# Influence of Experimental Parameters on the Determination of Asphaltenes Flocculation Onset by the Titration Method

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# Influence of Experimental Parameters on the Determination of Asphaltenes Flocculation Onset by the Titration Method

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The present work studied the effects of crude oil solution concentration, reservoir temperature, and *n*-heptane addition flow rate on asphaltenes flocculation onset by using an automatic titration system. These effects were evaluated through the application of a central composite design that allows the simultaneous evaluations of the experimental parameters under study. Results showed that the onset measurements were strongly affected by the crude oil solution concentration, mainly on unstable crude oil samples. This phenomenon can be used to estimate the crude oil stability. On the other hand, temperature of the sample reservoir and precipitant addition showed a slight effect on the flocculation onset.

## 1. Introduction

Heavy organic deposition during petroleum and oil production, transport, and processing is related to the stability of the crude oils, and it has tremendous economic impact in the industry. It is well-known that in crude oil production facilities the formation of asphaltic sludge has resulted in partial or complete plugging of the well. This fact increases the downtime, cleaning, and maintenance fees of the producing crude oil fields.[1,2]

The major factor that governs the production of heavy organic deposits is the asphaltenes flocculation mechanism, which is initiated by changes in the crude oil composition, pressure, and temperature of the reservoir. Alterations of any of these parameters give as result an increase in the interaction between small-sized asphaltenes colloids, inducing the formation of large asphaltenes flocs.[3−8]

Studies concerning the deposition mechanisms of asphaltenes and other heavy organics compounds in crude oils can be found in the literature.[9−14] These works explain the crude oil stability based on thermodynamic and colloidal models for asphaltenes aggregation−flocculation process. Essentially, the thermodynamic models consider the asphaltenes stability as a function of temperature and pressure variations at equilibrium conditions. On the other hand, the colloidal models take into account the composition and chemical behavior of the asphaltenes in solutions.

Experimentally, the tendency of asphaltenes to flocculate has been monitored by their behavior at different additions of paraffin hydrocarbon.[15] Briefly, the asphaltenes flocs grow in size as result of the addition of *n*-heptane or hexadecane. However, there is an upper size limit where the colloids are considered stable in the medium. Over this limit, the asphaltenes colloids start to flocculate and produce heavy organic deposits as a result. This change from a dispersion of asphaltenes colloids to asphaltenes flocs is known as the flocculation onset.[11−17,19]

Different techniques have been used to evaluate the asphaltenes flocculation onset. Among these techniques, it can be mentioned: the Oliensis spot test;[16] optic microscopic inspection or Shell P-Value;[17] and methods based on physical properties such as conductivity,[18] capillary viscosity,[2,20−24] solubility,[25,26]

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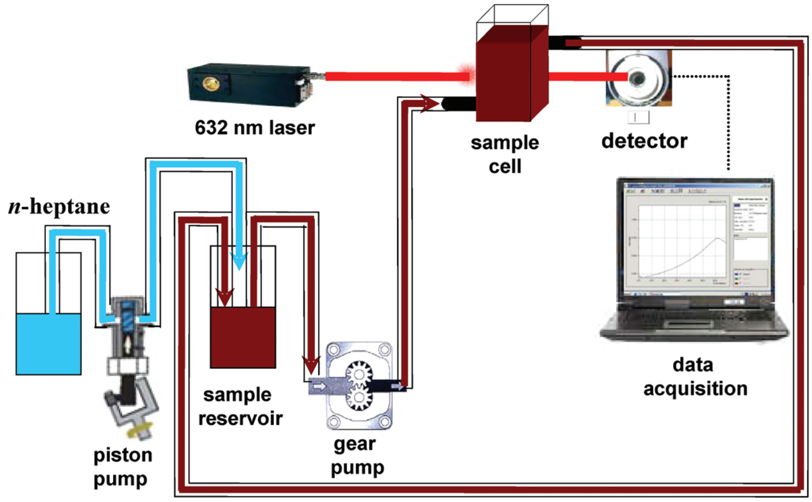


