

Petroleum Asphaltene—Properties, Characterization, and Issues

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Importance of asphaltene characteristics, the characterization techniques, and the practical issues regarding industrial operations are briefly reviewed. The properties are viewed from macroscopic and microscopic length scales. Techniques used for characterizing such properties and their relevance to upstream and downstream operations are introduced. Finally, a conceptual approach for predicting asphaltene miscibility with lighter components is proposed.

I. Introduction and Brief Historical Background

Petroleum asphaltene represents a solubility class of petroleum liquids. It is the most refractory and often the heaviest component. Because of these fundamental characteristics, asphaltene is considered an important factor that causes hindrance in many petroleum operations—production, transportation, refining, even wax crystallization, crude oil emulsification, and de-emulsification. Though many of these claims are not fully proved or understood, asphaltene does have a negative effect on many of the above operations. It is natural to attribute these negative impacts to particular molecular and thermodynamic properties associated with asphaltene. Such properties may include molecular weight, structures, and charge content as the molecular parameters, and unusual short-range interaction and strong propensity of self-association as thermodynamic related characteristics. It has taken researchers over a century trying to understand asphaltene molecular and colloidal properties. Yet, many issues around asphaltene are still controversial and considered unsettled.

Asphaltene research may be categorized into fundamental properties research and field operational/processing research. In the following, research in these two areas will be discussed.

Since asphaltene was identified by Boussingault in 1837 from an ether-insoluble fraction of asphalt,¹ research has been very active. This is particularly true, in the early twentieth century, when petroleum mass production began. The first reported asphaltene characteristics study was likely that of Marcusson² who compared petroleum asphaltene and coal asphaltene via HCl adsorption. The separation method followed the same procedure suggested by Boussingault. Marcusson's conclusion was that petroleum asphaltene and coal asphaltene were similar. Berthelot had a similar work but was not as systematic but almost half a century earlier.³ After Boussingault and Marcusson, a remark-

able work of petroleum asphaltene was the separation procedure suggested by Nellensteyn in 1933 when he used a carbon tetrachloride solubility separation method.⁴ His method led to a modern asphaltene separation method using heptane or pentane as the solvent.⁵ Not only did he propose a new separation method, but also he proposed a “conceptual sketch” of the asphaltene structure in petroleum liquid. Nellensteyn suggested that asphaltenes are high molecular hydrocarbons forming a colloidal system adsorbed by lighter components on the surface. This was an incredibly accurate revolutionary idea. This concept, though being questioned, persists even today. The success of this proposal led to the first asphaltene research era between 1933 and 1945. However, there was negative impact as well. The down side of Nellensteyn's proposal was that a considerable amount of effort was directed to studying fundamental properties of asphaltene molecules, such as molecular weight, structure, and the related characteristics of asphaltene. This more or less slowed the research that tried to link asphaltene molecular properties to field operations, e.g., the production efficiency. In the meantime, a group of investigators suspected that asphaltene molecular properties might not be as important to the field operation efficiency as it was believed by many others. This group of researchers was practical and their thinking was in line with the concept proposed by the asphaltene discoverer, Boussingault.¹ However, research inevitably went bi-directional after the 1930s with fundamental research focusing on molecular weight study and petroleum and field engineer studying the impact of asphaltene on production, transportation, and refining.

On the fundamental research, the booming era was 1930s when the colloidal concept was introduced. Un-

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fortunately, most of the characterization methods were "mechanical" measurements and largely focused on molecular weight measurement.⁶⁻¹⁴ Although the techniques used for measurements were limited, it was during this era that the colloidal concept was proposed and established by Nellensteyn.⁴ From an academic point of view, understanding molecular weight of asphaltene is an important subject, but is not necessarily so from an industrial point of view, in particular, the upstream production. Rather, the colloidal properties and inter-colloidal interactions were found to be much more relevant. In this regard, much of the pioneer work should be credited to Nellensteyn and later to Pfeiffer and Saal.¹¹ Because of their concept of resin-peptized colloidal model,¹¹ the investigators began looking into the microscopic world of asphaltene liquids, even though the measuring techniques were still on the macroscopic length scale. It was this challenge that led to Eiler's empirical viscosity work,¹⁵ which is useful and accurate, as we know today.¹⁶

The research advancement on asphaltene was closely related to instrumentation development, which took a quantum leap when mechanical measurement became more accurate in the 1940s. This prompted Eiler to propose the famous empirical formula,¹⁵ which allowed one to peek into some microscopic world using simple viscosity data. While viscosity was nearly the sole technique for physical property measurement, numerous techniques were engaged to study asphaltene molecular weight. They include the ultracentrifuge, osmotic pressure, monomolecular film method, ebullioscopy, cryoscopy, and vapor pressure measurement. Among these methods for molecular weight measurement, the only semi-microscopic technique was the light transmission/adsorption method,¹⁷ but that was nearly a decade after the laser was developed in the physics community, and several years after the pioneer X-ray work of Dwiggins in 1965.¹⁸ This marked the beginning of the next era of asphaltene, the microscopic measurement. It is interesting to note that the scattering technique was developed by physicists in the late 1940s to early 1950s but was adopted by asphaltene researchers approximately 15 years later when the techniques flooded the physics community. Unfortunately, the X-ray technique was applied to asphaltene only in the solid phase while its behavior in liquid (solvent or crude oil) is more essential to petroleum operations.

