

# Identification and measurement of petroleum precipitates

D. Vazquez, G.A. Mansoori \*

*Department of Chemical Engineering, Thermodynamics Research Laboratory, University of Illinois at Chicago, 202 CEB, M / C 110, 810 S. Clinton Street, Chicago, IL 60607-7000, USA*

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## Abstract

A number of procedures to identify and measure the precipitates that result from petroleum fluids are presented. The fractions considered in this study include those in the categories of asphaltenes, resins, saturates (paraffin/wax), aromatics, inorganic minerals and diamondoids. A combination of deposition techniques, separation by centrifuge, filtration, gas chromatography, gel-permeation chromatography, and SARA (LC-HPLC) separations, and a number of other techniques are utilized to identify each fraction and quantify their concentrations. These procedures provide an understanding of the overall behavior of the species that precipitate as well as of the interactions among them. The results of such analysis are the cornerstone of any predictive and preventive measures for heavy organics deposition from petroleum fluids. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* petroleum precipitates; deposition techniques; concentration

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## 1. Introduction

Solid precipitation during production, transportation, and storage of petroleum fluids is a common problem faced by the oil industry throughout the world. Through complex phase transformations, dissolved and suspended solids (asphaltenes, resins, paraffin/wax, diamondoids, formation solids, etc.) precipitate out of solution. Such phase segregations are sometimes followed by flocculation of the resulting precipitates. In many instances, these deposition phenomena render in complete clogging of flow lines and serious damages to storage vessels and

processing equipment. The solution or alleviation of the many technological problems posed by such depositions lies on a good understanding of the multi-phase behavior of the species that precipitate. It is also necessary to understand the interactions amongst these various species in the local environment where phase segregation and flocculation take place (Kawanaka et al., 1991; Mansoori, 1997).

The procedures presented in this report are complimentary to the other procedures already in the literature. The results of all such experimental measurements will be especially useful for the better modeling and prediction (Kawanaka et al., 1991; Mansoori, 1997) of the behavior of heavy organics in petroleum fluids. In the following sections of this report, the procedures along with the results of a crude-oil analysis as performed by each procedure are presented.

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\* Corresponding author. Tel.: +1-312-996-5592; fax: +1-312-996-0808.

*E-mail address:* mansoori@uic.edu (G.A. Mansoori).

## 2. Analysis of suspended materials in a crude oil

Microscopic inspection of crude oil samples is generally performed as a preliminary step. A microscope with a minimum magnification of  $200\times$  and equipped with a photo camera may be used. Photographs are obtained by placing small samples of the crude oil in a micro-chamber that is then perfectly sealed with a glass cover to prevent evaporation of the lighter fractions. This test will determine whether a crude oil contains suspended solids. If not, measurements of the onsets of asphaltene precipitation, flocculation and deposition (Vuong, 1985; Escobedo and Mansoori, 1995, 1997) and other related measurements can safely be performed. Otherwise, such measurements cannot be performed unless the suspended solids are found to be without asphaltene. It may be also necessary to establish the nature of the droplets (or bubbles) present in the crude. A number of procedures may be devised to study these droplets through microscopic techniques (Vazquez and Mansoori, in press). These experiments may demonstrate whether some of the species present in crude oil show surface activity at brine–oil interface indicative of stable water-in-oil emulsions in crude oil. It must be noted that some of the species contained in a crude oil, especially asphaltene, may exhibit surface activity that renders in the formation of stable water-in-oil emulsions. This emulsion seems to be stabilized by a film that surrounds the brine droplets. Generally suspended solids in the crude oil interact with these droplets such that lumps of several droplets are held together by solid aggregates. The amounts of water and sediment content of a crude oil can be measured following the IP 359/82 (ASTM D4007-87) standard procedure using a centrifuge (IP 359/82, 1985).

For quantitative analyses, it is important to prevent material loss due to evaporation during sample preparation. It is necessary to devise an appropriate procedure to draw aliquots from the main sample, such that uncertainties introduced by evaporation will be minimized.