**Figure 1.** Automatic titration system by light dispersion for determination of asphaltenes flocculation onset.

interfacial tension,[27] fluorescence, particle size, heat transfer,[19,28−31] optical transmission, and light scattering.[32]

The transmitted light through a crude oil solution as a function of the addition of a paraffin hydrocarbon is one of the most common methods for the onset determination. This method allows the determination in real time with higher precision when compared to the others techniques. However, this onset value can be affected by the experimental parameters of the instrumental setup, such as temperature of the system and sample dilution. In addition, there are some discrepancies in the literature concerning the effect of the experimental parameters.[26,28,33−36] For example, Gharfeh et al.[35] observed that the crude oils become more unstable with temperature; however, Ghloum and Oskui[36] observed the opposite trend. It is also important to state that the works found in the literature used univariate methods (modifying one factor while keeping the others constant) to present the results. Such procedures omit the interactions among the experimental factors that may have significant influence on the flocculation onset value.

For all the above-mentioned results, this work evaluates the effect of some experimental parameters on the flocculation onset of Venezuelan heavy crude oils solutions using an automated titration system. The following parameters were considered: crude oil concentration of the solution, temperature, and titrant (*n*-heptane) addition flow rate. These effects were evaluated by using a central composite design. This statistic methodology generates a surface response that allows the simultaneous evaluation of all the experimental parameters (or factors) under study. It was also related the stability of some Venezuelan crude oils, measured as Shell P-value, with the asphaltene aggregation mechanism.

## 2. Experimental Section

**Instrumental Setup.** The asphaltenes flocculation point is determined by measuring the transmitted light through crude oil samples during the flocculation induction by continuous addition of *n*-heptane. Figure 1 shows the instrument setup for the automatic determination of asphaltenes flocculation onset in crude oil samples. The beam from a He−Ne laser (632 nm, 5 mW) passes through a 2 mm path length flow cell. The transmitted beam is continuously detected by a photodiode. The detector signal is acquired and processed in real time by custom-made software. The crude oil solution is recirculated through the cell by using a stainless steel gear pump. Heptane is added at constant rate by using a piston pump. In a typical experiment 10 mL of solution of crude oil diluted in toluene is added to the sample reservoir and the gear pump starts to recirculate the solution through the flow cell at 14 mL/min flowrate. Once the beam intensity remains stable, the piston pump is activated at 0.7 mL/min for the addition of *n*-heptane. At this point begins the induction of the flocculation process in the sample reservoir. It is important to state that the continuous agitation of the sample and the high recirculation flow rate, when compared to *n*-heptane addition, avoid any local asphaltenes flocculation. The onset value is automatically obtained based on the measured quantity of *n*-heptane required to reach the maximum transmitted light.

This instrument allows the titration of crude oil solutions having high optical densities (low dilution factor) due to the light intensity of the laser and the short path length of the recirculation cell.[28,32]

**Samples and Sample Preparation.** Samples of Venezuelan crude oils having different API gravity and SARA composition were used in this work, and they are presented in Table 1. The crude oil samples were diluted with toluene (HPLC grade, Riedel-Haën), to reduce the viscosity and to diminish their optical density. The

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**Table 1. API Gravity and SARA Composition of Venezuelan Crude Oils Used in This Work**

| crude oil | API gravity | saturates, % | aromatics, % | resins, % | asphaltenes, % |
|---|---|---|---|---|---|
| Bachaquero | 9 | 25 | 33 | 29 | 13 |
| Lagunillas | 15 | 30 | 26 | 32 | 12 |
| Boscan | 8 | 10 | 23 | 48 | 19 |
| Sur mediano | 15 | 25 | 28 | 35 | 11 |
| Hamaca | 8 | 11 | 19 | 57 | 13 |
| Merey 16 | 20 | 25 | 24 | 36 | 15 |
| CNS | 21 | 21 | 27 | 37 | 15 |
| PTZL | 28 | 35 | 33 | 28 | 4 |
| Mesa 30 | 20 | 44 | 25 | 21 | 10 |
| UD-672 | 21 | 22 | 30 | 44 | 4 |
| Furrial | 21 | 35 | 24 | 32 | 9 |