At this point, it is necessary to mention another important asphaltene contributor, Yen,¹⁹⁻²³ whose im-

pact on many aspects of asphaltene is truly essential and pertinent. Moreover, his research spans nearly four decades and he is still active as of today. He provided a better and systematic model for asphaltene in different stages, linking Nellensteyn's colloidal concept and Pfeiffer and Saal's resin-peptized model to modern self-association and continuously network forming structure. To date, Yen's model has been confirmed from various macroscopic and microscopic measurements.^{16,24,25}

In 1973, the first energy crisis brought many opportunities for energy research and asphaltene was certainly one of the topics laid out by top energy strategists, hoping to improve production efficiency and refining yields. Since then, ROSE process, hydrocracking, and H-oil technologies were developed, and delayed coking technology was refined to boost refining yield. Many of these development projects were directly or indirectly related to asphaltene. Because of the research needs during this energy crisis period, a fundamental understanding of asphaltene became urgent. On the production side, asphaltene inhibitors became one major item on the field chemistry list and the well treatment business boomed.

After the first energy crisis, the fundamental research on petroleum liquids became active, and gradually lost communication with the field research investigators. Fundamental research made great progress after the 1980s on the subject of asphaltene molecular weight, chemical structures, colloidal properties, self-association,^{16,22-30} etc. Again, the progress was in parallel to the instrumentation advancement. On the other hand, the field researchers also made great progress in understanding wells, reservoir formation, and production control. More importantly, several models were developed to predict the thermodynamic conditions below and above the wellbore. This advancement was obviously from the computer capability when simulation became possible.³¹⁻³³

The past decade of the twentieth century was a particularly fruitful period for asphaltene researchers.

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On the molecular level, details of asphaltene molecules were examined,^{34–36} the colloidal properties were well characterized,^{16,25,37–39} and the simulation of asphaltene self-association became available.^{31–33}

On the production side, more challenge arrived when the horizontal well technique was commercialized and offshore exploration and production became routine. During this period, models for production control became more sophisticated and accurate.^{40–45} The focus was switched to in-situ controlled production to combat problems such as wax crystallization, deposition, and hydrate and asphaltene deposition.

Now that the 21st century has arrived and the energy crisis becomes a norm, the more important issue regarding petroleum research and operation is to bring the knowledge from basic research to the field. This is essential because field researchers still frequently suffer inaccuracy from model calculation when dealing with different wells.

In this article, macroscopic and microscopic properties of asphaltene are briefly reviewed, followed by characterization of asphaltene properties, history, and techniques. Techniques were categorized into microscopic and macroscopic measurements. Microscopic measurements mainly focus on molecular weight and structural determination, more downstream operation relevant. Macromolecular methods are largely for colloidal properties and thermodynamics, and are more upstream related. Models developed for asphaltene flocculation and precipitation are briefly described in the next section, and finally, a new approach for predicting asphaltene flocculation and precipitation is proposed.

II. Understanding Asphaltene—Properties and Characterization

There are at least two levels of understanding of asphaltene. One is on the macroscopic level and the other is on the microscopic length scales. Each has its

practical meaning. The microscopic characterization of asphaltene aims to understand molecular properties of asphaltene, both chemically and physically, and to deal with the hindrance it may cause in refining operation. It is important to emphasize the linkage of microscopic measurement to refining. Catalysts play a very important role in modern day refining operations, but asphaltenes poison catalysts, particularly at elevated pressure and temperature where asphaltenes are likely to be in their molecular form. The dominant parameters in this case are short-range interactions between asphaltene molecules and catalyst surfaces. On the other hand, the macroscopic characteristics of asphaltene are more upstream related (production and transportation) because asphaltenes are likely in colloidal form or in network-like fractal structures where inter-colloid interactions are more relevant. Thus, it is advantageous to discuss the microscopic and macroscopic measurements separately.

A. Microscopic Characterization of Asphaltene.

The most sensible approach to characterizing asphaltene was to evaluate its molecular weight when asphaltene was first identified and was practically the first parameter researchers investigated.^{1–14} It was naturally the first parameter thought to correlate with the behavior of asphaltene. To date, there are still a number of research reports on this subject, but not necessarily for the same reason as a few decades or a century ago. If one examines the definition of asphaltene more closely, it is clear that molecular weight is not necessarily a good parameter to characterize asphaltene, simply because asphaltene is defined through the solubility in pentane or heptane. Other than the molecular weight, relevant parameters include polarity, unpaired electrons, aliphatic chain lengths, or the combination of them. Therefore, one should not use molecular weight to solely describe asphaltene. The molecular weight, though important for many aspects, may not be as important for upstream operations and for characterizing asphaltene behaviors as we once thought.

Having said so, one should note that asphaltene colloids are formed through self-association of asphaltene molecules. Thus, while it is advantageous to discuss the microscopic and macroscopic measurements separately, it is not wise to completely ignore their linkage, and the linkage is the self-association propensity. It turns out that the self-association propensity jeopardized many techniques that have been routinely used for determining asphaltene molecular weight. This is because asphaltene was found to self-assemble when the concentration is above a certain threshold, similar to a surfactant critical micelle concentration (CMC),^{29,30} and many techniques for molecular weight measurement are operated at a concentration much higher than the CMC.

