Measurement of property relationships of nano-structure micelles and coacervates of asphaltene in a pure solvent

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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 asphaltenes 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. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Coacervates of asphaltene; Nanostructure micelles; Property relationship; Solvent; Measurement

1. Introduction

Asphaltene, resin, wax, etc. are heavy organic compounds which may exist in petroleum, heavy oil, tar sand, etc. 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 non-volatile products will remain in the bottom of the refinery's fractionation column as a very complex mixture known as "resid" (Yen & Chilingarian, 1994). 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 was originally stimulated by a desire 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, Leontaritis, Park, & Mansoori, 1989, Chapter 24; Mansoori, 1999).

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

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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 & 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 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. The coacervation process was originally discovered and developed into practical applications by Green and Schleicher (1957). Coacervation and phase separation from organic and aqueous media involve many properties, materials and processes such as phase-inducing agents, stirring rates, core-to-wall ratios, polymer characteristics, core characteristics (wettability, solubility), cooling rates and rates of addition.

MOLECULES ↔ MICELLES

↔ COACERVATE ASPHALTENE

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, Rimaev, Gubaidullin, & Khakimov, 1980; Sachanen, 1945; Sheu & Mullins, 1995; Yen & Chilingarian, 1994).

The classic definition of asphaltenes is based upon the solution properties of petroleum residuum in various solvents. The word *asphaltene* was coined in France by Boussingault (1837). Boussingault described the
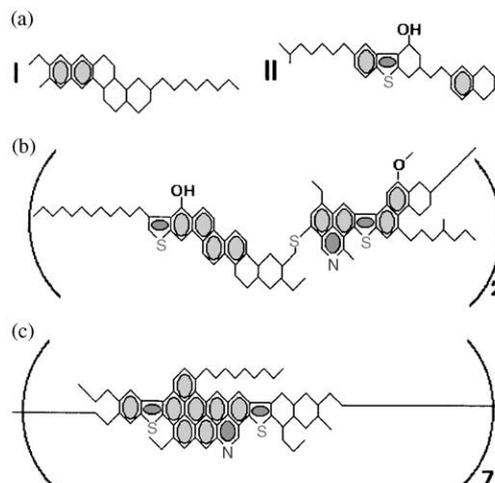

Fig. 1. Average molecular structural models of the fractions of Athabasca tar-sand bitumen and petroleum bitumen: (a) resin fraction; (b) asphaltene fraction of tar-sand bitumen; and (c) asphaltene fraction of bitumen proposed by Suzuki et al. (1982).

constituents of some bitumens (asphalts) found at that time in eastern France and in Peru. He named the alcohol insoluble, essence of turpentine soluble solid obtained from the distillation residue "asphaltene", since it resembled the original asphalt. The asphaltene fraction of a petroleum fluid is defined according to Nellensteyn (1924) as the fraction insoluble in low boiling point paraffin hydrocarbons, but soluble in carbon tetrachloride and benzene. Later, Pfeiffer (1950) defined asphaltene as the fraction insoluble in *n*-heptane but soluble in toluene. Presently, there are standard methods available for separation and characterization of asphaltene such as IP 143 (Institute of Petroleum, 1966).

A number of investigators have constructed model structures for asphaltenes, resins, and other heavy fractions based on physical and chemical methods. 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 Atabasca tar-sand bitumen and petroleum bitumens (Suzuki, Ito, Takegami, & Watanabe, 1982) and includes carbon, hydrogen, oxygen, nitrogen, sulphur as well as polar and non-polar groups as it is shown in Fig. 1.