**Table 2. Factor Levels for the Central Composite Design Used to Evaluate the Effects of the Experimental Parameters on the Asphaltenes Flocculation Onset**

| factor | | | |
|---|---|---|---|
| sample reservoir temperature, °C | crude oil solution concentration, mg/L | $n$-heptane flow rate, mL/min | codified level[a] |
| 11 | 30 000 | 0.40 | −1.4 |
| 25 | 40 000 | 0.50 | −1 |
| 45 | 55 000 | 0.65 | 0 |
| 65 | 70 000 | 0.80 | +1 |
| 78 | 80 000 | 0.90 | +1.4 |

[a] Determined by: $2[((X - \bar{X})/(X_{max} - X_{min}))]$.

asphaltenes flocculation was induced by addition of $n$-heptane (HPLC grade, Riedel-Haën).

**Methodology.** *Effects of the Experimental Parameters.* The asphaltenes flocculation onset determination can be affected by the experimental parameters of the instrumental setup: light source, temperature of the system, sample dilution, addition flow rate, type of paraffin hydrocarbon, and recirculation flow rate.[33] In this connection, some experiments were implemented to study the effect of experimental parameters of the titration system on the flocculation onset of Venezuelan heavy crude oils solutions. The following parameters were considered: crude oil concentration in toluene solution, reservoir temperature, and $n$-heptane addition flow rate. These factors were selected because they have a significant effect on the absolute onset flocculation value.[19,25,32,40] The experimental parameters effects were evaluated by using a central composite design. This statistic methodology generates a surface response that allows the simultaneous evaluation of all the experimental parameters (or factors) under study.[37] The factor levels used in this study are listed in Table 2. These values were selected considering the optical density of the heavy crude oils solutions, the boiling point of $n$-heptane, and the generation of turbulence by the gear pump. The $n$-heptane temperature was always fixed at the same value of the sample reservoir, and the recirculation of the solution was predetermined at 14 mL/min. The surface response was obtained for Furrial and Bachaquero crude oils, low and high stability crude oils, respectively.[32]

**Relation of the Asphaltenes Flocculation Onset with Crude Oil Stability.** The stability of the crude oils is always a relative measurement. The Shell P-value is one of the most-used parameters to evaluate stability, from an operational point of view.[17] At this point, it is necessary to remind that the Shell P-value consists in the examination of the presence of flocculated asphaltenes in mixtures of diluted crude oil samples with varying amounts of hexadecane and, after a heating at 100 °C for 1 h, by means of a microscope.[17] Crude oils with a P-value larger than 1.6 are considered stable, whereas lower values are indicative of low stability. In this sense, the stability of 11 Venezuelan crude oils samples were related, expressed as Shell P-value with the experimental flocculation onset considering the results of the central composite design.

**Table 3. Flocculation Onset at Different Experimental Parameters of the Titration System[a]**

| experiment number | sample reservoir temperature | $n$-heptane addition flow rate | crude oil solution concentration | Furrial onset, % v/v | Bachaquero onset, % v/v |
|---|---|---|---|---|---|
| 1 | +1 | +1 | +1 | 65.9 | 73.2 |
| 2 | 0 | +1.41 | 0 | 66.0 | 74.0 |
| 3 | 0 | 0 | +1.41 | 66.3 | 72.8 |
| 4 | −1.41 | 0 | 0 | 67.6 | 73.2 |
| 5 | −1 | −1 | −1 | 71.6 | 73.4 |
| 6 | −1 | +1 | −1 | 68.5 | 74.0 |
| 7 | 0 | 0 | 0 | 67.5 | 73.8 |
| 8 | 0 | 0 | 0 | 67.8 | 73.6 |
| 9 | 0 | 0 | 0 | 65.2 | 72.0 |
| 10 | 0 | 0 | 0 | 66.0 | 73.4 |
| 11 | 0 | 0 | 0 | 66.8 | 73.5 |
| 12 | −1 | −1 | +1 | 67.3 | 72.2 |
| 13 | 0 | 0 | 0 | 66.2 | 73.6 |
| 14 | +1.41 | 0 | 0 | 66.8 | 73.8 |
| 15 | +1 | +1 | −1 | 67.5 | 74.0 |
| 16 | −1 | +1 | +1 | 66.6 | 73.8 |
| 17 | 0 | 0 | 0 | 66.4 | 73.7 |
| 18 | 0 | 0 | 0 | 66.4 | 73.1 |
| 19 | +1 | −1 | −1 | 68.5 | 74.1 |
| 20 | 0 | 0 | −1.41 | 69.6 | 75.1 |
| 21 | +1 | −1 | +1 | 65.8 | 72.7 |
| 22 | 0 | 0 | 0 | 66.3 | 73.6 |
| 23 | 0 | −1.41 | 0 | 66.5 | 73.2 |