The onset concentration of asphaltene self-association can be determined by measuring surface tension as described in ref 29. Figure 1 shows a surface tension measurement of Messaoud asphaltene in toluene. One can see a clear breaking point at concentration ~0.18 wt % where the CMC was observed. Due to this self-association propensity, molecular weight measured using vapor pressure osmometry (VPO), gel permeation chromatography (GPC), and many other methods^{6–14}

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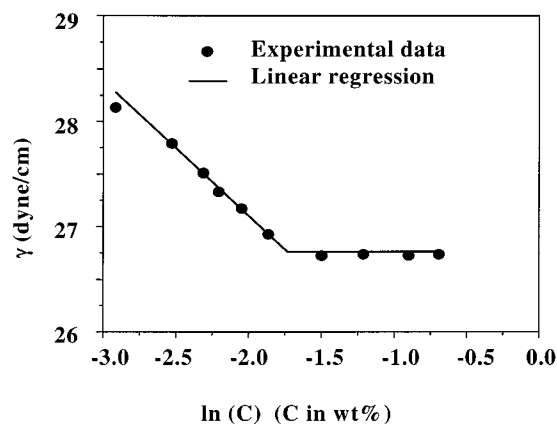


Figure 1. Surface tension as a function of asphaltene concentration in wt %. A clear break was observed, signifying the onset of aggregation.

may be misleading. Likely, the measured quantities are molecular weights of the aggregates. Self-association problems encountered in VPO measurements may be attributed to poor solvents used. However, CMC of asphaltenes is in general much lower than 2 wt %, which often is the lower limit of VPO measurements. This is true, even in good solvents. Thus, the solvent issue becomes irrelevant and the problem of measuring aggregates rather than molecule will still exist.

Because of the self-association phenomena, the molecular weights of asphaltenes were constantly re-visited, hoping to find the "real" asphaltene molecular weights. There are compelling reasons to accurately determine the molecular weights. For one, the aggregated molecular weight and the real molecular weights, if they can be determined, will allow us to calculate the aggregation number in an aggregate, the thermodynamics involved in the association, and even the cavity volume fraction of an aggregate. The practical value of these quantities is that one may be able to evaluate the percentage of potential refinable components entrapped in an asphaltene aggregate, provided all relevant parameters of the aggregate are well characterized. Practically, one needs three pieces of information, namely, the aggregate molecular weight, the true molecular weight, and the aggregate size. Numerous research efforts were on molecular weight measurement in the 1990s.^{46–50} The aggregate structure was found to lie between 2 and 25 nm in diameter.^{16,25,26} The molecular weight obtained from modern techniques, after taking great caution of asphaltene self-association into account, tends to suggest that the asphaltene molecular weight is considerably smaller than we once thought.^{48–51} This issue is not completely settled yet but more findings are coming in every day. Through studying various asphaltenes, the molecular weights appear to be no more than 1500 Daltons and mostly around 600 to 1000 Daltons.^{48–51} Surface tension is one of the methods leading to this result. It is a simple method and often operates at very

low concentration below the aggregation onset.⁵² For example, the data in Figure 1 can be used to calculate the molecular weight using a different molecular model for the asphaltene molecule at the toluene/air interface.

The starting point of molecular weight calculation using the surface tension data is the Gibbs adsorption equation.⁵³ It calculates the area per molecule at the interface using the measured surface tension data below CMC. The Gibbs adsorption equation for a reversible system reads:

$$\Gamma = (-1/RT) \times (d\gamma/d(\ln C)) \quad (1)$$

where $d\gamma$ is the surface tension variation, and $d(\ln C)$ the logarithmic concentration variation (C expressed in wt %). One should note that Gibbs equation is applicable only to the concentration below CMC (critical micelle concentration). Once Γ is obtained, the average area occupied by an asphaltene molecule at the toluene/air interface can be easily calculated,

$$\Gamma = 1/(NA) \quad (2)$$

where N is Avogadro's number and A is the molecular area. From A , one can construct a conformational model for the molecule at the interface to compute the molecular volume; and from the volume, one can determine the average molecular weight,

$$MW = \text{density} \times N \times \text{particle volume} \quad (3)$$

Equations 1–3 provide a simple method for molecular weight estimation. This method was applied to Ratawi asphaltene by Taylor⁴⁷ to obtain molecular weight ~2000 Dalton. Later, Sheu and Storm⁴⁸ pointed out that the solvation effect from pyridine and the intermolecular interaction at the interface were not taken into account in Taylor's calculation. They recalculated the surface tension data to obtain the molecular weight ~800 Daltons, very different from Taylor's results. This demonstrates the importance of intermolecular interactions, solvation, and the molecular shape near the interface. These effects were evaluated via viscosity measurement, which is a macroscopic measurement. This is to say that macroscopic and microscopic measurements may be combined to better characterize a complex fluid like the asphaltene systems. Details of how to extract the molecular weight with all relevant effects taken into account will be discussed in the macroscopic section.

