, this study is conducted by keeping asphaltenes in their natural environment (that is, in the petroleum fluid). We also study the effect of DBSA on asphaltene precipitation from the same petroleum fluids at different concentrations. The effects of resins and DBSA are compared and discussed. Another objective of this work is to show the differences between asphaltenes and resins in a petroleum fluid. Accordingly, we perform solubility tests on resins in different media and examine the effect of asphaltene addition to a petroleum fluid on precipitation from the same petroleum fluid.

Experimental

We used three different petroleum fluids (data are listed in Table 1) to investigate the effect of various resins and DBSA on asphaltene precipitation. The three petroleum fluids are medium mixed-base type and their chemical composition is provided in our previous paper (Goual and Firoozabadi, 2002). The resins are separated by adsorption liquid chromatography (ASTM D2007) from petroleum fluids C, TK, U, and are named after the respective petroleum fluids. Table 2 presents the dipole moment of the resins and the corresponding n-C_5 asphaltenes. Resins C have the highest dipole moment, while resins U have the lowest dipole moment. The effectiveness of resins is evaluated from the onset point of asphaltene precipitation, as well as the precipitation amount. Precipitation data are measured with n-C_5/petroleum fluid ratios varying from 1 wt/wt to 20 wt/wt. The resins are added to the petroleum fluids at three different concentrations. Prior to the precipitation tests, we measure the solubility of resins C in n-C_5, oils C, and petroleum fluid C, as well as the solubility of resins TK and C in petroleum fluids TK and C, respectively. The effect of asphaltenes U on precipitation by n-C_5 from petroleum fluid U is measured and compared to that of resins U. In addition, precipitation measurements are performed with DBSA at concentrations of 0.3, 0.5, 1, 3, and 5 wt. % in the petroleum fluid. We could not determine the dipole moment of DBSA by dielectric spectroscopy because of strong association in toluene even at very small concentrations.

Chemicals

The data for the chemicals used in this study are listed below.

- n-Pentane (n-C_5): J. T. Baker, HPLC grade, MW = 72.15, purity > 99%, density at 25°C = 0.63 g/cm^3, water content = 0.01%.
- Toluene: J. T. Baker, HPLC grade, MW = 92.14, purity > 99.5%, density at 25°C = 0.87 g/cm^3, water content = 0.05%.
- DBSA: TCI, MW = 326.5, purity = 95%, density = 1.0 g/cm^3.

Equipment

The asphaltene filtration setup consists of a filtration flask and funnel connected to a vacuum pump through rubber tubings. To avoid solvent infiltration into the pump, a trap is used at a temperature of −60°C to liquefy n-pentane in the air. Asphaltenes are filtered using a Whatman glass microfibre filter paper (7 mm diameter and 1.5 μm pore size). The weight is measured with a Sartorius analytical balance with an accuracy of 0.001 g.

Procedure

Resins and DBSA are first transferred in equal amounts into eight different flasks. The weight of resins and DBSA is measured and an appropriate quantity of petroleum fluid is added to each flask. The mixture is left for 24 h after which n-C_5 is added in different proportions. The concentration of n-C_5 is varied to provide the n-C_5/petroleum fluid ratios of 1, 2, 4, 6, 8, 10, 15, and 20 wt/wt. After standing overnight, the mixtures are filtered and asphaltenes are washed extensively with n-C_5 and then dissolved in toluene. Once the solvent is evaporated, asphaltenes are dried and weighed. The procedure used to measure the amount of resins soluble in different fluids consists of mixing resins with each fluid at various concentrations (from 1 wt. % to 20 wt. %) and recording, after several days, the amount of resins soluble in the fluid as a percent of total resins. The amount of insoluble resins is measured by taking into account the portion of resins that remain on the wall of the test tube as well as the amount filtered from the petroleum fluid. Note that the filtrate had the appearance of resins (brown, shiny, and nonfriable).

Results

First we present the results of resin solubility in different fluids. Once the solubility behavior of resins is defined, the effect of resins U, TK, and C on precipitation from petroleum

Table 2. Dipole Moment (in D) of Asphaltenes and Resins

Petroleum Fluid	U	TK	C
n-C_5 asphaltenes	4.4	5.2	6.7
Resins	2.4	2.8	3.2

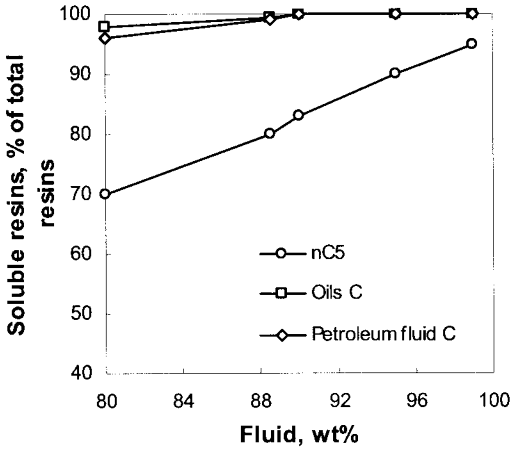

Figure 1. Solubility of resins C in n-C_5, oils C, and petroleum fluid C.