[a] Results were obtained according to a central composite design. The onset values have a precision less than 1% expressed as relative standard deviation. See Table 2 for the original values of the codified levels.

## 3. Results and Discussion

Table 3 presents the flocculation onset obtained at different operating experimental parameters, according to the central composite design for a Furrial and Bachaquero crude oils. The results generate the pareto charts and response surfaces presented in Figure 2. The pareto charts show the level of significance of the experimental parameters on the asphaltenes flocculation onset. One parameter has a significant effect when its value is higher than the standard error of the experiment (vertical line).[37] It can be noticed that crude oil solution concentration is the factor that has the most significant influence on the flocculation onset ($i_A$, $iii_A$). The unstable crude oil (Furrial, $i_{AA}$) showed a significant quadratic effect when compared to the stable one (Bachaquero, $iii_{AA}$). That means the crude oil solution concentration has a strong impact on the unstable crude oil, and this fact can be clearly appreciated in response surfaces (ii, iv).

Temperature of the sample reservoir showed a slight effect on the flocculation onset for unstable crude oil ($i_B$). The onset point slightly reduces until approximately 45 °C and then starts to increase (ii). Such effect was more evident at lower concentration. On the other hand, the stable crude oil (Bachaquero) did not present any effect with the temperature ($iii_B$ and iv). It seems that this effect mainly depends on the type of crude oil (the combined effects are not significant, $i_{AB,\ AC\ and\ BC}$). Also, these results can help explain the discrepancies found in the literature.[28,33,35,36]

The $n$-heptane addition flow rate had no significant effect on the onset under the experimental conditions used in this work (Figures $i_C$ and $iii_C$). The values were lower or similar than the standard error of the experiment.

Following the above results, a new set of experiments was realized where the flocculation onset dependence on crude oil

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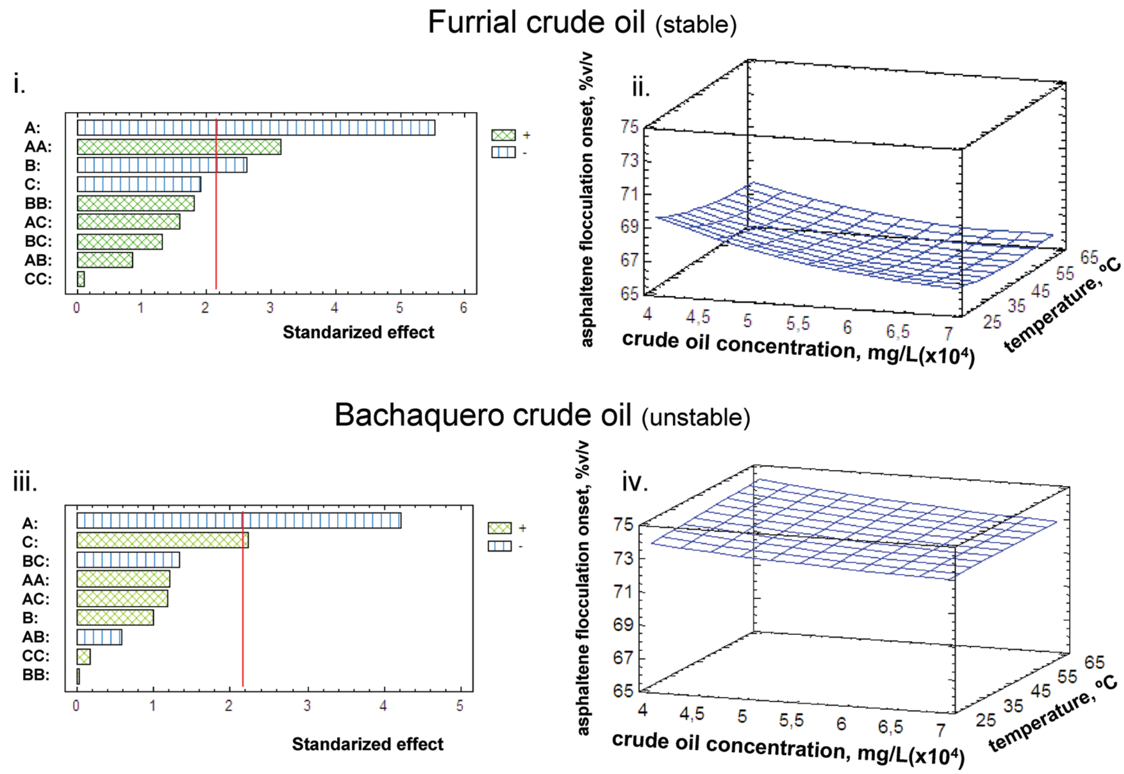