Molecular weight can of course be determined using mass spectrometry (MS), VPO, or GPC but should be used with great caution to avoid measuring the apparent molecular weight, which is the molecular weight of the aggregates. In 1990, Storm et al. investigated the Ratawi asphaltene molecular weight using ion-impact MS.⁴⁶ The drawback of this technique is that the sample inlet system is far from perfect, leaving a substantial amount of asphaltene un-sublimed. Moreover, the spectrum clearly shows fragmentation. Both effects favor

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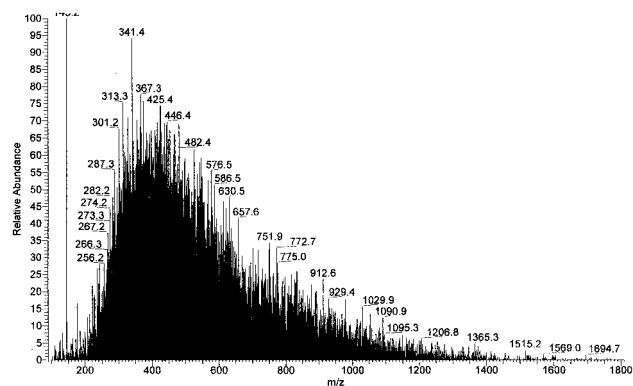


Figure 2. Mass spectrum of Furrial crude oil. The distribution is similar to a Schultz distribution and the molecular spans from 200 to nearly 1800 Daltons.

smaller molecular weight. An average molecular weight of ~ 800 was obtained. To overcome the drawback from sample sublimation and the fragmentation, the authors used a mathematical method to back-calculate the contribution and arrived at an estimate of the upper bound molecular weight at ~ 1600 Daltons. Because many mathematical assumptions involved and data were somewhat over-analyzed, this work was not able to convince the community that average asphaltene molecular weight should be lower than 1600. Later, Hunt re-visited the molecular weight using a laser desorption technique, which avoided the problem of fragmentation.⁵⁰ Hunt obtained an average molecular weight of ~ 500 – 800 Daltons. In this work, atmospheric pressure chemical ionization (APCI) mass spectrometry (MS) was used to determine the molecular weight distributions of Furrial crude oil and asphaltene. The sample inlet system is far simpler than Storm's work. The samples were dissolved in THF at 2.5 mg/L, much lower than the aggregation onset. Since the samples were wholly injected, there is no reason to argue that parts of the samples did not arrive at the ionization chamber. Figures 2 and 3 show the spectra for Furrial crude oil and its pentane-soluble fraction. It is interesting to note that there is a dip in the pentane-soluble fraction (between 650– 1000 Daltons) compared with the crude oil, indicating that there is substantial amount of missing material with molecular weight between 650 and 1000 Daltons. The only possibility is that these molecules are pentane insoluble, thus, are pentane asphaltene. Figure 4 gives the pentane-insoluble fraction where the majority of pentane asphaltene molecules have molecular weights between 200 and 650 Daltons. One notes that the signals at any molecular weight are considerably lower than the pentane soluble. This is because the solution was prepared at 0.5 mg/L to prevent any aggregates from forming in the chamber. With this spectrum, it is reasonable to argue that asphaltene molecular weights detected here are low, like what we know about coal asphaltene. Fluorescence depolarization (FD) measurements by Groenzin et al. also showed "small" asphaltene molecular weight.⁵⁴ They interpreted the molecular weight and asphaltene structure through combination of FD, fluorescence

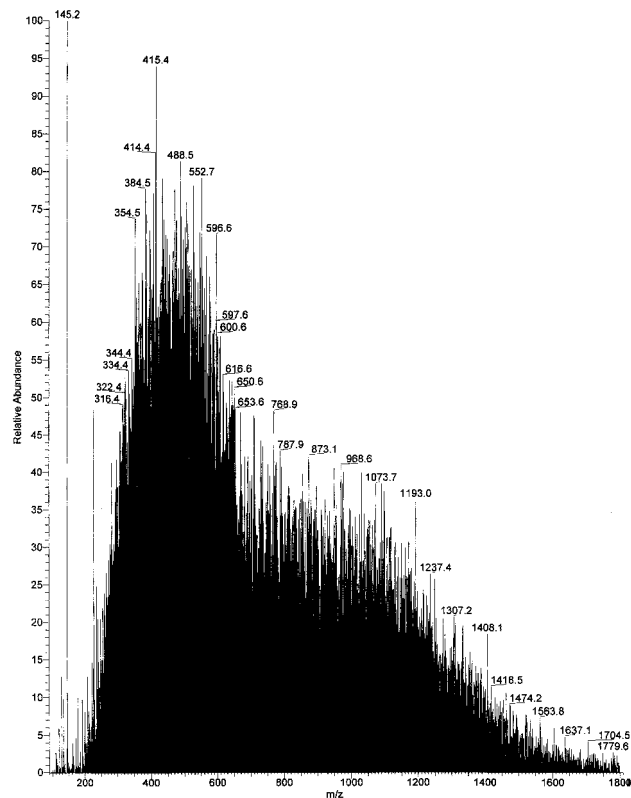


Figure 3. The pentane-soluble fraction of the Furrial crude oil. A clear dip is observed near 650– 1000 , indicating that substantial amount of mass with molecular weight in the range are pentane insoluble.

emission spectroscopy, ^{13}C NMR, IR, and molecular architecture argument.⁵⁵ From the techniques used and the interpretation, it is likely the molecular weight of asphaltene is less than 1500 Daltons.

