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STUDY OF ASPHALTENE AGGREGATION IN TOLUENE/n-HEPTANE/CO$_2$

MIXTURES AT HIGH PRESSURE CONDITIONS.

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ABSTRACT

In this work we present a novel experimental method to obtain asphaltene precipitation envelope (APE) of complex systems composed by toluene/n-heptane mixture in presence of CO_2 at high pressure and different temperatures. The method has the feasibility to detect phase changes of asphaltenes in a pressure range from 1 to 100 MPa and temperatures from 283 to 473 K. For the first time a complete APE using experimental data was obtained. The solubility behavior of the asphaltenes with the pressure of the system is in agreement with previous studies. However the temperature aggregation behavior at high pressure showed a minimum near to 353 K that contrasts with reported data. This complex tendency can be explained by changes in viscosity, density and aggregate composition with temperature. Also, the coexistence of two sub-fractions A1 and A2 in the asphaltenes and their differences in solubility modifies the solubility and the entropy variation of the system can help to understand the asphaltene aggregation behavior at higher temperatures.

Keywords: Asphaltene aggregation, CO_2 injection, asphaltene phase envelope (APE), temperature.

INTRODUCTION

Asphaltene are defined as the heaviest aromatic fraction of crude oil. This is soluble, in organic solvents having solubility parameter values in the 17.5 – 21.6 MPa$^{1/2}$ range, like toluene and it is insoluble in saturated hydrocarbons, such as n-heptane or n-pentane. Consequently, asphaltenes are considered as a solubility class of complex mixture of thousands of compounds, which are highly polydisperse, with molar mass distribution covering range between 200 to 1000 g mol^{-1}.[1,2] From the molecular point of view, asphaltenes are represented by a mixture of polycyclic systems joined by flexible aliphatic chains, such as rosary- or archipelago-type molecules and condensed polycyclic structures, and bridging aliphatic rings or continental-type structure.[3-5] Acevedo et al. have presented evidence of two asphaltene sub-fractions using the p-nitrophenol (PNP) method.[6,7] One of these sub-fractions called A1, has a low solubility in toluene at room temperature (0.05 g L^{-1}) and molar mass around to 2600 g mol^{-1}.[3,8] The A2 sub-fraction has the usual toluene solubility of asphaltenes (between 57 and 100 g L^{-1} under the same conditions) and molar mass close to 1000 g mol^{-1}. According to these results, the authors propose a model where asphaltene colloids could be represented by particles with a core rich in A1 and a periphery rich in solvent media and A2 type molecules.[9] Fractal packing, mainly promoted by A2, allows the solvent penetration to the colloidal periphery, and this forms a barrier to inhibit the A1 sub-fraction particles interaction and therefore asphaltene

aggregation.[6, 10]

The tendency of asphaltene to flocculate and precipitate in presence of light liquid paraffin, like *n*-heptane and other incompatible fluids such as carbon dioxide (CO_2), is a well-known source of operational problems in the oil industry. Destabilization of asphaltene in crude oils can cause reservoir plugging, deposits formation in well production, generally around the bubble point depth or during the transportation and treatment.[11-14] In this fact, lies the importance to study asphaltene aggregation at high pressure in presence of CO_2

In recent years applications of enhanced oil recovery (EOR)[15] have been widely used to improve the oil recovery. One of the popular EOR procedures is the miscible-CO_2 flooding method. The CO_2 is more soluble in oil than water so, CO_2 acts as a solvent in this process,[16] lowering the oil viscosity and making it mobile.[17] However, CO_2 injection may cause undesirable effects which are favorable for the asphaltenes phase separation.[18,19] Consequently, precipitation of asphaltenes is a common event in most CO_2 flooding.[18-22] For this reason, the oil industry increment efforts to have a practical tool which enables to estimate asphaltene precipitation, especially in conditions of pressure and temperature during the CO_2 injection.