In order to ascertain reproducible results, all aliquots must be weighed in gas-tight vials.

The solids in a crude oil may be separated for further analysis by two different methods (Vazquez and Mansoori, in press). In the first method, the

suspended solids are separated using an appropriate filtration technique. In the second method, the solids are separated using a centrifuge. Then, the amounts of  $nC_5$ -soluble,  $nC_5$ -asphaltene, and insoluble fractions in the suspended solids are measured using a detailed procedure (Vazquez and Mansoori, in press).

Table 1 contains the results from the fractionation of the suspended solids in a crude oil named (A). Note from Table 1 that the suspended solids in crude oil A are mainly comprised of  $nC_5$ -soluble material that could very well be paraffin/wax in conjunction with resins and traces of oil trapped in the solid. Note also that these suspended solids contain a considerable amount of  $nC_5$ -asphaltenes as well as a considerable amount of insoluble material. The composition of the solid material contained in crude oil A suggests a strong interaction among insoluble material (minerals), asphaltenes, and paraffin/wax. The insoluble material contained in the suspended solids of crude oil A was further tested and found to be inorganic minerals from the formation. Differential scanning calorimetry is performed on the  $nC_5$ -soluble material in the suspended solids in order to establish its paraffin/wax molecular weight range (Letoffe et al., 1995). For crude oil A, the melting curve indicated that the maximum of the melting occurs in the range of 76.26–81°C. These temperatures correspond to  $nC_{36}$  (hexatricontane; mp = 76.26°C) and  $nC_{40}$  (tetracontane; mp = 81.00°C). Thus, the thermogram suggested the suspended solids in crude oil A contain mostly high-molecular-weight (HMW) paraffin/wax species.

It is not surprising that the suspended solids found in crude oil A are primarily comprised of para-

Table 1  
Characterization of the suspended solids contained in crude oil A

Fraction	Suspended solids	Whole crude oil
Total amount of solids	100	2.5909 ± 0.1156 wt.%
Total volume of solids	100	3.82 ± 0.06% (v/v)
$nC_5$ solubles (wt.%)	81.7669 ± 1.7794	2.1198 ± 0.1404 $nC_5$
Asphaltenes (wt.%)	10.9081 ± 1.4704	0.2815 ± 0.0253
Insoluble solids (wt.%)	7.3250 ± 0.3133	0.1892 ± 0.0032

ffin/wax since its cloud point is above room temperature ( $\sim 33^\circ\text{C}$ ). However, what is important here is the fact that this solid material also contains a substantial amount of precipitated asphaltenes. It is apparent from these results that mineral particles and paraffin/wax crystals assist the precipitation of asphaltenes. A plausible scenario would be the existence of attractive forces between mineral particles and asphaltenes, which would result in the formation of larger particles on which paraffin/waxes may deposit.

### 3. Total asphaltene content of a crude oil

The exact value of the total asphaltene content of a crude oil cannot be measured by any precipitation procedure because of the fact that it will not completely precipitate by the existing precipitation procedures. However, the asphaltene that precipitates using different normal paraffin hydrocarbon solvents can be measured. Then, using such data in an appropriate polydisperse deposition model for asphaltene, one may be able to estimate the true value of the total asphaltene content of a crude oil (Kawanaka et al., 1991; Mansoori, 1997).

Measurement of the asphaltene content of  $n\text{C}_5$ -insolubles, could be a challenging task. It is well known that some amount of resins will precipitate along with the asphaltene fraction and insoluble material. It is also known that HMW solid paraffin/wax will precipitate out of solution once the asphaltene starts to flocculate. The experimental procedure used here finds its basis in the IP143/90 (ASTM D3279-90) standard procedure (IP 143/90, 1985).