If one takes the molecular weight to be lower than 1500 Daltons, then, it is clear that molecular weight itself cannot fully describe many behaviors of petroleum liquid containing asphaltenes. These liquids exhibit the effect of asphaltene as if asphaltenes were large molecules. Recent investigation suggests that these effects may be attributed to polarity and charge-like interactions.^{54,55}

The above-mentioned microscopic parameters, molecular weight, polarity, charge-like interactions, are more relevant to downstream refinery than to upstream productions. This is because it is believed that the asphaltene form aggregates in a refining process. These asphaltene aggregates can entrap lighter components, thereby hindering the refining yield. To improve the refining yield, it is necessary to open up the aggregates to enhance the refining yield. This requires thorough characterization of asphaltene structure, average molecular weight, aggregation, and the energies involved in the aggregation process.

The ultimate parameter for resolving refining asphaltene problem is to quantitatively evaluate the energies involved in the self-association process. It is a difficult subject and is still an open question. A possible route is to determine the molecular weight, the aggregate size, and packing conditions of the aggregates

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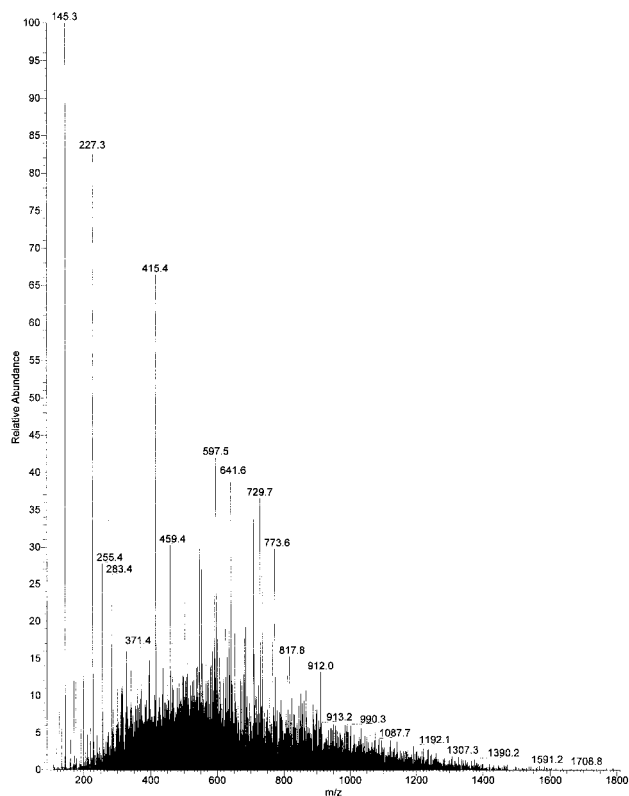


Figure 4. Pentane-insoluble fraction of Furrial crude oil. The average molecular weight is near 500 Daltons, indicating a much smaller molecular weight than obtained from VPO, GPC, and many other measurements.

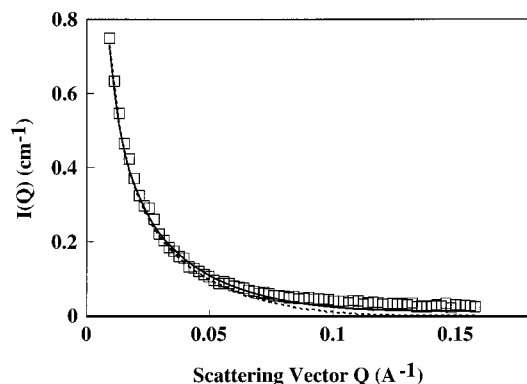


Figure 5. Small angle neutron scattering data fitting using spherical Schultz model (solid line [book]) and the mono-disperse cylindrical model (dash line).

so that a corresponding thermodynamic model can be developed to account for the energies into the self-association process. Once the model is established experiments needed to determine the relevant parameters can be conducted. For example, molecular weight can be measured using mass spectroscopy; the size of the asphaltene aggregates can be determined accurately using scattering techniques.^{16,25,26,29} Figure 5 shows a typical scattering spectrum (the intensity distribution function) of an asphaltene solution. One can extract structure of asphaltene from the intensity distribution function.

The packing condition of an asphaltene aggregate is another parameter needed to determine the self-association energy, and is a hard subject. There is neither experiment nor theory that can fully character-

ize this particular energy for asphaltene aggregate. In addition, a proper thermodynamic model for asphaltene aggregation process with built-in association energy is not available.

B. Macroscopic Characterization of Asphaltene.

Asphaltene in field operation shows physical phenomena that are macroscopic and directly affect production efficiency. It is thus important to macroscopically characterize asphaltene, at least to a point a field engineer can use this information for operational decision and optimization. Macroscopic characterization is a natural approach from the field operation point of view. In the early stage of asphaltene research, most efforts were geared toward solving field problem or improving process. Many of the parameters measured, e.g., temperature, pressure, phases, viscosity, etc., are either thermodynamic or transport properties (flow and viscosity, etc.). They are certainly macroscopic properties.

