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Resins: The Molecules Responsible for the Stability/Instability Phenomena of Asphaltenes[†]

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Resins are reported to be able to contribute to both the stabilization and destabilization of asphaltenes. Resin adsorption isotherms were carried out on different substrates such as silica particles or asphaltenes and silica–asphaltene fraction A₂ complexes extracted from different Venezuelan crude oils, which either show evidence of precipitation problems (Furrial) or do not (Hamaca and Guafita). Experimental evidence indicates that resins from Furrial crude oil display a much higher tendency to adsorb on the different substrates than resins from the two other crude oils, even on silica particles with the same surface area for all of the resins, thus indicating a higher self-interaction. This self-interaction of resin molecules is shown to be the key factor in determining whether these molecules do or do not stabilize asphaltene colloidal particles against aggregation. The experimental results are interpreted according to a simple repulsion/adhesion alternative model.

Introduction

Traditionally, resins have been associated with the stabilization of asphaltenes in crude oils through a peptization mechanism, in which resin molecules adsorb at the periphery of asphaltene colloidal particles. This allows for a smooth transition from polar asphaltene to apolar oil, which prevents agglomeration from taking place and stabilizes asphaltene particles through some steric dispersing effect.

The word “asphaltenes” stands for a widely studied crude oil fraction corresponding to a solubility class rather than a chemical one, which is precipitated from petroleum by the addition of a large excess of liquid paraffinic hydrocarbons, such as *n*-heptane. As a matter of fact, this solubility class makes up the most polar fraction of crude oil. It is generally accepted that it is present as a colloidal dispersion,^{1–5} which contains

submicrometer particles consisting of a few aggregated asphaltene molecules mainly bounded by π – π van der Waals interactions among their polyaromatic clusters. As one can see in the literature, many questions about asphaltenes have been resolved; however, many more questions are still unanswered about their properties and their different aspects of the phenomena that they undergo, such as the mechanism of aggregation and the best way of avoiding it.

Among many others reasons, asphaltenes have become an important subject of study because of the multiple problems that they cause in the petroleum industry as a result of their precipitation and related phenomena. These generate trouble along the whole petroleum production operations from the reservoir to surface facilities and transport operations and even in refinery processes. Their significant economic impact has been the strong motivation behind the research dedicated toward better understanding their adsorption, aggregation, precipitation, and related phenomena.

It has been reported that changes in the temperature,^{6,7} pressure,^{7,8–11} and oil composition¹² can cause asphaltene precipitation. In the presence of aromatic hydrocarbons, they are known to self-associate by forming colloidal aggregates,^{3,13–15}

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which could remain stable or eventually be destabilized by a variety of factors. As suggested first by Nellensteyn et al.¹ in 1933, asphaltene stability is probably associated with the presence of resins. Because resins have an intermediate polarity between asphaltenes and the rest of the crude oil, they are likely to adsorb on the surface of the asphaltene colloidal particles and act as a steric dispersant. This is why resin-like substances such as alkyl-benzene lipophilic surfactants are often used to inhibit or remediate asphaltene fouling. Some relevant studies on the resin–asphaltene interactions and related asphaltene stability issues are available to help with the understanding of the dispersion/aggregation phenomena.

Ekulu et al.¹⁶ detected the aggregation–dissociation phenomena through differential scanning calorimetry (DSC) and showed that temperature is able to change the asphaltene microstructure in crude oil.

Evdokimov et al.³ showed through different experimental techniques that the threshold concentration for self-assembly of asphaltene monomers is below 10 mg/L. These results suggest the existence of a solvophobic asphaltene subfraction (fraction A₁), as shown by Acevedo et al.,^{17,18} singled out by its extremely low solubility. Therefore, asphaltene aggregation appears to be controlled by a solvent-mediated attraction, determined by the solvophobic effect. Thus, “insoluble” asphaltenes are thought to form the stacked core of colloidal particles, whereas the more soluble asphaltene fraction (A₂)^{17,18} makes up the surrounding stabilizing shells/coronas.