The total  $n\text{C}_5$ -,  $n\text{C}_7$ -, and  $n\text{C}_9$ -asphaltene contents of crude oil A were measured according to this procedure. These results are summarized in Table 2. The total content of insoluble material in crude oil A

Table 2  
Total  $n\text{C}_5$ ,  $n\text{C}_7$ , and  $n\text{C}_9$  asphaltene content of crude oil A

Paraffin solvent	wt.% Asphaltene
<i>n</i> -Pentane	$1.0833 \pm 0.0050$
<i>n</i> -Heptane	$0.5167 \pm 0.0059$
<i>n</i> -Nonane	$0.3982 \pm n/a$

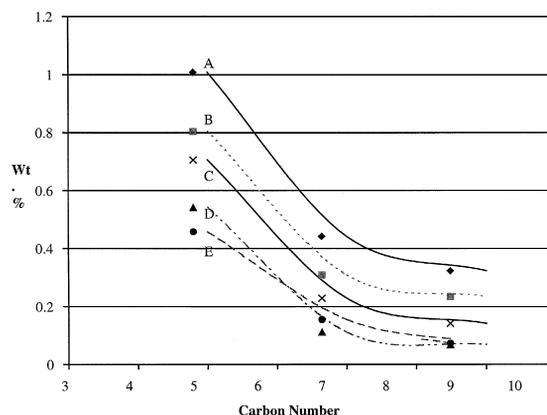


Fig. 1. Normalized amounts of asphaltenes precipitated with various paraffin solvents. The values reported in this figure were normalized with respect to the content of insoluble material present in crude oil A.

is determined by the same procedure as for asphaltene precipitation. Fig. 1 shows the normalized total  $n\text{C}_5$ -,  $n\text{C}_7$ -, and  $n\text{C}_9$ -asphaltene content of crude oil A along with four other crude oils.

### 4. Gel permeation chromatography (GPC) studies of precipitated asphaltenes from a crude oil

Adsorbed resin material on the precipitated asphaltene particles may lead to discrepancies in the MW determination. Therefore, a given precipitated asphaltene fraction of a crude oil must be purified before the measurement (Vazquez and Mansoori, in press).

For any particular method of determination, the observed molecular weights suggest that asphaltenes form molecular aggregates, even in dilute solutions. This association is influenced by solvent polarity, asphaltene concentration and temperature. The most widely used method for determining the MW of asphaltenes is GPC. It is understood, however, that GPC provides relative molecular weights and depends entirely on the calibration standards used (Leontaritis and Mansoori, 1989).

The molecular weight distribution of the  $n\text{C}_5$ -,  $n\text{C}_7$ -, and  $n\text{C}_9$ -asphaltene fractions precipitated from the crude oil A were obtained by a GPC procedure designed specifically for asphaltene. Each asphaltene

fraction was dissolved in tetrahydrofuran (THF) at a defined concentration. A similar solution of the whole crude oil A was also prepared. All samples were equilibrated using continuous mixing for a prescribed duration. Care was taken to avoid contact of the samples with open air. It must also be pointed out that all samples were filtered through appropriate membrane filters to remove any insoluble materials from the solutions. Three injections of each solution were run through a GPC system. The mobile phase for these analyses was THF at an appropriate flow rate. The mobile phase was degassed by filtration and subsequent *sonication* with dry helium. The temperature for all the runs were kept constant and the eluant was analyzed. The raw GPC data were processed using a size exclusion chromatography software. Calibration curves were obtained using narrow-dispersity polystyrene standards.

The molecular weight distributions of the  $nC_5$ -,  $nC_7$ -, and  $nC_9$ -asphaltene fractions of the crude oil A are reported in Fig. 2. Since asphaltenes are solubility-class compounds, properties of the precipitated asphaltenes vary according to the solvent used for their precipitation. The resin content in the pre-

cipitate increases as the number of carbons in the precipitating solvent decreases. When *n*-pentane is used HMW paraffins co-precipitate with the asphaltenes and resins. Therefore, it is expected that these three types of asphaltenes will exhibit very different MW distributions. The MW distributions will depend on the level of interactions among asphaltenes, resins, and co-precipitated HMW paraffins.

