



Structure & Properties of Micelles and Micelle Coacervates of Asphaltene Macromolecule*

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Key Words: Micelles, Micelle Coacervates, Asphaltene, Macromolecules

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ABSTRACT

We have made some progress in studies towards formation and measurement of the behavior of asphaltene micelles nano-structures that might be formed to serve as elements of nano-materials and also on synthetic strategies for creating such structures. An investigation of the micellization and coacervation measurements of some well-characterized asphaltene molecules in polar solvents at various concentrations and temperatures are made. The critical micellization concentration (CMC) and the micelle coacervation point (MCP) of nano-structure asphaltene micelles are measured using viscometry. At concentration above the CMC, asphaltene in the solution will self-associate, saturation phase will be formed and then at a higher concentration asphaltene nano-structure micelles in the solution will coacervate represented by a second sharp point of inflection corresponding to the asphaltene MCP and finally, at a higher concentration the aggregation of asphaltenes coacervates will occur.

As a result of these measurements, for the first time it has become possible to produce phase diagrams for the whole range of asphaltene micellization and micelle coacervation.

INTRODUCTION

Asphaltene, resin, wax, etc. are heavy organic compounds which may exist in petroleum, heavy oil, tar sand and coal in different quantities. Such compounds could precipitate out of petroleum fluids due to various forces causing fouling in the oil reservoir, in the well, in the pipeline and in the oil production and processing facilities. During refining of petroleum heavy organic compounds, including asphaltene, other heterocyclic compounds, heavy hydrocarbons and nonvolatile products will remain in the bottom of the refinery's fractionation column as a very complex mixture known as "resid". Our group is investigating unusual behavior of asphaltene molecules in petroleum fluids and in model systems that use pure solvents and well-characterized asphaltene molecules. Our interest in these molecules is to characterize their various phase transitions. These molecules are found to be the basic reason for fouling in the flow of petroleum fluids. The focus of the work on these unusual molecules is to characterize their structure, dynamics and thermodynamics, and to establish the relationship between these properties and petroleum fluid behavior. Asphaltene particles are believed to exist in petroleum partly dissolved and partly in steric-colloidal and / or micellar 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 (Kawanaka et al 1989, Mansoori, 1997).

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 consist 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 solution. These surface active materials, known as surfactants, tend to self-assemble into 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). The change in properties that occur as micelles form is marked by sharp transitions in many physical quantities such as the surface tension, viscosity, conductivity, turbidity and nuclear magnetic resonance of the solution (stupp et al 1997). Although micellization represents a self-association phenomenon in general, it is conventionally limited to the self-association initiated by the hydrophobic-hydrophilic imbalance. The hydrophobic part of the surfactant molecule tends to avoid contact with water, while the hydrophilic ionic head group tends to be strongly hydrated. Self-association of surfactant molecules into micelles can be seen as resulting from a compromise between the two different properties of the surfactant molecules (Jones and Gormally, 1983).

If one starts with a solution of micelles in an appropriate solvent, then as a result of increase in micelle concentration a large part of the micelles can be separated out into a new phase. The original one phase system becomes two phases. One is rich and the other is poor in micelle concentration. The micelle-rich phase in a dispersed state appears as amorphous liquid droplets called coacervate droplets. Upon standing these coalesce into one clear homogenous micelle-rich liquid layer, known as the coacervate layer which can be deposited.

MOLECULES \longleftrightarrow **MICELLES** \longleftrightarrow **COACERVATE**

Whether the asphaltene particles are dissolved in petroleum, in steric-colloidal state or in micellar form, depends, to a large extent, on the presence of other particles (paraffins, aromatics, resins, etc.) in the petroleum. The existence of various nano-structures of asphaltenes in petroleum has been extensively discussed in numerous publications (Mansoori, 1997, Rogacheva et al 1980, Sachanen 1945, Sheu and Mullins 1995, Yen and Chillingarian, 1994).

A number of physical and chemical methods are available for construction of model structures for asphaltenes. Physical methods include IR, NMR, ESR, mass spectrometry, x-ray, ultra centrifugation, electron microscopy, small angle neutron scattering, small angle x-ray scattering, quasi elastic light scattering spectroscopy, VPO, GPC, etc. Chemical methods involve oxidation, hydrogenation, etc. Two of the representative structures for the asphaltene molecule belongs to the the Atabasca tar-sand bitumen and petroleum bitumens (Suzuki, et al 1982) and includes carbon, hydrogen, oxygen, nitrogen, sulphur as well as polar and non-polar groups as it is shown by Figure 1.