Similarly, Oh et al.¹⁹ showed, through near-infrared absorbance, the effect of the aliphatic/aromatic ratio of the solvent on the onset of asphaltene precipitation. Their results showed that, when solid polyaromatic compounds (naphthalene and phenanthrene) were dissolved in the oil, more aliphatic solvent was required to initiate precipitation.

Goncalves et al.¹⁴ showed through fluorescence spectroscopy that asphaltene aggregation can start at a concentration as low as 50 mg/L for asphaltene from Furrial and approximately at 75 mg/L for that from Hamaca. These experimental results are consistent with the fact that Hamaca asphaltenes have a lower tendency to aggregate compared to those from Furrial.

Auflem et al.²⁰ showed that natural and synthetic naphthenic acids tend to disperse the asphaltenes and reduce the asphaltene particle size just as resins do. However, in this case, the asphaltene dispersion takes place through an acid–base interaction.

Porte et al.²¹ proposed a model in which asphaltene aggregation–precipitation phenomena occur in well-differentiated steps, in a completely reversible process. Aggregation comes from specific strong interaction sites located at the periphery of the asphaltene molecules, which drive the reversible association in two-dimensional sheets. Precipitation, however, is determined by van der Waals attractions between colloidal aggregates, when the solubility parameter of the solvent is shifted. This model

proposes a completely reversible scheme to explain how resins are able to solubilize asphaltenes.

Through computational chemistry simulation and on the basis of arguments from the molecular structure, Ortega-Rodríguez et al.⁴ showed that the medium has an important effect on the resin–asphaltene mixture stability. The effect of different solvents on the resin–asphaltene aggregates was assessed through potential barriers. The results showed that aggregates were formed when using *n*-heptane and toluene but mixtures with pyridine behave as a homogeneous solution. It is also important to mention that, when *n*-heptane was the solvent, the aggregate dispersion was unstable, while it remains stable when toluene was used.

Al-Sahhaf et al.²² found that the capacity of different molecules and petroleum fractions to inhibit asphaltene precipitation increases as follow: dodecyl resorcinol > dodecyl benzene sulfonic acid > nonyl phenol > resin > toluene > desasphalted oil. The results show that toluene and desasphalted oil are not effective inhibitors, while resins provided a modest inhibition effect. On the other hand, lipophilic surfactants produce a strong inhibition probably because they favor the dispersant effect, so-called peptization, even more than resins.

The present paper has two goals: (1) to rebut the traditional paradigm, which states that “resins are responsible for asphaltene stability”, by proposing alternatively that this petroleum fraction is also able to destabilize them in certain cases and (2) to explain how asphaltene stability/instability phenomena could be simply linked to resin adsorption and self-association. Experimental evidence on the adsorption behavior of resins from three different crude oils on three different substrates is reported to sustain the discussion.

Experimental Section

Materials and Instruments. Resins, asphaltenes, and asphaltene fraction A₂ were extracted from Hamaca [11% of asphaltene, 8° American Petroleum Institute (API)], Guafita (2% of asphaltene, 25° API), and Furrial (7% of asphaltene, 21° API) Venezuelan crude oils, with the later being the one that exhibits serious precipitation problems. All of the analytical-grade reagents (cumene, toluene, heptane, methanol, and chloroform) were purchased from J.T. Baker. Silica, 70–230 mesh, 60 Å (pore size), for column chromatography, was purchased from Merck. On the other hand, the UV–vis spectra were taken by a diode array HP spectrophotometer, model 8452 A, with a 1 cm width quartz cell. For temperature control, a continuously agitated thermostatic bath is kept at 25 °C.