Nowadays, the macroscopic characteristics of asphaltene are still the main theme because the theoretical development in the past century enables us to investigate a complex fluid to the colloidal length scale using only macroscopic data. With this capability, carefully measured and analyzed macroscopic properties can be as powerful as microscopic measurements without analysis. Realistically, there are many microscopic measurements routinely performed without much data analysis. Therefore, the theoretical advancement of analyzing macroscopic data to investigate microscopic properties truly opens up a new chapter for studying complex fluids.

In the 1940s Eiler had seen the power of data analysis and had applied various empirical viscosity formulas to characterize petroleum systems. He was able to quantitatively determine the intrinsic viscosity using simple plots of the low shear viscosity data. Eiler's work substantially improved understanding of complex fluids at the time. However, information obtained from his analysis scheme cannot satisfy modern needs, if only macroscopic measurements are to be used. An alternative route is to combine several theories with built-in microscopic parameters to analyze macroscopic data. This approach allows one to extract microscopic parameters less ambiguously. Sheu et al.⁵⁶ reported one such example where six viscosity theories were adopted for analysis of a single set of viscosity data. In the following, another example is demonstrated where viscosity was analyzed to obtain the solvation of an asphaltene aggregate and interaction between aggregates. From these parameters, more accurate asphaltene molecular weight can be estimated using surface tension data as described earlier.

As mentioned above, Taylor analyzed Sheu's data⁴⁷ without taking into account the effect of solvation and intermolecular interaction, thus, over-estimating the molecular weight of Ratawi asphaltene. These effects can be taken into account by factoring the solvation and inter-aggregate interactions,

$$MW_c = MW/(S)(\xi)^3 \quad (4)$$

where S represents the degree of solvation, and ξ and MW_c stand, respectively, for the interparticle inter-

Table 1. Comparison among Various Models Used for Analyzing Viscosity Data

model	shape (p = aspect ratio)	solvation	interactions	total effect (linear term)	MW (spherical model)	MW (cylindrical model)
Pal & Rhodes	sphere-like	$K = 2.89$ (qualitative)	N/A	$2.89 \times 2.5 = 7.22$	~800	~520
Eiler	$[\eta] = 8.4$	89% swelling	N/A	$([\eta]/2) \times 2.1.89 = 7.9$	~400	~290
Huggin/Jeffery	$p = 1.33$, $[\eta] = 2.56$ (sphere-like)	58% swelling	$k_H = 2.51$	$1.33 \times 2.1.58 \times 2.2.56 = 5.38$	~690	~400
Mooney	$[\eta] = 7.6$	N/A	N/A	7.7	~830	~490
Khun & Khun ^a	$[\eta] = 7.7$, $p = 7.35$ (dilute limit)	N/A	N/A	7.5		

^a MWs were not calculated because the asphaltene aggregates should be spherical-like.

action⁵⁶ and the corrected molecular weight. S can be estimated from

$$S = (0.74/\phi_m) \quad (5)$$

where ϕ_m is the maximum packing volume fraction. ϕ_m can be determined from analysis of the viscosity measurement using Euler's approach. The number 0.74 was chosen because it represents the maximum packing of a face centered cubic (FCC) crystal. The factor ξ can be extracted from the viscosity measurements provided an appropriate model for the interparticle interaction is in place and that the interaction parameter obtained from the bulk analysis can be used for the intermolecular interaction at the surface. For different asphaltene systems, this interaction factor may differ. There are a number of theories available for evaluation of inter-aggregate interactions.

Table 1 shows the results using different theories with the solvation effect taken into account. Regardless of the models used, the molecular weight was found to be between 300 and 800 Daltons.

Other than molecular weight, viscosity data can be used to evaluate the shape of the aggregates, the inter-aggregate interactions,⁴⁹ and even the flocculation phenomenon.¹⁶ In fact, asphaltene flocculation is a major subject for upstream operations and macroscopic measurements can make great impact. Asphaltene flocculation, precipitation, and deposit near the well-bore have been long known to hinder the production efficiency. In the following, an example of using viscosity to evaluate the flocculation kinetics and the resulting fractal structure of the flocs are demonstrated.

The consensus of asphaltene flocculation, precipitation and deposit is that asphaltene solubility in the live oil decreases when oil is depressurized. In practical applications, knowing when the flocculation occurs, how fast it may progress, and to what extent the precipitation can impact the formation, downpipe, etc., are essential because it can provide an early warning sign for field engineers to take proper actions. Thus, it is important to detect the phase of the petroleum liquid and asphaltene flocculation phenomenon as early as possible.

From measurement point of view, it is crucial to know what flocculation can change the system so that one can select the right parameters to measure. Obviously, flocculation changes the asphaltene structure on a colloidal length scale. The measurable parameters to be impacted by this change are structure, conductivity, viscosity, and dynamics, such as diffusion, dielectric behavior, even the IR, UV, or Raman characteristics, and many others. Among these parameters, viscosity appears to be a simple one. The author had developed

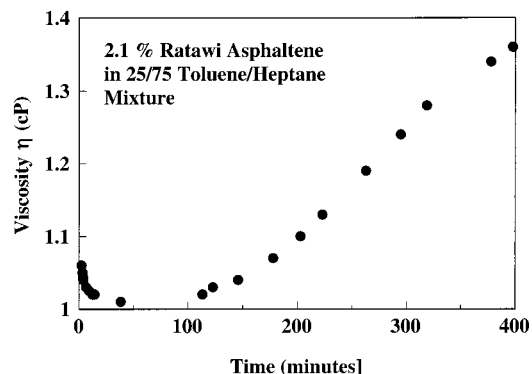


Figure 6. Viscosity as a function of time from 2.1 wt % of Ratawi asphaltene in 75/25 toluene/heptane mixed solvent.