According to Fig. 2, the MW distributions for all the three types of asphaltenes are bimodal. The distribution for the  $nC_5$ -asphaltenes exhibits two distinguishable peaks: one narrow HMW peak [6751] and one broad low-molecular-weight (LMW) peak [2663]. The HMW peak exhibits little tailing towards high molecular weights. The shape of these two peaks suggests the existence of, at least, two different types of species in the solution.

The MW distribution for the  $nC_7$ -asphaltenes also exhibits two distinct peaks: a narrow HMW peak (9383) with considerable tailing towards the high molecular weights, and one broad LMW peak (3383). Note that this distribution also suggests the coexistence of, at least, two types of species in the solu-

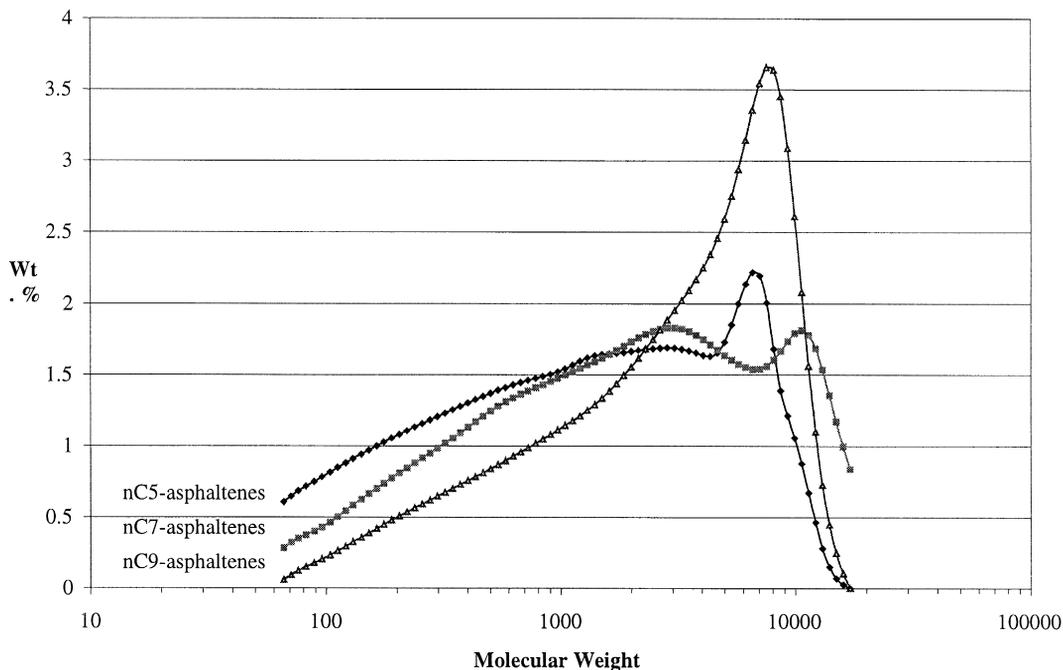


Fig. 2. Molecular weight distributions obtained by GPC for the various asphaltene fractions derived from five different crude oils.

tion. The LMW peak for the  $nC_9$ -asphaltenes is not easily observed as in the previous two cases. One prominent peak with a peak molecular weight of 7747 is observed with little tailing towards high molecular weights. The shape of this peak suggests that in this case, the amount of LMW species is much smaller than in the case of  $nC_5$ -, and  $nC_7$ -asphaltenes. This suggests rather strong interactions among asphaltene molecules such that very HMW species/aggregates are formed. The average molecular weights obtained for the  $nC_5$ -,  $nC_7$ -, and  $nC_9$ -asphaltenes were 2725, 6198, and 5607, respectively.