Methods: Fractioning Resins, Asphaltenes and Asphaltene Fraction A₂. Asphaltenes are extracted from crude oil through precipitation according to the following procedure. A large excess (40 volumes) of *n*-heptane is added to an aliquot of crude oil while keeping the mixture stirred. Then, the stirring is maintained for an additional 6 h, and the mixture is left to rest overnight. Finally, the precipitated solid, mainly containing asphaltene and resins that have coprecipitated, is then filtered and placed within a Soxhlet extractor, under continuous operation for about 24 h, with boiling *n*-heptane to remove most of the resins. When this methodology is applied, the yield of asphaltenes is around 11, 2, and 7 wt % for Hamaca, Guafita, and Furrial crude oils, respectively. It is worth noting that, for the Hamaca case, the precipitation of the asphaltenes in crude oil diluted with the same volume of toluene takes place when 60 volumes of *n*-heptane are added instead of 40 volumes.

On the other hand, the resins are substances coming from the maltene fraction (a mixture containing paraffins, aromatics, and resins), which remain soluble in heptane together with those

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obtained from the Soxhlet extraction. The mixture is then fractionated by liquid chromatography on a silica column. The first two fractions of this mixture, i.e., saturated and aromatic compounds, are sequentially eluted and collected using the following solvents: *n*-heptane and toluene. Finally, resins are obtained by eluting the still retaining mixture with a toluene–methanol blend at a 7:3 volume ratio.

To obtain asphaltene fraction A₂, the following experimental procedure is carried out: A solution of asphaltene in cumene and *p*-nitroaniline (PNA) saturated in cumene is separately prepared and then mixed in 100 mL volumetric flasks such that the final concentration of asphaltene is 5 g L⁻¹. The solution thus obtained is then allowed to stand for 5 days at room temperature, and then, the solvent (cumene) is evaporated in a rotavapor until the volume reaches 50 mL. Next, an equal volume of *n*-heptane is added under stirring. The precipitated solid is separated as the so-called fraction A₁, while the resulting solution is washed once with aqueous hydrochloric acid (10%) to extract the PNA. Next, the organic phase is washed with water until its pH comes to about 7. Then, cumene is evaporated from the filtrate, and the resulting dry solid is dissolved in chloroform; traces of water are removed by means of anhydrous magnesium sulfate, which is then filtered. Finally, the chloroform is evaporated, and the resulting solid (so-called fraction A₂) is dried under vacuum conditions.

Absorbent Materials. Silica particles and asphaltenes are used with no treatment, as adsorbent materials; complex adsorbent substrates are prepared by adsorbing asphaltene fraction A₂ from Hamaca and Furrial, on silica particles. For the later case, the procedure is as follows: Solutions of the different adsorbents are prepared at 200 mg L⁻¹ in chloroform. Then, silica particles are added to these solutions under continuous stirring such that the asphaltene/silica ratio is 1:25. The mixture is kept under stirring for 8 h. Next, the solid is separated by filtration and washed with chloroform until the filtrate becomes colorless. The separated solids are the different adsorbent materials.

Adsorption Isotherms. The different isotherms are plotted as the amount of adsorbed resin versus the resin equilibrium concentration in the bulk liquid. To do so, the following procedure is carried out: First, different resin solutions are prepared in *n*-heptane at concentrations between 0 and 400 mg L⁻¹. Next, a 10 mL aliquot of the above solution is added to 10 mg of adsorbent previously introduced in a test tube. Then, the tube is closed with a lid, and the suspension is gently stirred in a thermostatic bath at 25 °C during 18 h. It is worth remarking that this time span is long enough for the adsorption of resin on asphaltene to reach equilibrium conditions.²³ Next, the samples are centrifuged, and the equilibrium concentration in the liquid phase is estimated by visible spectrometry at 400 nm. All calibration and actual concentration absorbances are measured twice. Finally, the adsorbed resin is calculated from the depleted amount in the mass balance.