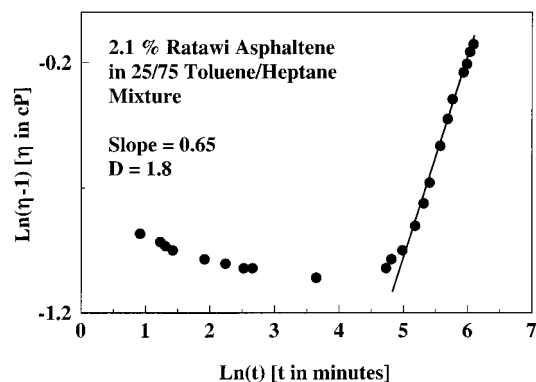


Figure 7. Analysis of Figure 1 according to eq 8. A fractal dimension of 1.8 was obtained.

a simple viscosity formulation to detect the dynamic structural change of asphaltene containing fluids.¹⁶ The formulation is based on the change of fractal dimension when flocculation occurs, and on an assumption that the flocculation process is diffusion limited. The formulation reads

$$\ln\left\{\frac{[\eta_r(t) - 1]\nu}{20kW}\right\} = \left(\frac{3}{f} - 1\right) \ln[t] \quad (6)$$

where η_r is the relative viscosity, t is the time, and the rest of variables are known experimental quantities. This simple formula provides an opportunity to apply zero shear viscosity for evaluating the dynamics of flocculation. Figure 6 shows the viscosity change as a function of time when flocculation is initiated by adding poor solvent (heptane) to an asphaltene solution (2.5 wt % in toluene). Figure 7 shows the analyzed data. The fractal dimension can be extracted using eq 6.

Other than the viscosity method, there are a number of methods available for characterization of asphaltene flocculation and precipitations.^{40–44} The index of refraction method is a relatively new one and appears to be

promising though there are still some doubts of its extrapolation mechanism, assumption, and sensitivity. This method is a microscopic technique, so are laser transmission in a PVT cell, IR, UV, Raman, while gravimetric and conductivity are considered macroscopic. From a field operation point of view, simple macroscopic methods probably fit the practical requirement better than the microscopic ones. Thus, future development should focus on macroscopic methods for characterizing asphaltene flocculation, precipitation, and deposition.

III. Asphaltene Issues

A. Downstream. Downstream operation is relevant to asphaltene due to its hindrance on refining yield. It is likely due to entrapment of light components into asphaltene aggregates. Other hindrance includes poisoning catalysts, depositing to the vessel, delayed coker and fluidized bed catalytic cracker, etc. Clearly, the issue of entrapping light component is not as important because modern delayed coker design and operation has made great progress in yield. This is more from a financial point of view than technological point of view. In the delayed coking process the aliphatic chains attached to the heavy end component are clipped off to improve the yield. As long as the yields are satisfactory, delicate technology development to open up the asphaltene aggregates may not be necessary because one may have to pay a high energy price to open up these tightly packed aggregates. The deposition of asphaltene on catalysis is more severe and needs some attention. Dispersants are available for reducing deposit but not enough details on the molecular level about the interactions between these dispersants and asphaltene are available. In addition, claims made by the dispersant suppliers often are controversial. Thus, deposition of asphaltene is an issue to be addressed.

When one addresses the deposition problem, it inevitably requires a good understanding of asphaltene molecular weight, polarity, and charge-like interactions, to quantitatively evaluate the deposition kinetics and the deposition energy. This brings back the point made earlier that it is not sufficient to use molecular weight alone to model the asphaltene behavior. This is particularly true when dealing with a complex problem encountered in downstream operation.

One may argue that molecular weight is a good indicator in chainlike polymer properties using the scaling concept and proved useful from the Staudinger time⁵⁷ to the de Genne era.⁵⁸ However, the interaction in asphaltene is very or completely different from polymers from the following two stand points: (1) asphaltenes are generally not chainlike, and likely have polynuclear aromatic cores, which introduces π - π interactions and inter-molecular van der Waal forces; (2) there are heteroatoms associated with asphaltenes which perturb interaction and likely relate to the existence of unpaired electrons. These are what chainlike polymers do not have. This confirms that molecular weight alone is not sufficient for characterization of asphaltene molecules.

One possible way to combat such a complex problem is to artificially create a parameter, which lumps all energies that are related to asphaltene-catalyst interactions. Then, develop an experimental method to measure this parameter, either qualitatively or quantitatively, as long as it can indicate what properties a dispersant needs to prevent or reduce deposition or even just help to screen the dispersant or any actions that can be taken to improve the process. This approach is conceptually true and possible but might need tremendous effort before being put into commercial practices.