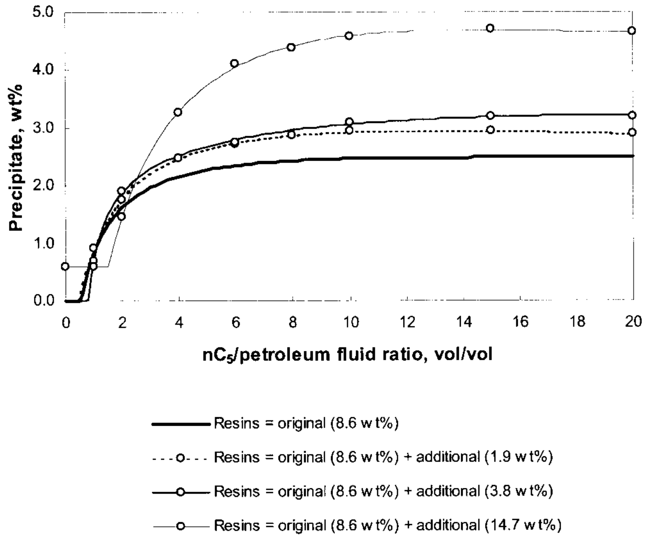

Figure 3. Precipitation by n-C_5 from petroleum fluid U for various concentrations of resins U.

fluids U, TK, and C at three concentrations is presented. To better illustrate the difference between asphaltenes and resins, the effect of asphaltenes U on n-C_5 precipitation from petroleum fluid U is also described. We also measured, the effect of DBSA amphiphile on precipitation from all the petroleum fluids; the results are discussed and compared with those obtained with resins. All precipitation measurements are repeated a minimum of three times.

Resin solubility tests

Figure 1 presents the solubility of resins C in three different fluids: n-C_5, oils C, and petroleum fluid C. The oils C represent the nonvolatile fraction of saturates and aromatics in petroleum fluid C; this fraction is only 40% of the total oils. For all three fluids, the amount of soluble resins increases with the fluid concentration. The measurements were repeated twice, and the average value is plotted in Figure 1. For concentration higher than 90 wt. % in the petroleum fluid and oils, resins are completely soluble; however, resins become partially soluble for lower petroleum fluid and oils concentrations. Data show that when resins are mixed with a petroleum fluid or with oils at a concentration of 20 wt. %, 14% of the resins are insoluble in the petroleum fluid and 6% are insoluble in oils. Resins are generally believed to be soluble in n-C_5, but our results show that this is not the case even at a low resin concentration. Indeed, when 80 g of n-C_5 is mixed with 20 g of resins, about 70% of the resins are soluble, that is, only 14 g.

Figure 2 depicts the solubility of resins U, TK, and C in petroleum fluid TK, as well as the solubility in petroleum fluid C. Resins C are more soluble in the petroleum fluids than resins TK and U. In addition, resins U show the same solubility behavior as resins TK. This may imply that resins with a high dipole moment are more soluble in petroleum fluids than resins with a low dipole moment. In all cases, additional resins revealed to be completely soluble in the petroleum fluid at a concentratin lower than 7 wt. %.

Effect of resin concentration on asphaltene precipitation

Figures 3, 4, and 5 show the effect of resin amounts on precipitation by n-C_5 from three different petroleum fluids. Resins are added to each petroleum fluid at three concentra-

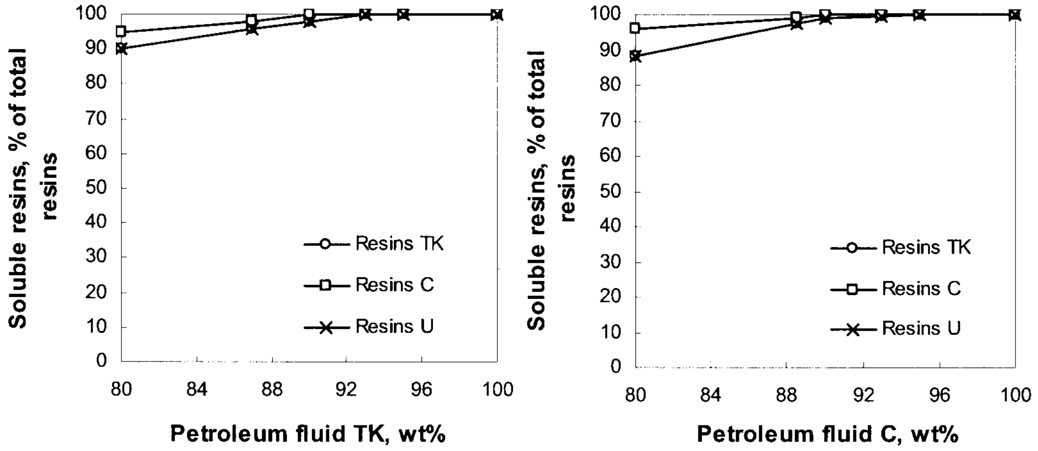

Figure 2. Solubility of resins in petroleum fluids TK and C.

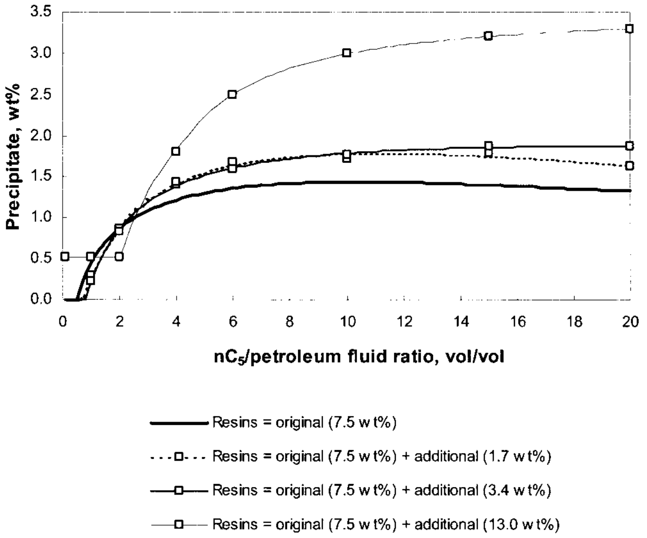

Figure 4. Precipitation by n-C_5 from petroleum fluid TK for various concentrations of resins TK.