Results and Discussion

Resin adsorption studies are carried out on asphaltene particles, as generally reported in the literature.^{23–25} Differences in adsorption behavior of resins extracted from three different Venezuelan crude oils are scrutinized to try to establish a correlation with the asphaltene-stabilizing agent. Isotherms are shown in Figure 1. It is seen that the amount of adsorbed resins from Furrial at a high equilibrium concentration is much larger than those observed for resins extracted from Hamaca and Guafita. It is also observed that the isotherm for Furrial resins exhibits a linear variation in the studied range, a pattern that has also been found for resins from others “unstable” crude

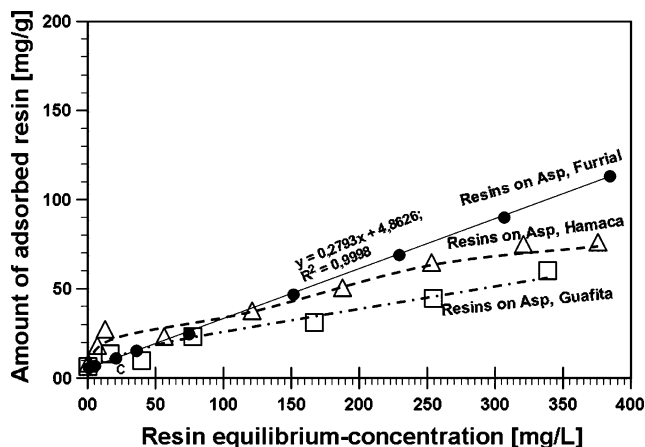


Figure 1. Adsorption isotherms of resins on asphaltenes. Resins and asphaltenes were extracted from the Venezuelan crude oils: Furrial, Hamaca, and Guafita. The adsorption isotherm experiments were carried out at room temperature, and *n*-heptane was used as the solvent.

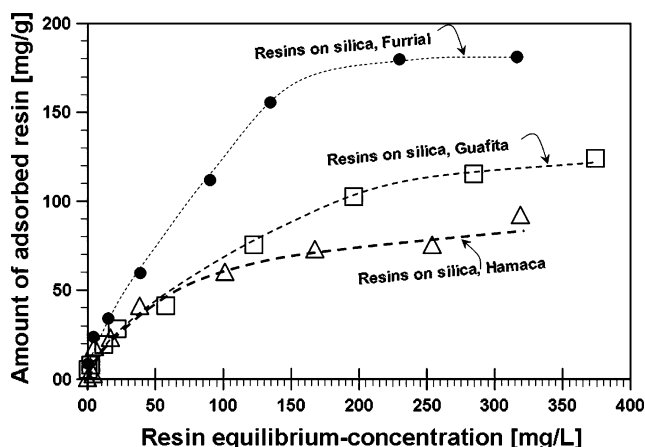


Figure 2. Adsorption isotherms of resins on silica particles. Resins were extracted from the Venezuelan crude oils: Furrial, Hamaca, and Guafita. The adsorption isotherm experiments were carried out at room temperature, and *n*-heptane was used as the solvent.

oils.²³ It is also worth mentioning that this linear adsorption pattern has been correlated to resin pore penetration,²³ i.e., adsorption in the inner pore network of the asphaltene particles.

Next, the adsorption behavior of the same resins is studied again but this time on silica particles. The idea behind this change is to remove some of the drawbacks found in resin adsorption experiments on asphaltene particles, such as the dissolution of the substrate, its porosity, its unknown surface area, and its unidentified surface composition. Indeed, silica particles offer a homogeneous and insoluble substrate with a large surface area for adsorption with perfectly known composition (SiO₂). The corresponding isotherms are shown in Figure 2.

Before we discuss Figure 2 data, it is important to highlight that, for this case, the amount of adsorbed resins in equilibrium with a very low resin concentration in the bulk, e.g., the very first data points, is some kind of estimate of the interaction forces between the resin molecules and the silica surface. Similarly, it may be said that the initial slope of the isotherm somehow is a measurement of the combined effect of the silica–resin interaction forces and the number of active sites.^{26–29} Furthermore,