Asphaltene particles can assume various forms when mixed with other molecules depending on the relative sizes and polarities of the particles present. Their structure can vary from source to source as it is studied by Yen et al. (1994). In addition, they behave as lyophobic and steric, and they posses electrostatic and associative forces. Asphaltene molecules have a high degree of polynuclear
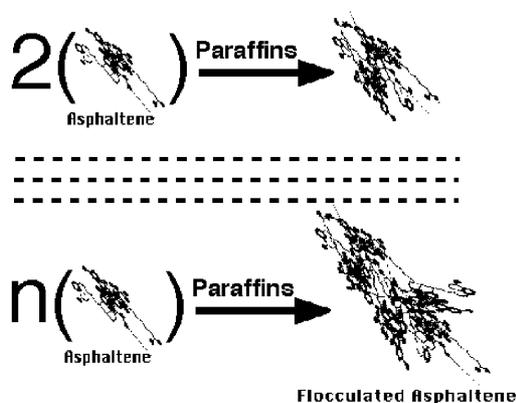
Fig. 2. Flocculation of asphaltene due to increase in paraffin (non-polar) content of petroleum.
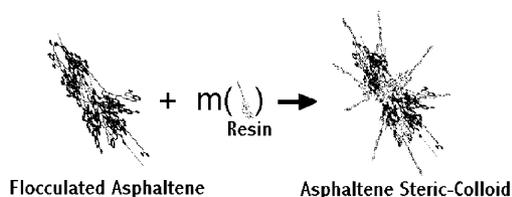

Fig. 3. Steric-colloid formation of asphaltene flocs (random aggregates) in the presence of excess amounts of resins and paraffin hydrocarbons.
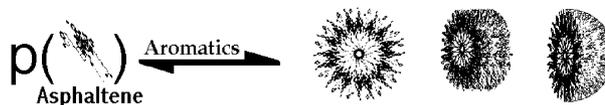

Fig. 4. Micellization (self-association) of asphaltene due to increase in aromaticity (polarity) of its medium.

aromaticity. It has been recognized that petroleum asphaltene may form micellar particles in aromatic and/or polar solvents such as toluene and methyl-naphthalene (Galtsev, Ametov, & Grinberg, 1995; Mansoori, 1997; Rogacheva et al., 1980; Sachanen, 1945; Sheu & Mullins, 1995; Yen & 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 Fig. 2. Flocculation of asphaltene in paraffinic petroleum are known to be irreversible, having hysterises when the conditions are returned to pre-flocculation point (Abedi, Seyfaie, & Shaw, 1998; Acevedo, Ranaudo, Escobar, Gutierrez, & Ortega, 1995; Birket, 1997; Fuhr, Cathrea, Coates, Kalra, & Majeed, 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 & Waxman, 1995; Kim, Boudh-Hir, & Mansoori, 1990; Pacheco-Sanchez & Mansoori, 1997). Asphaltene flocs (random aggregates) can form steric-colloids in the presence of excess amounts of resins and paraffin hydrocarbons (Park & Mansoori, 1988; Mansoori, 1997) as shown in Fig. 3. In this report, the micellization and coacervation of asphaltene after it is separated from petroleum fluids and then dissloved in specific organic solvents are studied.

Furthermore, the phenomenon of self-association in asphaltene/toluene systems has been confirmed through measurements of surface tension. With small concentration of asphaltene (< 0.1–1.0 mg/g of solvent) true solutions are formed (Rogacheva et al., 1980). Rogacheva et al. (1980) have reported some experimental data for the phase diagram of asphaltene micelle formation when

asphaltene is dissolved in toluene. They indicate that mixing a purified asphaltene with pure toluene results in the formation of a true solution for asphaltene concentrations in the range 0–1 mg per gram of toluene. Their 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-loving and the solvent-hating 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. Even though the possibility of coacervation of asphaltene micelles are reported by Rogacheva et al. (1980), neither they nor other investigators report any data for the micelles coacervation point (MCP) of asphaltene.

Asphaltene molecules may have an average molecular diameter around 5 N m. The size distribution of asphaltene micelles may have an average size around 25 N m, whereas micellar coacervates may have sizes > 25 N m. Several experimental investigations have indicated that asphaltene micelles could be of spherical-like, cylindrical-like or disk-like form (Espinat & Ravey, 1993; Yen & 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 Fig. 4. An example of asphaltene micelle coacervation is depicted in Fig. 5.