Table 3. Concentration of Additional Resins in Petroleum Fluids U, TK, and C

Additional Resins, wt. %			Total Resins, wt. %		
U	TK	C	U	TK	C
0.0	0.0	0.0	8.6	7.5	6.5
1.9	1.7	1.6	10.5	9.2	8.1
3.8	3.4	2.9	12.4	10.9	9.4
14.7	13.0	11.5	23.3	20.5	18.0

tions (see Table 3). In Figures 3–5, the thick solid curves represent the precipitation of asphaltenes from the petroleum fluids without the addition of resin. Examination of the data in Table 3 and Figure 2 suggests that resins added at the first two concentrations are completely soluble in the petroleum fluid, while resins added at the highest concentrations are partially soluble in the petroleum fluid. Indeed, asphaltene precipitated upon addition of low resin concentration does not have the same appearance as asphaltene precipitated upon addition of high resin concentration. In the first case, the precipitate is black, shiny, and friable and resembles the asphaltenes precipitated from the petroleum fluids without resin addition. In the second case, the precipitate is brown, shiny, and nonfriable, which reveals the presence of some resins with asphaltenes. Nevertheless, high resin concentrations are considered in order to examine the effect on the onset point of precipitation and the amount of precipitate. The main observation from Figures 3–5 is that the additional resins at low concentration increase the onset point of precipitation, as well as the amount precipitated. The effect of resins on the onset point of precipitation at low concentration is in line with published data (Hammami et al., 1998; Carnahan et al., 1999). However, the increase in the amount of precipitation was not expected and has not been reported in the literature, to the best of our knowledge. Previous studies (Murzakov et al., 1981; Lian et al., 1994) examined the effect of resins on solutions of asphaltenes in aromatic solvents. In this study, we examine the effect of additional resins on precipitation from petroleum fluids. Our results reveal that asphaltenes interact differently with resins according to the medium in which they are present.

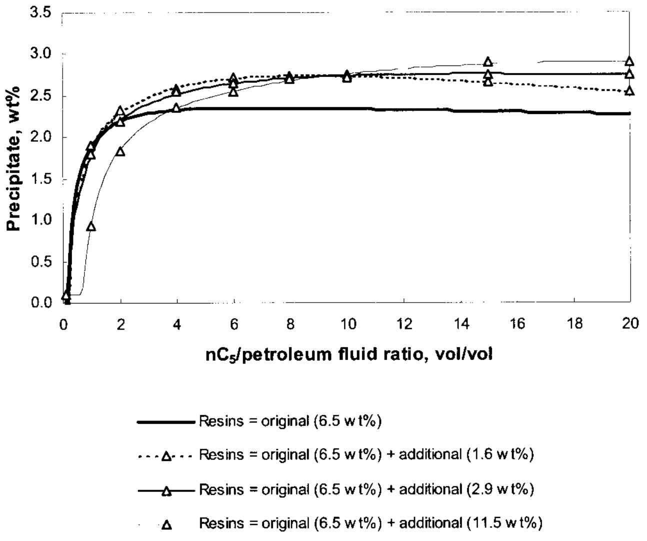

Figure 5. Precipitation by n-C_5 from petroleum fluid C for various concentrations of resins C.

Figure 3 shows the effect of different concentrations of resins U on precipitation by n-C_5 from petroleum fluid U. The increase in the amount of precipitation is proportional to the concentration of additional resins and becomes substantial (about 89% difference) when the total concentration of resins in the petroleum fluid is 23.3 wt. % instead of 8.6 wt. % in the original petroleum fluid. On the other hand, the high resin concentration causes early precipitation. The precipitate is mainly composed of resins that are not soluble in the petroleum fluid (see Table 4).

Figure 4 portrays the effect of different concentrations of resins TK on precipitation by n-C_5 from petroleum fluid TK. The same behavior as in Figure 3 is observed; the maximum precipitation of 3.3 wt. % occurs with 13 wt. % additional resins TK as compared to 1.3 wt. % in the original petroleum fluid. At high concentration, precipitation occurs upon resin addition.

Figure 5 depicts the effect of the different concentrations of resins C on precipitation by n-C_5 from petroleum fluid C. One can observe the high slope of the precipitation curve with the addition of small concentrations of resins, which increases the uncertainty in the reading of the onset points. Nevertheless, the effect of resins in increasing the onset point of precipitation is not substantial at low resin concentration. Also, the amount of precipitation does not increase appreciably with the addition of 11.5 wt. % resins. At this concentration, the percent of soluble resins in the petroleum fluid is 99% for resins C and 97.5% for resins TK and U, leading to 0.29 wt. % precipitated resins TK and U and 0.115 wt. % precipitated resins C in petroleum fluid C, as shown in Table 4. In other words, with low resin concentration, the onset is moved to the right in Figure 5; however, at high concentration, the onset is moved to the left, like the results in Figures 3 and 4. This is also the first report in the literature of the effect of resins at high concentration on the onset point of precipitation.

Table 4. Resin Precipitation from Petroleum Fluids U, TK, and C

	Petroleum Fluid U			Petroleum Fluid TK			Petroleum Fluid C		
	Addtional Resins			Additional Resins			Additional Resins		
	U	TK	C	U	TK	C	U	TK	C
Additional resins, wt. %	14.7	14.7	14.7	13.0	13.0	13.0	11.5	11.5	11.5
Petroleum fluid, wt. %	85.3	85.3	85.3	83.0	83.0	83.0	88.5	88.5	88.5
				Resin Precipitate					
% of additional resins*	4.0	4.0	2.0	4.0	4.0	2.0	2.5	2.5	1.0
wt. % of additional resins	0.59	0.59	0.29	0.52	0.52	0.26	0.29	0.29	0.12

*Determined from Figure 2.

Effect of various resins on asphaltene precipitation

Figures 6, 7, and 8 present the effect of additional resins on precipitation by n-C_5 from three different petroleum fluids at different concentrations (see Table 3).