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the final amount of adsorbed resins, i.e., the saturation plateau value, is an indication of the number of active sites on the silica surface for the resins to adsorb. The isotherms clearly indicate differences in the behavior of the resins extracted from the three crude oils. This is probably due to variations in chemical composition despite similarities in the interaction forces with the substrate evidenced by the coincidence of the data at low concentrations. When the initial slopes of the isotherm are compared, it is seen that, for Hamaca and Guafita resins, the adsorption rising trend is lower than that for Furrial. Actually, for Hamaca and Guafita, the slope quickly dwindles, and as expected as a consequence of a Langmuir-type isotherm, the final adsorption density value at the plateau is lower. Hence, it may be stated that, when all active sites are covered by adsorbed resin molecules, a much higher adsorption density is attained for Furrial resins. This result may be due to two alternative causes. First, the silica particle surface could present a higher number of active sites for Furrial resins than for the other two resins. This eventuality could probably be ruled out, because the silica particles have been found to exhibit the same adsorption surface area for all resins. The second possible explanation is to attribute these differences to the van der Waals forces²¹ between resin molecules and not between resin molecules and the silica surface. This is probably the case, because all resins present similar weak interaction forces with silica particles as evidenced by the same low tendency to adsorb at a very low resin equilibrium concentration. Therefore, resin molecules from Furrial crude oil are likely to exhibit higher self-interaction forces than resin molecules from the other two crude oils. As a consequence of the previous arguments, the adsorbed resin layer is probably thicker in the Furrial resin case and may be a part of a multilayer or expanded layer structure.

To find out a correlation between resin adsorption activity and asphaltene stability in crude oils, experiments were carried out in which resins from Furrial and Hamaca were adsorbed on complex adsorbents obtained by adsorbing A_2 fractions from their respective crude oils on silica particles (see the Experimental Section). The reason underlying this choice is to take into account one of the most accepted models to explain asphaltene colloidal behavior; i.e., asphaltene fraction A_1 is surrounded by asphaltene fraction A_2 ^{3,17,18} according to a so-called peptization mechanism. Consequently, fraction A_2 is the one that interacts with resins and other crude oil components. The corresponding isotherms are shown in Figure 3. Once again, resins from Furrial present a much higher tendency to adsorb than those from Hamaca.

The results of Figures 1–3 suggest an unconventional assertion about the resin role; that is, resins are not only responsible for asphaltene stability but also for asphaltene instability. This statement constitutes the main point of this paper. It is surely not the first time that resins are found to not always provide asphaltene stability. For instance, González et al.³⁰ reported that the resin–asphaltene interaction does not necessarily provide stability to asphaltene dispersions in a crude oil, at least at the concentrations at which dispersing agents are expected to be effective, and other authors have reported similar results.²² However, as far as we know, this is the first time that resins are blamed to induce asphaltene instability. This claim is sustained by a resin adsorption dual effect, which elucidates how resins can both stabilize and destabilize asphaltene dispersion. Whenever the resins have a “weak tendency” to adsorb,

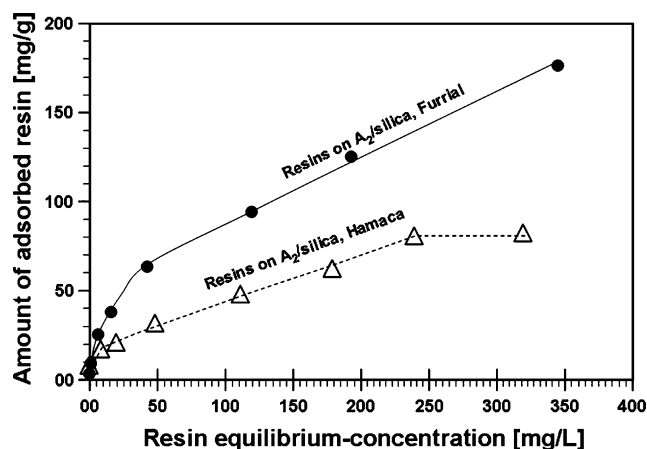


Figure 3. Adsorption isotherms of resins on silica–asphaltene fraction A_2 complexes. Resins and asphaltene fraction A_2 were extracted from the Venezuelan crude oils: Furrial and Hamaca. The adsorption isotherm experiments were carried out at room temperature, and *n*-heptane was used as the solvent.