**Figure 2.** Pareto Charts (i, iii) and response surfaces (ii, iv) of the asphaltenes flocculation onset as a function of the experimental parameters of the titration system. A: crude oil solution concentration in toluene; B: temperature of sample reservoir; C: *n*-heptane flow rate addition. AA, BB, CC, and AB, AC, BC are quadratic and combined effects of the experimental paremeters, respectively.

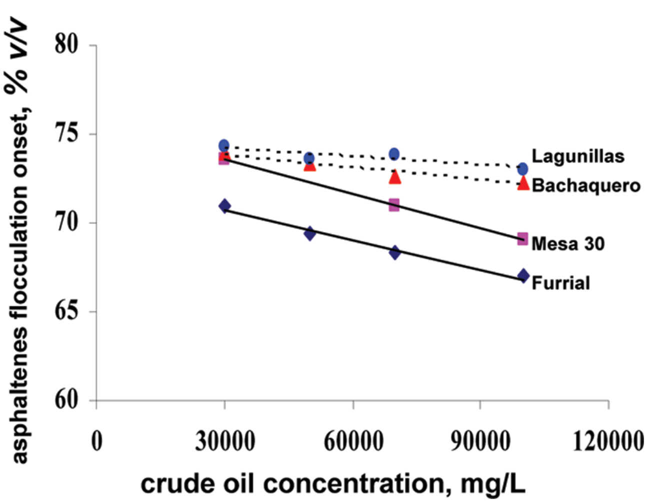


**Figure 3.** Behavior of asphaltene flocculation onset as function of crude oil solution concentration in toluene.

sample concentration was carefully established. Two unstable crude oils (Furrial and Mesa 30) and two stable crude oils (Bachaquero y Lagunilla) were selected for these experiments. The concentrations ranged from 30 000 to 100 000 mg/L. High stability crude oils present small changes (low slope) on the flocculation onset as the concentration increases; in contrast, low stability crude oils present a strong reduction, as can be observed from Figure 3.

For all above-mentioned, the flocculation onset of 11 Venezuelan crude oils at two concentrations (30 000 and 100 000 mg/L) with Shell P-value were associated; the results are presented in Table 4. Figure 4 contrasts the onset obtained at 30 000 mg/L with the Shell P-value of the samples. It can be appreciated that there is no clear tendency between these parameters. For example, Mesa 30 and UD-672 have similar