Figure 6 presents the precipitation results for petroleum fluid U after addition of various resins at two concentrations. The maximum increase in the precipitation amount is with resins U, and the minimum increase is with resins C. Thus, resins with a high dipole moment result in less precipitation than resins with a low dipole moment. In addition, the onset point of precipitation is higher upon addition of resins C, and it is lower upon addition of resins TK and U. This suggests that resins with high dipole moment are more effective than resins with relatively low dipole moment in increasing the onset point of precipitation at low resin concentrations.

Figure 7 presents the precipitation results for petroleum fluid TK by the addition of resins at two concentrations. The same correlation between the amount/onset point of precipitation and the dipole moment of resins is found as with petroleum fluid U. At the two concentrations of resins, comparable effects on the amount of precipitate are observed for resins U and TK and for resins C; the highest amount of precipitate corresponds to the addition of resins with the lowest dipole moment (that is, resins U). The effect of the resin dipole moment on the onset point is also noted. A gradual increase in the onset point is obtained with the increasing dipole moment of resins, and a maximum value of about 1.8 wt/wt is found upon addition of 1.6 wt. % of resins C as compared to 0.3 wt/wt in the original petroleum fluid.

Figure 8 depicts the precipitation results for petroleum fluid C after addition of resins at two concentrations. Petroleum fluid C contains approximately the same amount of n-C_5 asphaltenes as petroleum fluid U; however, the effect of resins on the two petroleum fluids is different. The first observation is the contrast in the amount of precipitation between resins TK and U and resins C. Addition of 11.5 wt. % resins C to petroleum fluid C slightly increases the amount of precipitation; however, the amount becomes significant with resins TK and C, and reaches 4.9 wt. % with resins U. It is also found that resins U do not affect the onset point of precipitation much when added at low concentration.

Comparison of the results reveals that the difference in the amount precipitated with the addition of resins at low concentration increases from petroleum fluid U to petroleum fluid TK

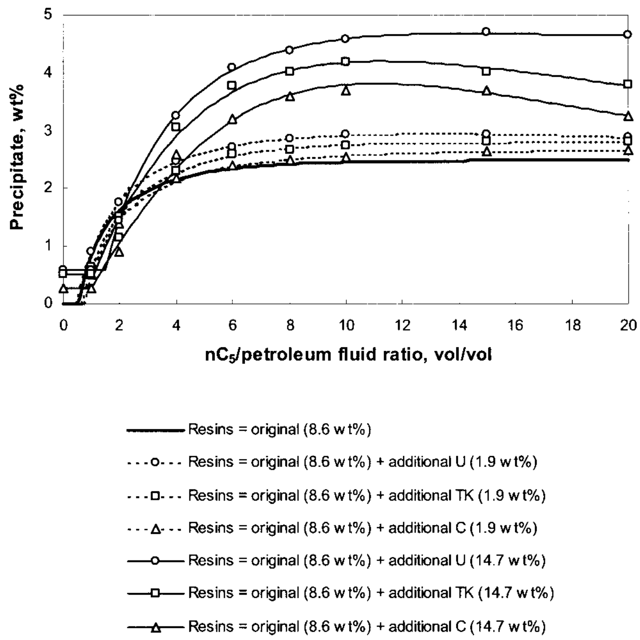

Figure 6. Precipitation by n-C_5 from petroleum fluid U for various additional resins.

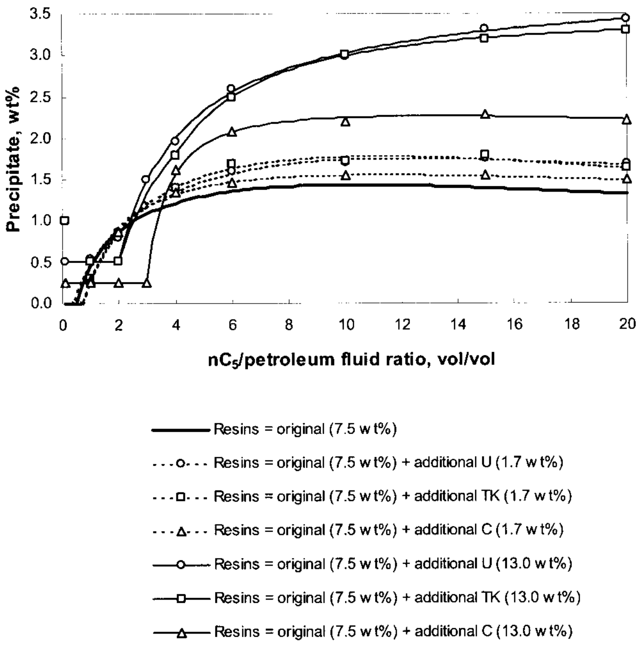

Figure 7. Precipitation by n-C_5 from petroleum fluid TK for various additional resins.

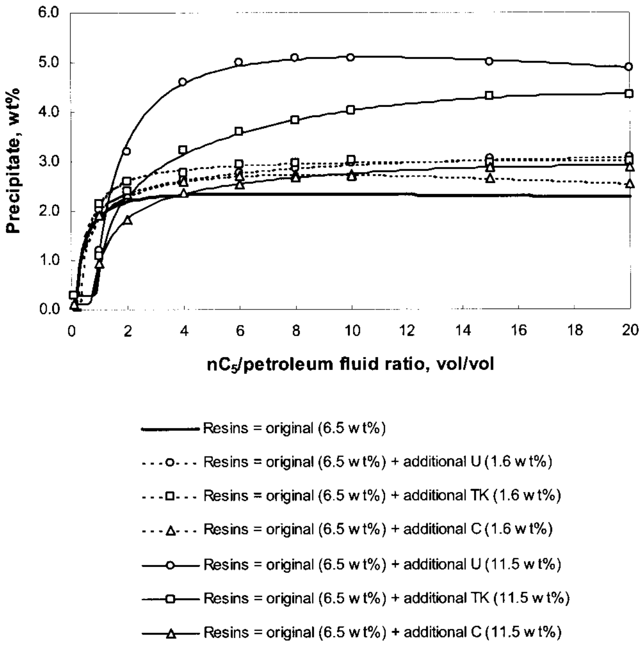

Figure 8. Precipitation by n-C_5 from petroleum fluid C for various additional resins.