While the mechanisms of asphaltene flocculation and steric-colloid formation are well understood and modeled (Kawanaka et al., 1989; Mansoori, 1997), the phase behavior of asphaltene micelle formation is not well characterized and in many cases in recent years it is confused with the asphaltene steric-colloids and asphal-
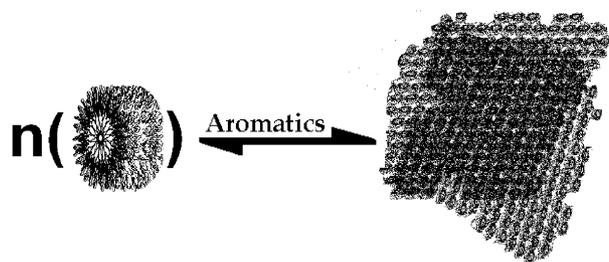
Fig. 5. Coacervation (self-association) of asphaltene micelles due to increase of micelle concentration in an aromatic (polar) medium.

tene flocs. Despite the experimental evidence on the micellization of asphaltenes, to our knowledge no experimental data is available for the MCP of asphaltene. The theories of micellar solutions of oil/surfactant/water may be used to explain the micellization of asphaltenes in aromatic solvents if it is assumed that the properties of these systems are similar to those of oil/surfactant/water systems. 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. 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.

2. Experimental procedure

There exist several methods for the experimental measurement of CMC of asphaltene micelles in polar solvents including the use of surface tension, microcalorimetry, small angle X-ray scattering method, and the use of visometry (Sheu & Mullins, 1995; Rogacheva et al., 1980; Escobedo & Mansoori, 1997). Rogacheva et al. (1980) described the dependence of surface tension on the concentration of asphaltene, there is a sharp point of inflection, which corresponds to the CMC. Surface tension of asphaltene-containing solvents decreases with the addition of asphaltene concentration and it remains fairly constant after CMC is reached (Sheu & Mullins, 1995). They also stated that with small concentration, below the CMC, the dilutions of asphaltenes are in a molecular state, while above the CMC, associated asphaltenes are formed. Measurements of the surface tension of asphaltenes in toluene in interval concentration of 0.1–1 mg/g were studied by Rogacheva et al. The investigation of Rogacheva et al. (1980) reveals that a decrease in CMC of asphaltene/toluene dilution as temperature increases. In their investigation, they used asphaltene in toluene dilution in the interval temperatures

of 20–150°C. While Rogacheva et al. (1980) explain the formation of asphaltene micelle coacervates there are no experimental data reported for the MCP of asphaltene. This seems due to the fact that surface tension technique may not be appropriate for such a measurement.

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.

The viscometry technique developed by Escobedo and Mansoori (1995, 1997) is used here for determination of the micellization and coacervation of asphaltene in polar solvents. Two ranges of concentrations were used in this investigation: the low concentration range of 0.1–1.0 mg/g asphaltene in solvent and 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 h 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 versus concentration of asphaltene in 1-methyl naphthalene at various temperatures, corresponding to the CMC and MCPs, 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
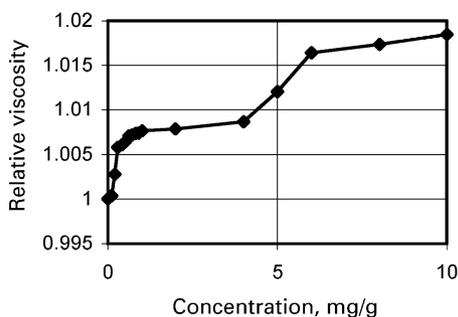
Fig. 6. The effect of concentration on the relative viscosity of pentane insoluble-asphaltene in 1-methyl naphthalene at 90°C.
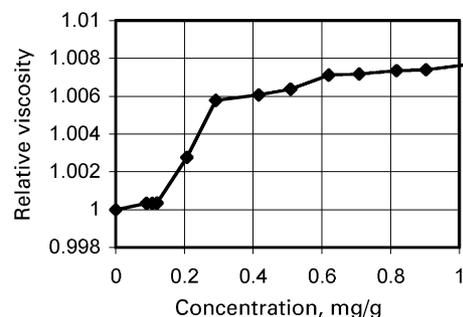

Fig. 7. The effect of concentration on the relative viscosity of pentane insoluble-asphaltene in 1-methyl naphthalene at 90°C.