These studies also indicate that the precipitated fractions contain a considerable amount of LMW species in solution. This is clearly indicated by the continuous distribution throughout the chromatogram until the lower exclusion limit (i.e. 100) for the setup used. When asphaltenes are dissolved in aromatic or polar solvents, even at low concentration, there seems to be a complex equilibrium: (Rogacheva et al., 1980; Pacheco-Sanchez and Mansoori, 1998)

Molecules  $\leftrightarrow$  Micelles  $\leftrightarrow$  Micelle aggregates

In this equilibrium, the first species (molecules) may exhibit molecular weights up to 4000; the second species (micelles) could have molecular weights from 4000 to 10,000; and the third species (micelle aggregates) may possess molecular weights up to 40,000,000. The existence of two distinct families demonstrated in Fig. 2 are attributed to the asphaltene molecule and asphaltene micelle.

## 5. SARA separation

The SARA separation was originally designed for characterization of residuals (Jewell et al., 1974). The heavy end of a crude oil can be separated into four distinct fractions namely saturates, aromatics, resins, and asphaltenes using the experimental SARA procedure. A crude oil usually contains a considerable amount of volatile material that must be removed prior to performing SARA separation of the crude oil. This is accomplished by performing a vacuum batch distillation at 10 mm Hg and room temperature until the weight of the residue reaches a constant value. The first fraction to be separated

from the vacuum residue is the  $nC_5$ -asphaltenes. The filtrate collected from the separation of the  $nC_5$ -asphaltenes is commonly known as maltenes. It contains the remaining three fractions, saturates, aromatics and resins. These three fractions are separated using open-column liquid chromatography.

Saturate hydrocarbons on percolation in a  $n$ -pentane eluant, are not absorbed on activated silica under the conditions specified. The saturate fraction of the oil is eluted from the column with 1 l of  $n$ -pentane at 5 ml/min. The solvent is removed using a rotary vacuum evaporator to recover the saturates fraction.

Aromatic hydrocarbons are adsorbed on activated silica in the presence of  $n$ -pentane, and desorbed by toluene after removal of the saturates under the conditions specified. The aromatic fraction of the oil is eluted from the chromatographic column using toluene at 5 ml/min. The resin fraction of the oil is eluted from the chromatographic column using a 90/10 toluene/MeOH solution at 5 ml/min. This fraction is reported as wt.%. Solvent removal is to be performed using standard laboratory procedures.

The bulk composition of crude oil A from the two SARA separations performed on the vacuum residue is given in Table 3. Note from Table 3 that as much as 21.05% by weight was separated from this crude oil at 27°C and 10 mm Hg (vacuum distillation). These light ends were further analyzed by gas chromatography-mass spectroscopy (GC-MS) as will be discussed later. Also note that the SARA separation performed on the vacuum residue was successfully accomplished with an average recovery of about 99%. The resins content of crude oil A is very small

Table 3  
Results from the SARA separation of crude oil A

Fraction	wt.% of whole crude oil	wt.% of vacuum residue
Light compounds (separated at 27°C at 10 mm Hg)	21.0500 $\pm$ 0.1150	100
Saturates	55.2369 $\pm$ 1.6849	69.1949 $\pm$ 1.3650
Aromatics	19.9590 $\pm$ 1.5373	25.2788 $\pm$ 1.9488
Resins (or polars)	2.3242 $\pm$ 0.0108	2.9437 $\pm$ 0.0137
Asphaltenes ( $nC_5$ )	1.0833 $\pm$ 0.0050	1.3753 $\pm$ 0.0032
Total recovery (average)	99.6534	98.7927

compared to its total asphaltene content (see Fig. 1). The overall composition of this crude oil appears to be a hostile environment for the stability of its asphaltene content.

## 6. Diamondoids separation and characterization

Diamondoid (adamantane) has the same structure as the diamond lattice, highly symmetrical and strain-free. It is generally accompanied by small amounts of alkylated adamantanes. The isolation of a single compound, adamantane, from such a complex mixture as petroleum is a consequence of its highly unusual physical and chemical properties (Vazquez Gurrola et al., 1998).