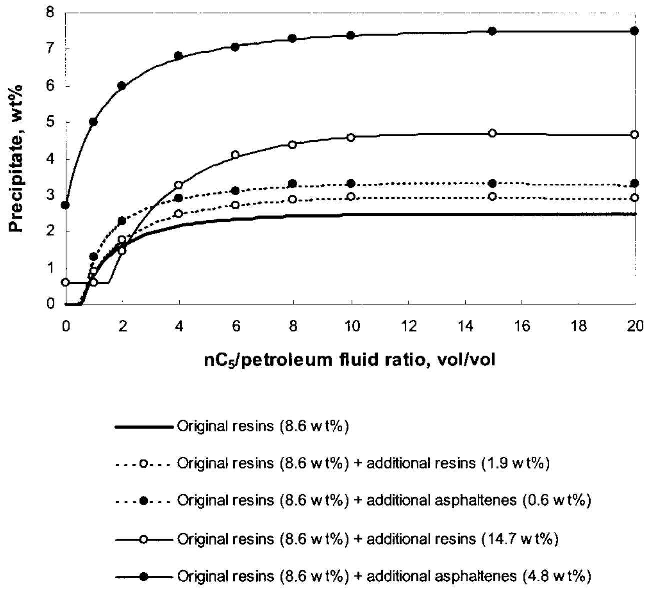

Figure 10. Precipitation by n-C_5 from petroleum fluid U for various concentrations of resins and asphaltenes U.

to petroleum fluid C, as shown in Figure 9. Thus, the increase in precipitation is more pronounced when the dipole moment of asphaltenes in the petroleum fluid is high. On the other hand, resins C (with the highest dipole moment) are the most effective with respect to the change in the onset point of precipitation in all petroleum fluids, and result in the least increase in precipitation.

Effect of additional asphaltenes on asphaltene precipitation

Figure 10 shows the effect of adding asphaltenes U on precipitation from petroleum fluid U. Results are shown for two concentrations of additional asphaltenes: 0.6 wt. % and 4.8 wt. %. For comparison purposes, we also include in the same figures the results of resin addition at two concentrations: 1.9 wt. % and 14.7 wt. %. In Figure 10, the addition of 0.6 wt. % of asphaltenes increases the amount of n-C_5 precipitate from 2.5 wt. % to 3.3 wt. %, which is 12% higher than the amount precipitated with the addition of 1.9 wt. % of resins. For the higher concentration of asphaltenes (that is, 4.8 wt. % asphaltene increase), results are substantially different. Prior to n-C_5 dilution, only 44% of additional asphaltenes are soluble in the petroleum fluid, that is, 2.1 wt. %. The amount of precipitate by n-C_5 is about 7.5 wt. %, almost three times higher than the original amount in the petroleum fluid and considerably higher than the amount obtained with the addition of 14.7 wt. % of resins. The addition of asphaltenes and resins at low concen-

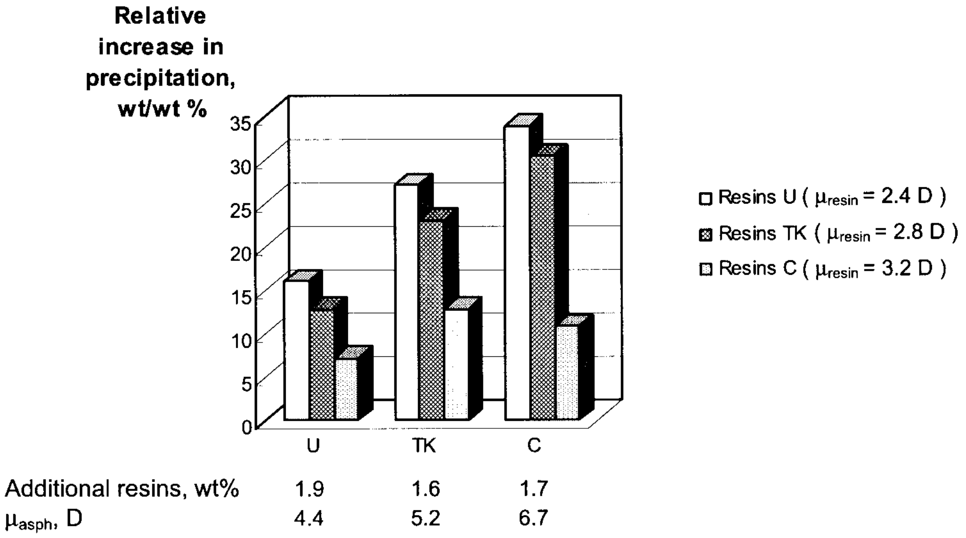

Figure 9. Relative increase in amount of precipitation by n-C_5 in petroleum fluids U, TK, and C.

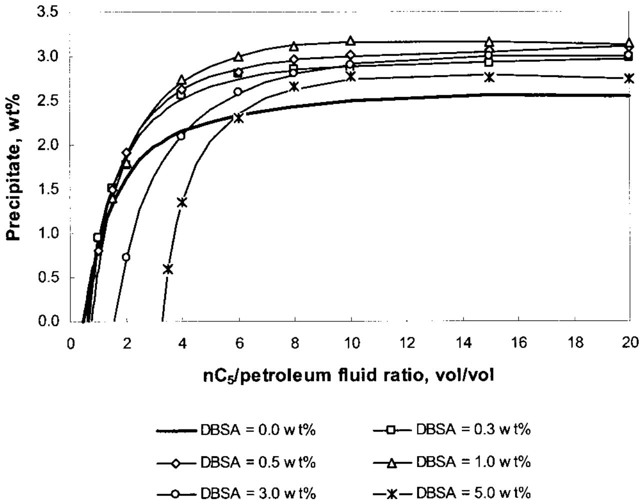

Figure 11. Precipitation by n-C_5 from petroleum fluid U for various concentrations of DBSA.

tration to a petroleum fluid has an opposite effect on the onset point of asphaltene precipitation. These observations, along with solubility analyses, corroborate the differences between asphaltenes and resins in the petroleum fluid.