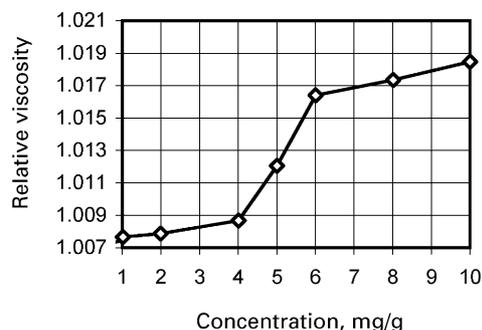Fig. 8. The effect of concentration on the relative viscosity of pentane insoluble-asphaltene in 1-methyl naphthalene at 90°C.

Materials July 1, 1953. The kinematics viscosity basis is 1.0038 mm^2/s (cSt) for water at 20°C. The gravitational constant, g, is 980.1 cm/s^2 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 was 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 & 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.

3. Results and discussion

The phase diagrams of AMHR asphaltene and PIBF asphaltene 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. Due to 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 have the limitation of measuring only the micellization, and not coacervation, and for smaller temperature ranges.

Fig. 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 in Fig. 6 are divided into two zoomed out sections (0–1 and 1–10 mg/g of asphaltene in solvent) and Figs. 7 and 8 are reported.

According to Fig. 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 CMC of asphaltene and the other (higher concentration) change of slope point represents the completion of micellization (or micellization saturation) point. According to Fig. 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 point corresponds to the 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°C, and various concentrations of asphaltenes in
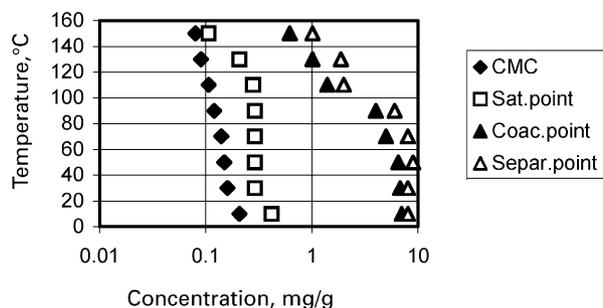
Fig. 9. The effect of temperature on the CMC, saturation point, MCP, and separation point of pentane insoluble-asphaltene from bitumen in 1-methyl naphthalene.
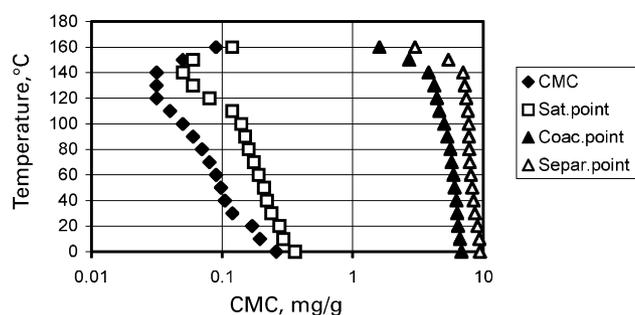

Fig. 10. The effect of temperature on the CMC, saturation point, coacervation point, and separation point of AMHR asphaltene in 1-methyl naphthalene.

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 nano-technology. 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. Nano-structured asphaltene with structural features in the nano-meter 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 nano-structure of asphaltene micelles and coacervates for future nano-technology 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.

Acknowledgements

polar solvents similar figures, as Figs. 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 Figs. 9 and 10.

Fig. 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. Fig. 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 nano-technology 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

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