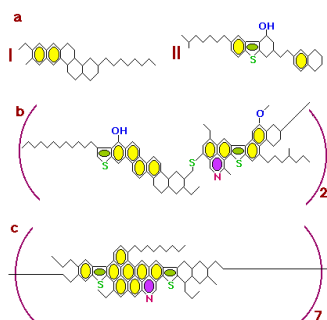


Figure 1

It has been recognized that petroleum asphaltene may form micellar particles in aromatic and/or polar solvents such as toluene and methyl-naphtalene (Galtsev1995, Mansoori, 1997, Rogacheva et al 1980, Sachanen 1945, Sheu and Mullins 1995, Yen and Chilingarian, 1994). Small-size asphaltene particles may be dissolved in a petroleum fluid, whereas relatively large asphaltene particles may flocculate out of the solution, due to high paraffin content of the oil, forming random aggregates as shown in Figure 2.

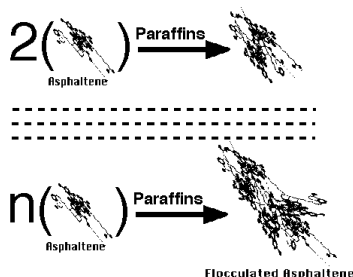


Figure 2

Flocculation of asphaltene in paraffinic petroleum are 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). Due to their large size and their adsorption affinity to solid surfaces asphaltene flocs (random aggregates) can cause

quite stable deposits which may not wash away by current remediation techniques. One of the effective and routine methods of remediation of heavy organic deposits is the use of strong aromatic solvents that could dissolve the asphaltene deposits (Acevedo et al 1995, Dubey and Waxman 1995, Kim et al 1990, Pacheco-Sanchez and Mansoori 1997). Asphaltene flocs (aggregates) can form steric-colloids in the presence of excess amounts of resins and paraffin hydrocarbons (Park & Mansoori, 1988, Mansoori 1997) as shown in Figure 3.

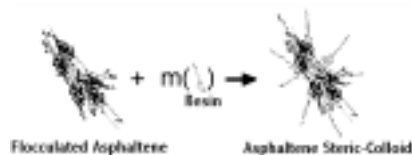


Figure 3

In this report the micellization and coacervation of asphaltene after it is separated from petroleum fluids and then dissolved in specific organic solvents are studied

Asphaltene molecules may have an average molecular diameter around 5 Nm. Asphaltene micelles may have an average size around 25 Nm. Whereas micellar coacervates may have sizes greater than 25 Nm. 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 form micelles in the presence aromatic hydrocarbons (or other polar solvents) as shown in Figure 4.



Figure 4

An example of asphaltene micelle coacervation is depicted in Figure 5.



Figure 5

The mechanisms of asphaltene flocculation and steric-colloid formation are well understood and modeled (Kawanaka et al 1989, Mansoori 1997). There exist also plenty of experimental data for asphaltene flocculation. Pacheco-Sanchez and Mansoori (1998) have developed a theoretical model to explain and quantify the phenomenon of asphaltene micellization and coacervation. This theory is also able to predict the nature of micelles from the phase diagram of the asphaltene micellization and coacervation. Despite the experimental evidence on the micellization of asphaltenes, to our knowledge no experimental data is available for the micelles coacervation point

(MCP) of asphaltene. In what follows an accurate and reliable technique for measurement of micellization and coacervation of asphaltene in pure solvents is reported and a number of representative measurements are made.

EXPERIMENTAL PROCEDURE

The experimental method proposed by Escobedo and Mansoori (1995 & 1997) to determine the onset of asphaltene steric-colloid formation in petroleum through viscometry is proven to be equally applicable for the detection of asphaltene micelle formation in polar solvents. In the present study the phase diagram of asphaltene micellization and micelle coacervation in polar-organic solvents (1-methyl naphthalene) is investigated in the temperature range of 0-160°C using the viscometry method.

Two ranges of concentrations were used in this investigation; The low concentration range of 0.1-1.0 mg/g asphaltene in solvent. The high concentration range of 1-10 mg/g asphaltene in solvent. 1-methyl naphthalene was chosen as the solvent. The solutions were aged for 24 hours before measurement. This method is based on observations of the trend in the relative viscosity variations with increase in the concentration of asphaltene in a solvent. The points of inflection on plots of relative viscosity vs. concentration of asphaltene in 1-methyl naphthalene at various temperatures, corresponding to the critical micelle concentration (CMC) and micelle coacervation points (MCP), were determined. In this study we also have produced, 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 never done before for asphaltene.