Effect of DBSA on asphaltene precipitation

Figures 11–13 present the effect of DBSA on asphaltene precipitation from petroleum fluids U, TK, and C, respectively. For each petroleum fluid, five precipitation measurements are made with n-C_5 at different concentrations of DBSA. During our experiments, visual observations indicate that the amount of resinous material in the precipitate decreases when the concentration of DBSA is increased in the petroleum fluid. At 5 wt. % DBSA in the petroleum fluid with an excess of n-C_5, very small dark black and dispersed particles deposit on the bottom of the flask. The filtration of the precipitated solid does not require extensive washing with n-C_5, indicating that the precipitate is almost resin-free.

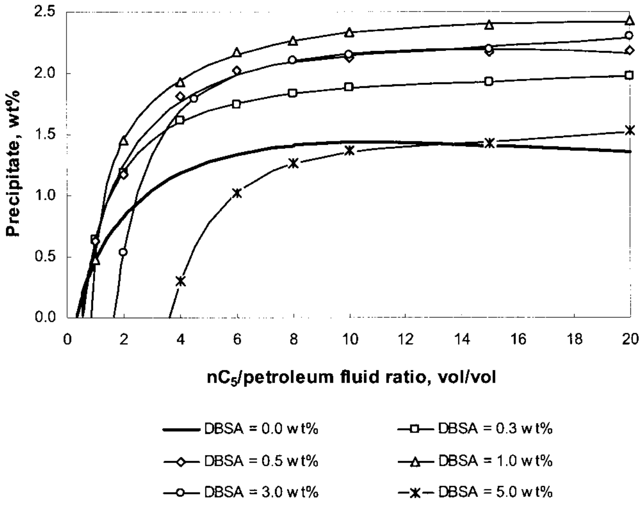

Figure 12. Precipitation by n-C_5 from petroleum fluid TK for various concentrations of DBSA.

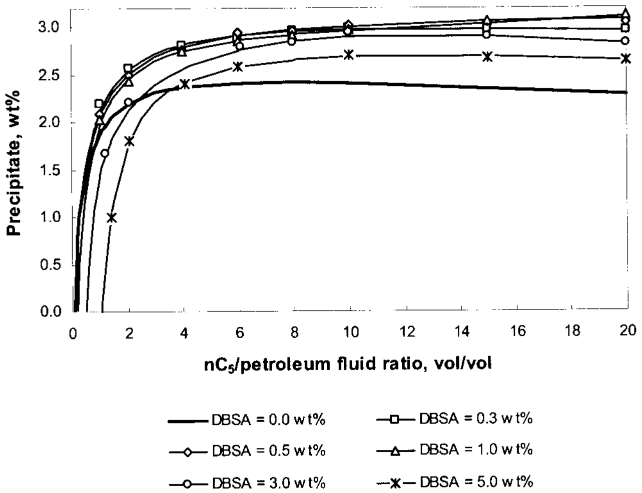

Figure 13. Precipitation by n-C_5 from petroleum fluid C for various concentrations of DBSA.

Figure 11 presents the effect of DBSA on asphaltene precipitation from petroleum fluid U. It appears that the amount of precipitate depends on the concentration of DBSA in the petroleum fluid. At concentrations of less than 1 wt. %, the effect is similar to that of resins. Addition of 0.3, 0.5, and 1 wt. % DBSA increases the amount of precipitate from 2.5 wt. % to approximately 3 wt. %. At these concentrations, the onset point of precipitation increases slightly with the concentration of DBSA. However, for concentrations above 1 wt. %, the effect of DBSA on precipitation is different. The precipitation amount decreases with DBSA concentration to only 2.4 wt. % when using 5 wt. % amphiphile. Moreover, increasing the concentration of the amphiphile above 1 wt. % has a significant effect on the onset point of precipitation. DBSA concentration of 3 and 5 wt. % increases the onset point of precipitation from 0.4 wt/wt, to about 1.6 and 3.3 wt/wt, respectively. Thus, DBSA is a suitable stabilizer for asphaltenes at high concentrations.

Figure 12 presents the effect of DBSA on asphaltene precipitation from petroleum fluid TK, which follows the same pattern as in petroleum fluid U. At 1 wt. % DBSA concentration in the petroleum fluid, the increase in the amount of precipitation is maximal and is almost two times higher than the original amount in the petroleum fluid. Conversely, a concentration of 5 wt. % DBSA reduces precipitation considerably to 1.52 wt. %, only 10% higher than the original amounts. As for the onset point of precipitation, DBSA shows high stabilization toward asphaltenes at increasing concentrations. The onset point increases significantly from 0.3 wt/wt to 3.6 wt/wt at 5 wt. % DBSA.

Figure 13 shows the effect of DBSA on asphaltene precipitation from petroleum fluid C. The effect of DBSA on precipitation is similar to that in petroleum fluid U. The variation in precipitation is not high at different concentrations. The precipitation data are very close to each other, especially when the concentration of DBSA is less than 1 wt. %. In addition, the data show approximately the same onset point of precipitation. However at 3 wt. % and 5 wt. % DBSA, the onset point is increased from 0.05 wt/wt, to about 0.5 and 1 wt. %, respectively.