B. Mid-stream. Midstream operations are largely transportation related. Again, it relates to asphaltene deposition and thickening when temperature decreases during transportation. There is nearly no rigorous research in this area because transportation was never weighted high enough for the petroleum industry to launch a solid research program. However, as the API of crude oils continues to drop, transportation becomes increasingly difficult. Conventional wisdom was to heat the pipeline, which is not an energy efficient approach. Developing dispersants and/or wetting agents to control the viscosity and wet the pipeline wall to reduce the pressure drop should be the goal. Drag reduction agents are available in the market place. Unfortunately, many of them have limited effect or are too expensive to be economically viable. Clearly, this is a subject that needs attention. For heavy oil fields at remote locations lacking infrastructure, the only effective transportation is via pipelines, which are susceptible to temperature change. This is becoming a problem in many high elevation oil fields or for heavy oils sensitive to subtle temperature change.

The relevant parameter in this case is the phase change upon temperature change. Clearly, development of additives to control the phase boundary is the subject to research.

C. Upstream. The asphaltene problem upstream is complex. The first problem is asphaltene flocculation and precipitation, which requires good models or accurate in-situ measurement methods to monitor the phase of the crude oils. Several models are available but they are not necessarily accurate under field conditions. Moreover, a model often can predict some wells accurately while it suffers severe inaccuracy on the others.

Most of the models are derived from the Flory-Huggins theory, which expresses the Gibb's mixing energy in terms of volume fractions, entropies, and solubility parameters of the mixing components,

$$\Delta G_{\text{mix}} = RT \left[n_m \ln \phi_m + n_a \ln \phi_a + n_m \phi_a \frac{V_m}{RT} (\delta_a - \delta_m)^2 \right] \quad (7)$$

Figure 8 shows the Gibb's energy of mixing for various combinations of solubility parameters. Whenever two minima are observed in the energy of mixing, the system is unstable. This approach appears to be very simple. However, the solubility parameters in the Flory-Huggins equation are not primary parameters and are structure dependent. Thus, it is difficult to calculate accurately the solubility parameter of a complex compound.

One other approach is to apply the statistical mechanical theory. In this case, the flocculation propensity

(57) Staudinger, H. *Die Hochmolekularen Organischen Verbindungen*; Springer: Berlin, 1932.

(58) de Gennes, P. G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.

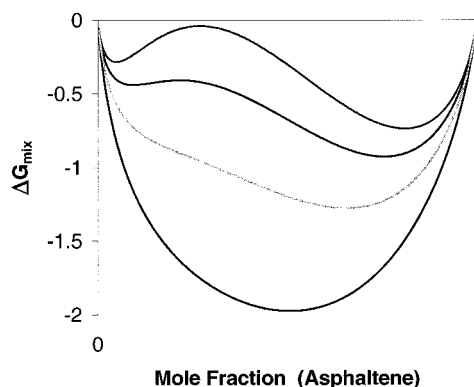


Figure 8. Gibb's energy of mixing for various combinations of solubility.

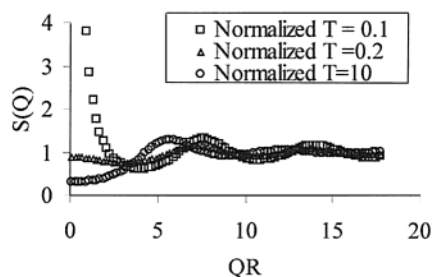


Figure 9. Structure factor at three normalized temperatures.

depends on the interactions between asphaltene aggregates. One can then solve the Ornstein–Zernike equation to obtain the structure factor from which the compressibility and other thermodynamic properties can be deduced. Figure 9 shows the structure factor of a stick hard-sphere model (radius = R) at volume fraction equal to 0.1. As one can see from this figure, when temperature increases the system may undergo liquid–vapor phase transition where structure factor $S(Q)$ diverges at small momentum transfer, Q .

This approach is still in its infancy and should be explored to see if a more well-independent model can be developed from this approach.

IV. Conclusion

Fundamental and practical research of petroleum asphaltene was reviewed. The molecular weight of asphaltene defined via solubility was discussed and evaluated using atmospheric pressure chemical ionization (APCI) mass spectroscopy. The results from Furrial crude oil show that asphaltene molecular weights are relatively low (~ 600 – 1000 Daltons). These results, together with those obtained from other techniques,^{46,49,51,54,55} indicate that the average asphaltene molecular weight is likely much lower than the results obtained from CPC, VPO, or pyrolysis. This further suggests that molecular weight should not be used as the sole parameter to describe asphaltene behavior in petroleum liquids. However, molecular level is important for downstream applications, especially, in a fluid catalytic cracker (FCC) where their interaction with catalysts more or less determines the efficiency of the catalytic reaction. While molecular weight cannot fully describe many downstream operations, other microscopic techniques may be used to further control the refining processes and improve the refining yields.

On the other hand, macroscopic measurements are more suitable for upstream where interaction between asphaltene aggregates are much more relevant. Macroscopic characterization techniques also provide less controversial results. However, it is not accurate enough to describe the complicated phase diagram encountered in upstream operations. A new approach using statistical mechanical theory (through the Ornstein–Zernike equation) for predicting asphaltene flocculation and precipitation is proposed.

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