The asphaltenes used in this study were two different kinds, Arabian medium heavy resid (AMHR) asphaltene obtained from Texaco Corp. and pentane-insoluble bitumen fraction (PIBF) asphaltene obtained from Syncrude in Canada. The 1-methyl naphthalene used in this study was produced by Aldrich Chemical Company, catalog no. M5,680-8 [90-12-0], 95% pure, BP. 240-243°C, MP. -22°C. The experiments were run at constant temperatures of 0-160°C with increments of 10°C for asphaltene in 1-methyl naphthalene (below boiling point of 1-methyl naphthalene). The solution viscosity was measured using glass capillary viscometer (Cannon-Fenske-Opaque) manufactured and calibrated by Industrial Research Glassware Ltd. for which calibration certificate was provided with the instrument. Two different viscometers, R14 and R15, were used to cover the viscosity ranges of all concentration of dilutions (low and high concentration). The viscometer constants were verified for accuracy using distilled water known viscosity data. Kinematics viscosities are based on the value for water adopted by the National Institute of Standards and Technology and the American Society for Testing and Materials July 1, 1953. The kinematics viscosity basis is 1.0038 mm²/s (cSt) for water at 20°C. The gravitational constant, g, is 980.1 cm/sec² at the Cannon Instrument Company. The gravitational constant varies up to 0.1% in the United States.

Each kinematic viscosity point of asphaltene in 1-methyl naphthalene were measured three times to ensure the reproducibility of the data. Enough time was allowed for the dilution in each sample to reach thermal equilibrium (Escobedo and Mansoori, 1994 & 1997) before measurement was made. The equilibration time was determined experimentally based on samples in which asphaltene dilution had already occurred and no variation in the viscosity. During the determination of the equilibration time, the open end of the cuvette cell was capped to prevent solvent evaporation.

RESULTS AND DISCUSSION

The phase diagrams of Arabian Medium Heavy Resid asphaltene (AMHR) and pentane-insoluble bitumen fraction asphaltene (PIBF) micellization and coacervation in 1-methyl naphthalene solvent are produced in the temperature 0-160°C and 0-180°C, respectively, with increments of 10°C. A series of experiments were performed to measure the effects of the changing concentration and temperature on asphaltene micellization and coacervation. Experimental observations 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 which can be accurately detected and measured. This experimental technique has an advantage over other techniques since the previous studies has the limitation of measuring only the micellization, and not coacervation, and for smaller temperature ranges.

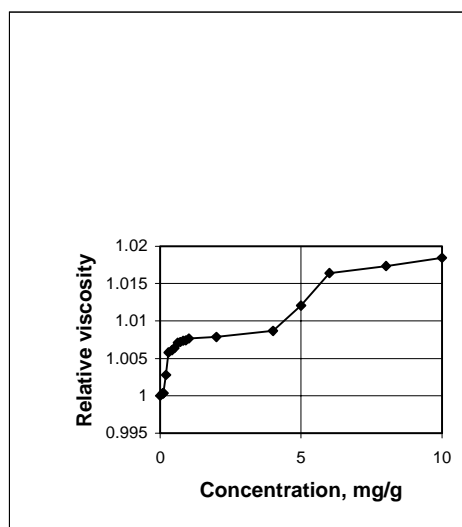


Figure 6

Figure 6 shows the results of relative viscosity measurements obtained for the PIBF asphaltene dissolved in 1-methyl naphthalene in the concentration range of 0 - 10 mg/g at the constant temperature of 90°C. As it can be seen from this figure 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 Figure 6 are divided into two zoomed out sections (0-1 mg/g and 1-10 mg/g of asphaltene in solvent) and Figures 7 and 8 are reported.