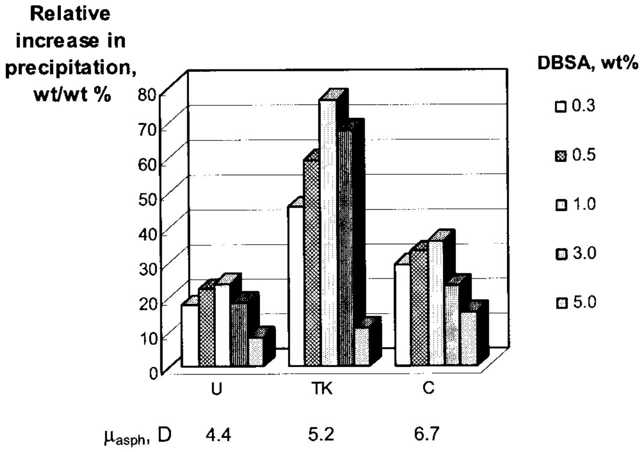

Figure 14. Relative increase in amount of precipitation by n-C_5 in petroleum fluids U, TK and C for various concentrations of DBSA.

Comparison of the amount of precipitation from the three petroleum fluids is presented in Figure 14. One can observe the increase in precipitation with increasing concentration of DBSA amphiphile first and then the decrease in precipitation. Differences with the original amounts are approximately the same for petroleum fluids U and C, but much higher for petroleum fluid TK. Furthermore, for a DBSA concentration of less than 1 wt. %, the effect of DBSA on precipitation is similar to that of resins, and it is likely that the interaction of DBSA and resin molecules are the same with other species. However, at greater concentrations, due to their high polarity, DBSA molecules may interact with themselves and with resins and asphaltenes through a different mechanism. The reasons underlying the effect of DBSA amphiphile on asphaltenes in petroleum fluids are the subject for future studies.

Electrostatic vs. London Interactions

A new finding in this work from the effect of the dipole moment of resins and asphaltenes on precipitation is that the electrostatic interactions may not be negligible. Let us calculate the relative contribution of the electrostatic and dispersion interactions between asphaltene molecules in a solvent medium using the van der Waals interaction energy U given by (Israelachvili, 1991)

$$U_{a-a}(r) = -\left\{3kT\left(\frac{\varepsilon_a-\varepsilon_s}{\varepsilon_a+2\varepsilon_s}\right)^2 + \frac{\sqrt{3}h\upsilon_e}{4}\,\frac{(n_a^2-n_s^2)^2}{(n_a^2+2n_s^2)^{3/2}}\right\}\frac{R_a^6}{r^6} \qquad (1)$$

and between asphaltene and resin molecules in a solvent medium given by (Israelachvili, 1991)

$$U_{a-r}(r) = -\left\{3kT\left(\frac{\varepsilon_a-\varepsilon_s}{\varepsilon_a+2\varepsilon_s}\right)\left(\frac{\varepsilon_r-\varepsilon_s}{\varepsilon_r+2\varepsilon_s}\right) + \frac{\sqrt{3}h\nu_e}{2}\,\frac{(n_a^2-n_s^2)(n_r^2-n_s^2)}{(n_a^2+2n_s^2)^{1/2}(n_r^2+2n_s^2)^{1/2}((n_a^2+2n_s^2)^{1/2}+(n_r^2+2n_s^2)^{1/2})}\right\}\frac{R_a^3R_r^3}{r^6} \qquad (2)$$

where the subscripts a, r, and s refer to asphaltenes, resins, and solvent, respectively; ε is the dielectric constant; n is the refractive index; R is the molecular radius; r is the distance between polar molecules (asphaltenes or resins) and solvent interacting molecules; k is the Boltzmann constant; h is the Planck constant; T is the absolute temperature; and υ_e is the absorption frequency. The product $h\upsilon_e$ is called ionization potential I, and a typical value of I in the UV range is 2×10^{-18} J (Israelachvili, 1991). We assume here that asphaltenes, resins, and the solvent medium have the same absorption frequency. In the brackets, the first term on the righthand side of Eqs. 1 and 2 represents the electrostatic interactions, and the second term represents the London dispersion interactions. We will calculate the contribution of each term in the total van der Waals interactions and compare them. At a temperature of 298 K, the dielectric constant of asphaltenes can be as high as 18.0, and the refractive index is approximately equal to 1.7, the dielectric constant of resins is about 4.5, the refractive index is equal to 1.6, and the dielectric constant and refractive index of the petroleum fluid are approximately equal to 2.0 and 1.49, respectively (Goual and Firoozabadi, 2002). If we consider these values in Eqs. 1 and 2, then the first term on the righthand side representing electrostatic interactions is equal to 0.65×10^{-20} J in Eq. 1 and 0.26×10^{-20} J in Eq. 2, and the second term representing London dispersion interactions is equal to 1.96×10^{-20} J in Eq. 1 and 1.036×10^{-20} J in Eq. 2. The sum of these two terms is equal to 2.61×10^{-20} J and 1.29×10^{-20} J in Eqs. 1 and 2, respectively, and the ratio of the first term (electrostatic interaction) to the sum of the two terms is 0.25 for Eq. 1 and 0.20 for Eq. 2. Thus, electrostatic interactions represent 25% of the total van der Waals interactions between asphaltene molecules, and 20% of the total van der Waals interactions between asphaltene and resin molecules, which is significant and cannot be neglected.

Conclusions

Based on the extensive and careful measurements reported in the article we draw the following conclusions.

(1) Addition of resin to a petroleum fluid increases the amount of precipitation. Reported data in the literature indicate that resins decrease the amount of asphaltene precipitation. The effect of various resins on precipitation depends on the resin dipole moment. Resins with a high dipole moment do not increase the amount of precipitation significantly.

(2) The increase in precipitation upon resin addition is more pronounced when the dipole moment of asphaltenes in the petroleum fluid is high.