Adamantane (with freezing point of 269°C in sealed capillary) crystallizes in a face-centered cubic lattice that is quite unusual for an organic compound. The special properties of adamantane are reflected in its mass spectrum that is also quite unusual.

Deposition of diamondoids can be particularly problematic during production and transportation of natural gas, gas condensates and light crude oils. These compounds are common in petroleum fluids, in general. However, their presence in crude oils is usually ignored due to their low concentration. Nevertheless, even small concentration of these compounds could lead to problems of deposition and plugging of flow paths. The high amount of gas associated with crude oil A (gas-to-oil ratio = 220 m<sup>3</sup>/m<sup>3</sup>) suggests that diamondoids, if present in appropriate amounts, may cause problem during its production.

GC-MS analyses of diamondoids in petroleum fluids can be performed on the saturates fraction of SARA separation, rather than on the whole crude oil. This is because the aromatic interferences need to be removed by isolating the saturates fraction on silica gel. The light fraction of a crude oil, separated at 27°C and 10 mm Hg, must be also analyzed by GC-MS to determine whether it contains diamondoids. Adamantane is expected to elute from the GC column between *n*C<sub>10</sub> and *n*C<sub>11</sub>; diamantane is expected to elute between *n*C<sub>15</sub> and *n*C<sub>16</sub>; and triamantane is expected to elute between *n*C<sub>19</sub> and *n*C<sub>20</sub>. The same alkyl-substituted adamantanes found in the saturated fraction of crude oil A were also

Table 4  
Alkyl substituted adamantanes found in crude oil A

Compound	<i>M</i> +	Base peak	Retention time (min)
1-Methyl adamantane	150 (14%)	135 (M-CH <sub>3</sub> )	55.59
2-Methyl adamantane	150 (68%)	135 (M-CH <sub>3</sub> )	60.88
1,4-Dimethyl adamantane	164 (15%)	149 (M-CH <sub>3</sub> )	61.88
1,2-Dimethyl adamantane	164 (15%)	149 (M-CH <sub>3</sub> )	64.51
1-Ethyl adamantane	164 (9%)	135 (M-C <sub>2</sub> H <sub>5</sub> )	66.89

detected in this low-boiling fraction at similar retention times and in higher concentrations (see Table 4).

## 7. Conclusions

The experimental procedures presented in this report provide the means for understanding the amounts and behaviors of the species that precipitate as well as the interactions among them. A detailed procedure for the separation and analysis of the suspended solids in the crude oils is presented. The results of the procedure can also reveal whether such tests as cloud point, onset of flocculation of asphaltene and other onset/threshold of deposition tests can be proceeded for the oil sample under study.

Total asphaltene content of crude oils are measured using various precipitating agents and its relation with the nature of the precipitating agent is established. This data along with the onset/threshold data may be used to tune theoretical models (Kawanaka et al., 1991; Mansoori, 1997) of heavy organics deposition. GPC studies of asphaltene separated from a crude oil will produce the size distribution of asphaltene deposited as a function of the solvent used. Such data, along with GPC size distribution data (Leontaritis and Mansoori, 1989; Vazquez and Mansoori, in press) for resins can be quite useful for tuning theoretical polydisperse models of heavy organics deposition (Kawanaka et al., 1991; Mansoori, 1997). The SARA separation of the heavy and light fractions of a crude oil give the composition of the crude oil from the point of view of the four basic

families of compounds, namely saturates, aromatics, resins and asphaltenes. Interactions among these four families of compounds have a profound effect on the stability of a crude oil that must be understood and modeled in the stability analysis of crude oils. Characterization and concentration measurement of diamondoids can be particularly useful for petroleum reservoir fluids with high gas-to-oil ratios. The analytic techniques presented in this report can be used to find the composition and nature of such compounds present in a crude oil.

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