**Table 4. Variation of Asphaltenes Flocculation Onset at Two Crude Oil Concentration and Shell P-Value of the Venezuelan Crude Oil Samples**[a]

| crude oil | Shell P-value | flocculation onset at 30 000 mg/L, %[b] | flocculation onset at 100 000 mg/L, %[b] | $\Delta_{onset}$, %[b] |
|---|---|---|---|---|
| Bachaquero | 3.3 | 73.8 | 72.3 | 1.5 |
| Lagunillas | 3.1 | 74.3 | 73 | 1.3 |
| Boscan | 2.9 | 77.2 | 75.3 | 1.9 |
| Sur mediano | 2.8 | 80.0 | 78.1 | 1.9 |
| Hamaca | 2.3 | 65.2 | 64.4 | 0.8 |
| Merey 16 | 2.2 | 70.1 | 68.9 | 1.2 |
| CNS | 1.8 | 63.7 | 62.4 | 1.3 |
| PTZL | 1.6 | 65.2 | 69.3 | 4.1 |
| Mesa 30 | 1.4 | 73.6 | 69.1 | 4.5 |
| UD-672 | 1.5 | 78.5 | 75.6 | 2.9 |
| Furrial | 1.5 | 70.9 | 67.1 | 3.8 |

[a] The onset values and $\Delta_{onset}$ have a precision less than 1% expressed as relative standard deviation. [b] *n*-heptane added in % v/v.

P-values (both are unstable <1.6) but they have different values of asphaltenes flocculation onset. In contrast, Mesa 30 and Bachaquero, with different stability behavior (1.6 and 3.3, respectively), exhibited similar flocculation onset values. It is evident that the flocculation onset obtained at only one crude oil solution concentration can not be used as direct stability criteria, and this result is in agreement with those obtained by Leon et al.[38,39] Figure 5 shows the difference between onset values observed in the extremes of the concentration range ($\Delta_{onset}$ = onset value at 100 000 mg/L − onset value at 30 000 mg/L) of the crude oil samples versus Shell P-value. It can be appreciated that there are two groups of crude oil samples. The first one presents $\Delta_{onset}$ higher than 2.5. This group corresponds to the unstable samples. The other group presents $\Delta_{onset}$ lower

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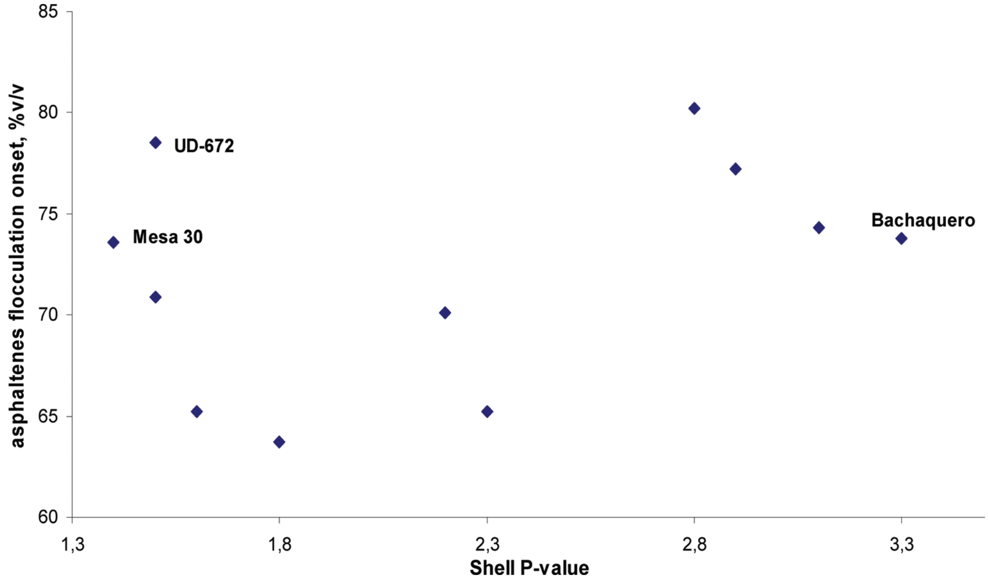


**Figure 4.** Relation of asphaltene flocculation onset with Shell P-value of some Venezuelan crude oils. Data from columns 2 and 3, Table 4.