(3) The addition of the DBSA amphiphile on precipitation by n-C_5 shows two different trends on the amount of precipitation. At low concentrations of DBSA, the amount of precipitation increases with increasing amphiphile concentration. This trend reverses with higher concentration (that is, as DBSA concentration increases, the amount of precipitation decreases). Therefore, before a certain concentration, the amphiphile is not effective.

(4) Electrostatic interactions between polar molecules such as asphaltenes and resins in a solvent medium may not be negligible in comparison to dispersion interactions.

Acknowledgments

This work was supported by the member companies of the Reservoir Engineering Research Institute (RERI). We thank Prof. J. M. Prausnitz (The University of California Berkeley) for his help and valuable comments during the course of this work.

Literature Cited

Al-Sahhaf, T. A., A. F. Mohammed, and A. S. Elkilani, "Retardation of Asphaltene Precipitation by Addition of Toluene, Resins, Deasphalted Oil and Surfactants," *Fluid Phase Equilibr.,* **194,** 1045 (2002).

Bardon, Ch., L. Barre, D. Espinat, V. Guille, M. H. Li, J. Lambard, J. C. Ravey, E. Rosenberg, and T. Zemb, "The Colloidal Structure of Crude Oils and Suspensions of Asphaltenes and Resins," *Fuel Sci. Technol. Int.,* **14**(1–2), 203 (1996).

Buckley, J. S., G. J. Hirasaki, Y. Liu, S. Von Drasek, J.-X. Wang, and B. S. Gill, "Asphaltene Precipitation and Solvent Properties on Crude Oils," *Pet. Sci. Technol. Int.,* **16**(3–4), 251 (1998).

Carnahan, N. F., J. L. Salager, R. Anton, and A. Davila, "Properties of Resins Extracted from Boscan Crude Oil and Their Effect on the Stability of Asphaltenes in Boscan and Hamaca Crude Oils," *Energy Fuels,* **13**(2), 309 (1999).

Chang, C., and H. S. Fogler, "Stabilization of Asphaltenes in Aliphatic Solvents Using Alkylbenzene-Derived Amphiphiles. 1. Effect of the Chemical Structure of Amphiphiles on Asphaltene Stabilization," *Langmuir,* **10**(6), 1753 (1994).

Clarke, P. F., and B. B. Pruden, "Asphaltene Precipitation from Cold Lake and Athabasca Bitumens," *Pet. Sci. Technol.,* **16**(3–4), 287 (1998).

Firoozabadi, A., *Thermodynamics of Hydrocarbon Reservoirs,* McGraw-Hill, New York (1999).

Goual, L., and A. Firoozabadi, "Measuring Asphaltenes and Resins, and Dipole Moment in Petroleum Fluids," *AIChE J.,* **48**(11), 2643 (2002).

Hammami, A., K. A. Ferworn, J. A. Nighswander, S. Overa, and E. Stange, "Asphaltenic Petroleum Fluid Oil Characterization: An Experimental Investigation of the Effect of Resins on the Stability of Asphaltenes," *Pet. Sci. Technol.,* **16**(3–4), 227 (1998).

Hiemenz, P. C., *Principles of Colloid and Surface Chemistry,* Dekker, New York (1986).

Huyskens, P. L., W. A. P. Luck, and T. Zeegers-Huyskens, *Intermolecular Forces: An Introduction to Modern Methods and Results,* Springer-Verlag, Berlin (1991).

Israelachvili, J. N., *Intermolecular and Surface Forces,* Academic Press, San Diego (1991).

Li, S., C. Liu, G. Que, W. Liang, and Y. Zhu, "A Study of the Interactions Responsible for Colloidal Structures in Petroleum Residua," *Fuel,* **76**(14/15), 1459 (1997).

Lian, H., J.-R. Lin, and T. F. Yen, "Peptization Studies of Asphaltene and Solubility Parameter Spectra," *Fuel,* **73**(3), 423 (1994).

Maitland, G. C., M. Rigby, E. B. Smith, and W. A. Wakeham, *Intermolecular Forces: Their Origin and Determination,* Clarendon Press, Oxford (1981).

Moschopedis, S. E., and J. G. Speight, "Investigation of Hydrogen Bonding by Oxygen Functions in Athabasca Bitumen," *Fuel,* **55**(3), 187 (1976).

Murgich, J., "Intermolecular Forces in Aggregates of Asphaltenes and Resins," *Pet. Sci. Technol.,* **20**(9–10), 983 (2002).

Murzakov, R. M., S. A. Sabanenkov, and Z. I. Syunyaev, "Influence of Petroleum Resins on Colloidal Stability of Asphaltene-Containing Disperse Systems," *Z. I. Khim. Tekhnol. Topl. Masel,* **10,** 40 (1981).

Permsukarome, P., C. Chang, and H. S. Fogler, "Kinetic Study of Asphaltene Dissolution in Amphiphile/Alkane Solutions," *Ind. Eng. Chem. Res.,* **36**(9), 3960 (1997).

Ratajczak, H., and W. J. Orville-Thomas, *Molecular Interactions,* Vol. 1, Wiley, Bath, UK (1980).

Rogel, E., "Simulation of Interactions in Asphaltene Aggregates," *Energy Fuels,* **14,** 566 (2000).

Rogel, E., O. Leon, J. Espidel, and Y. Gonzales, "Asphaltene Stability in Crude Oils," SPE Production and Facilities, **16**(2), 84 (2001).

Speight, J. G., *The Chemistry and Technology of Petroleum,* Dekker, New York (1999).

Swanson, J. M., "A Contribution to the Physical Chemistry of the Asphalts," *J. Phys. Chem.,* **46,** 141 (1942).

Wu, J., J. M. Prausnitz, and A. Firoozabadi, "Molecular-Thermodynamic Framework for Asphaltene-Oil Equilibria," *AIChE J.,* **44**(5), 1188 (1998).

Manuscript received Dec. 19, 2002, and revision received June 19, 2003.