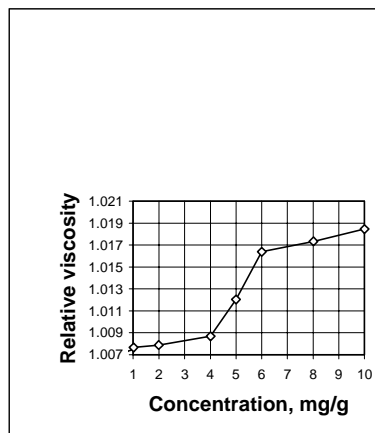
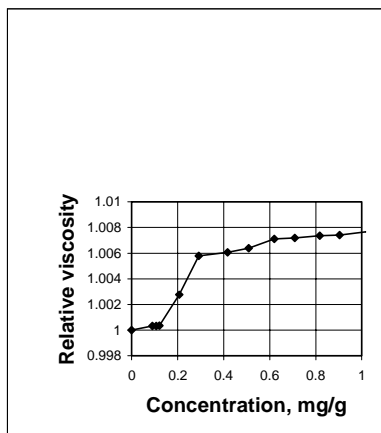


Figure 7

According to Figure 7, 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 Figure 8 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 corresponds to the micelles coacervation point (MCP) of asphaltene and the other (higher concentration) change of slope represents the coacervate separation point. By repeating the relative viscosity measurement at various other temperatures in the range of 0-160 oC, and various concentrations of asphaltenes in polar solvents similar figures, as Figures 6-8, were obtained which provided us with the necessary data to construct the micellization, saturation, coacervation and phase separation diagrams of asphaltene in polar solvents as reported in Figures 9 and 10.

Figure 8

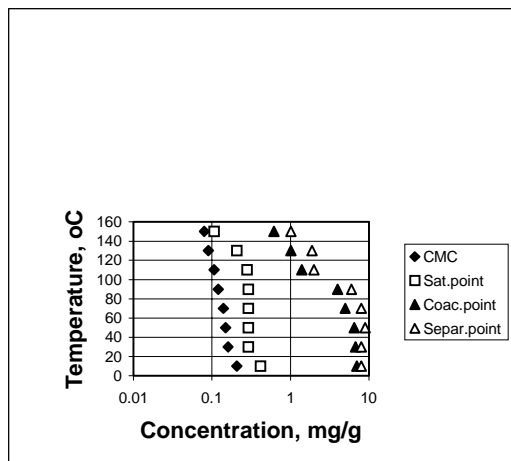


Figure 9

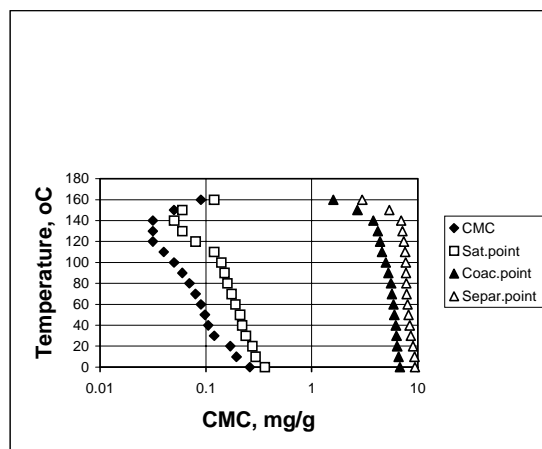


Figure 10

Figure 9 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 10°C increment. According to this figure the CMC, saturation point, MCP and separation point get closer to one another as temperature increases. Figure 10 shows the measured data obtained for the phase diagram of AMHR asphaltene which has concentrations of 1.0 - 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.

The essence of nanotechnology is the ability to work at the molecular level, atom by atom, to create large structures with fundamentally new molecular organization. The aim is to exploit these properties by gaining control of structures and devices at atomic, molecular, and supramolecular levels and to learn to efficiently manufacture and use these devices (NSTC 2000). Asphaltene micelles and coacervates are in this category of molecular-level structures which can have interesting and useful applications in nanotechnology. We have made some progress in

studies towards formation and measurement of the behavior of asphaltene micelles nano-structures that might be formed to serve as elements of nanomaterials and also on synthetic strategies for creating such structures. Nanostructured asphaltene with structural features in the nanometer range can be also found in the form of micelle clusters known as coacervates. In addition, progress has been made in predicting the behavior of asphaltene micelle nano-structures at various temperatures and compositions in pure solvents. Our primary focus is to establish all the details of the nanostructure of asphaltene micelles and coacervates for future nanotechnology application. Nano sized materials can often be prepared by precipitant clusters of atoms in a liquid. The asphaltene micelle process may be used to produce nano-structured materials. The ultimate goal is to achieve a better understanding of the fundamental molecular processes and properties of these nano-structures which are dominated by grain boundaries and interfaces. In understanding the behavior and the properties of these nano-structures the potential for technological applications will be considered.

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