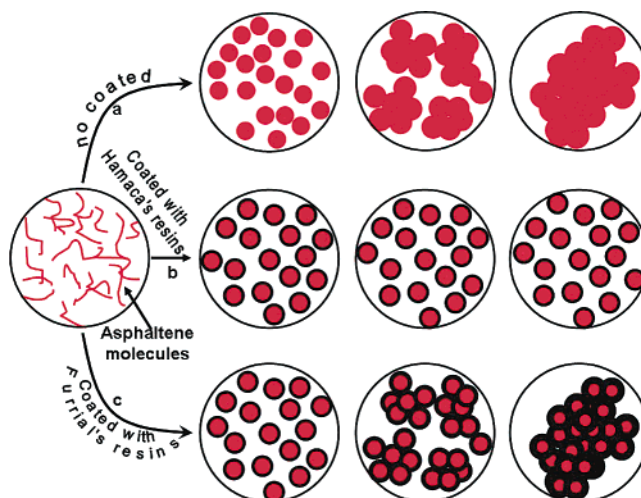


Figure 4. Three alternatives to explain asphaltene stability/instability phenomena. In all cases, asphaltene molecules associate to form colloidal particles. (a) Asphaltene particles are not protected against flocculation and readily aggregate. (b) Adsorbed resin molecules provide steric repulsion and protect particles against aggregation by the conventional peptization mechanism. (c) Thick and sticky layer of adsorbed resin molecules favors adhesion upon contact of colloidal particles and thus promotes their aggregation.

as observed in Hamaca and Guafita cases (see Figures 1 and 2), the asphaltenes happen to be stabilized; in contrast, if resins have a “strong tendency” to adsorb, as in the Furrial case, the asphaltenes become unstable. This relationship is in direct agreement with the fact that flocculation is a phenomenon driven by van der Waals attraction between colloidal particles,²¹ which is similar in nature to self-interaction between resin molecules. Parts a–c of Figure 4 schematically illustrate the three different alternatives that explain the dual role of the resins on asphaltene stability/instability phenomena. Asphaltenes are fairly polar molecules;^{1,2} hence, when colloidal asphaltene particles are dispersed in a nonpolar liquid-like petroleum in the absence of a stabilizing agent, they will immediately start flocculating and forming large-scale aggregates,¹ ending up in a precipitate as shown in Figure 4a. In the presence of a dispersing agent, peptization takes place, as frequently reported in the literature.^{2,5,21} This conventional mechanism is illustrated in Figure 4b, where resin molecules are seen to stabilize the asphaltenes by adsorbing at the surface of the particles. That is, weakly polar

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resin molecules surround the asphaltene colloidal particles, conformed by relatively highly polar molecules. Because these resin molecules have a low tendency to self-interact (weak van der Waals interaction forces between them),²¹ they are able to produce a protective “wrapping” around the asphaltene colloidal particles and prevent their aggregation by some steric repulsion mechanism. Finally, Figure 4c exemplifies the case in which resins are responsible for asphaltene instability. Resin molecules still surround the asphaltene colloidal particles as in the previous case, but this time, the surrounding resin layer is “thick and sticky” because of the strong self-interaction forces between resin molecules. Consequently, the asphaltene colloidal particles are likely to aggregate upon contact because their surrounding resin layer effect is adhesive rather than repulsive. This will eventually end up in the formation of a precipitate, causing fouling and the many associated petroleum production troubles.

Conclusions

Resins from the three different Venezuelan crude oils, both with and without precipitation problems, are found to exhibit different adsorption patterns in identical situations.

The results suggest a correlation between the resin adsorption behavior and asphaltene stability/instability phenomena in crude oil. Moreover, it seems that the resin molecular self-interaction intensity plays a key role in the asphaltene stability/instability issue. Resins with weak self-interaction (as in the Hamaca case) exhibit a low adsorption tendency and tend to stabilize asphaltenes against flocculation by the conventional peptization mechanism. In contrast, resins that strongly self-interact (as in the Furrial case) exhibit high adsorption and produce a thick and sticky adsorbed layer, which favors flocculation of contacting asphaltene particles.

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