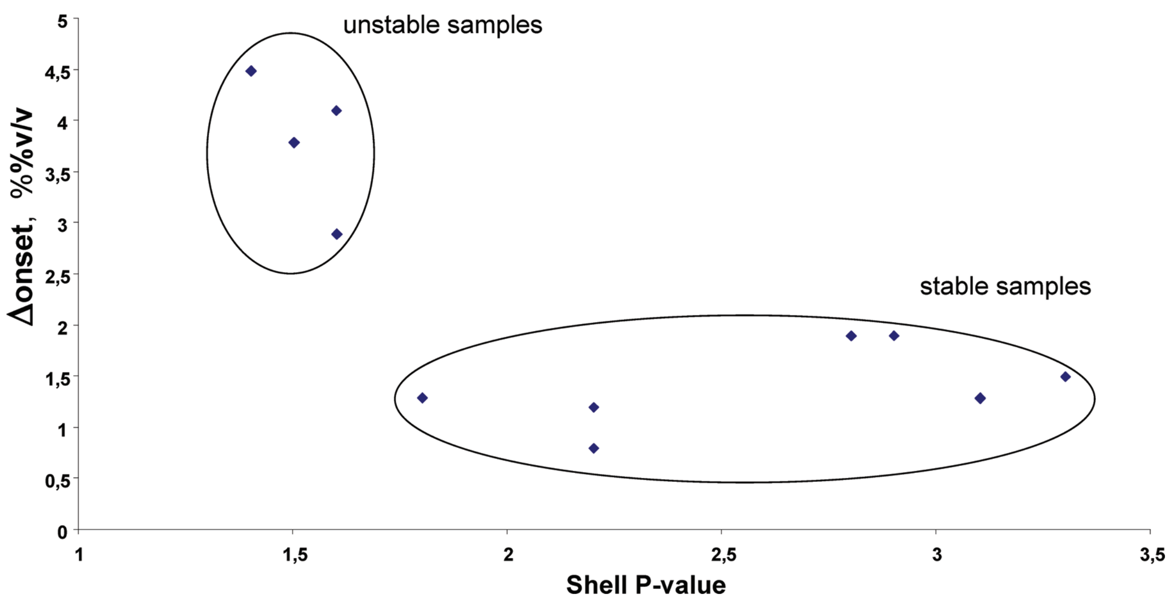


**Figure 5.** Relation on asphaltene flocculation $\Delta_{onset}$ with Shell P-value of Venezuelan crude oils.

than 2, and they correspond to stable crude oil samples. It is clear that the $\Delta_{onset}$ provides information about the stability of the crude oil with the main advantage that the titration system provides reproducible measurements in a very short time.

The observed dependence of $\Delta_{onset}$ with crude oil concentration can be explained in terms of asphaltenes solubility.[32,40−42] Hung et al. reported that the variations in solubility of the asphaltenes from stable and unstable crude oils depend on the differences in their aggregation mechanisms.[40] Asphaltene aggregation is a typical example of a nonequilibrium process that theoretically can be described by diffusion-limited colloidal aggregation (DLCA) or reaction-limited colloidal aggregation (RLCA).[40] In the DLCA, the aggregates growing process is governed by Brownian diffusion: that means the phenomena depends only on the diffusion of particles in the media. The repulsive forces between particles are minimal and all the encounters colloids will form aggregates. In RLCA, the growing process depends on the encounter probability and the effective interaction between particles. The unstable crude oils tend to form aggregates of low density, increasing in number faster than in size. This behavior is typical of reactions controlled by the kinetics,[32,40−42] and for that reason the dependence of the flocculation point with the concentration is remarkable. In contrast, for stable crude oils, the flocs grow in size faster than in number, showing the independence of the flocculation with concentration. This is characteristic of the kinetics controlled by diffusion.

## 4. Conclusions

Flocculation onset can be easily obtained in a homemade titration system based on light dispersion in a simple, precise,

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and fast way. The crude oil concentration in toluene solution is the experimental parameter of the titration system that has a significant effect on the asphaltenes flocculation onset. Temperature of the sample reservoir showed a slight effect on the flocculation onset for unstable crude oil. The *n*-heptane addition flow rate does not have any significant influence on the measurement of the onset. The stability behavior of crude oils can be estimated by measuring the difference on asphaltenes flocculation onset at two sample concentration in toluene solution, $\Delta_{onset}$. Samples with low stability produce $\Delta_{onset}$ larger than 2.5%. In contrast, high stability crude oils produce $\Delta_{onset}$ below 2%.

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