Asphaltenes aggregation behavior as function of pressure, temperature and composition is a complex process and still not fully understood. Hence, there are various models reported in the literature for predicting the amount of asphaltene precipitation. Some of the developed models are based on Flory-Huggins polymer solution theory,[25,26] thermodynamic colloidal models,[11] and thermodynamic micellization models,[17,18] and application of advanced equations of state (EOS).[27-30] However, apply these models to real samples need an enormous experiment and time-consuming work to analyze the results.

Asphaltene aggregated phase formation during natural production process depends strongly on pressure and temperature.[31] The asphaltene phase behavior at reservoir conditions can be represented in a pressure vs. temperature graph. The asphaltene onset at high pressure and temperature are used to draw a diagram that represent the phase stability.[32] This diagram has been called asphaltene phase envelope (APE).[31] The first experimental study about the effect of pressure in asphaltene precipitation was made by Bilheimer et al.,[33] in mixtures of bitumen with tetralin and using *n*-pentane as precipitant. The authors reported a constant decrease in asphaltene precipitation with the increase of pressure.

Buenrostro-González et al.,[31] studied the asphaltene precipitation by a series of high-pressure/high-temperature flocculation experiments in two Mexican crude oils. It was observed a dependence of the asphaltene onset with temperature

from experimental APE's. This behavior was related with the increases of asphaltene solubility with temperature so that the asphaltene onset requires an extreme reservoir condition to promote phase changes.

Verdier et al.,[34] studied the asphaltene phase behavior after injection of CO_2 in two dead crude oils (from South America and the Middle East) up to 383 K and 60 MPa using a high-pressure cell with a filtration technique to remove asphaltene precipitated. For both crude oil samples, the asphaltene was showed more stable at high pressure and low temperature.

González et al.[35] had been reported that CO_2 can destabilize or stabilize asphaltenes in oil depending upon the temperature of the system. They had been observed, a CO_2 inhibition effect on asphaltene precipitation with temperature in a range between 311 to 533 K. This phenomenon may be explained by changes in the solubility parameter of CO_2 around 422 K. At this temperature the solubility parameter of the mixture increase and the asphaltenes becomes more stables. On the other hand, at temperatures above this point, the solubility parameter of CO_2 is lower than the crude oil and it causes the asphaltene precipitation.

At this point and according to the literature, it is important to note that the asphaltene stability in presence of CO_2 is proportional with the pressure (i.e. at high pressure the asphaltenes are more soluble). However, the temperature effect on asphaltene behavior is a subject of controversy. There are three reported tendencies: a) an increase in asphaltenes solubility with temperature, b) a decrease of the solubility with temperature, and c) a temperature crossover point, where the CO_2 can act as a flocculation inhibitor or as an asphaltene precipitant. From our point of view, all these tendencies are correct and depend of pressure and crude oils properties. These effects are derived from the complex nature of asphaltene sub-fractions.

For all above mentioned, the main goal of this work is to study the asphaltene phase behavior in presence of CO_2 at high pressures as function of the temperature. In this effort we present a complete set of this type of experimental data at high pressures and temperatures. The sample was asphaltenes extracted from a Venezuelan unstable crude oil dissolved in toluene:*n*-heptane mixture (heptol) as synthetic model oil.[21] The asphaltene flocculation onset of solutions with 10, 15 and 20 wt % CO_2 were studied. The temperatures varied in the range 283 and 423 K using an especially designed high pressure cell system. Results reveals a critical temperature value around 353 K. Also, data showed an interesting behavior of the asphaltenes with temperature at pressures above bubble point. These results are strongly consistent with recent reports of the sub-fractions A1 and A2 influence in the asphaltene aggregation model.[10,31,36,37]

EXPERIMENTAL SECTION

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Experimental setup

Figure 1 presents a simplified scheme of the experimental setup used in this work. It was provided by Top Industries (Paris, France) and allows a visual detection of asphaltene flocculation onset and bubble point. The setup can be divided into three main parts. The first one corresponds to an automated high-pressure cell (2), designed to work a maximum pressure of 100 MPa and temperature up to 473 K. The volume of the cell is controlled by a mobile piston (11) to adjust the volume between 7.85 and 35.2 cm^3 and it automatically reach the pressure at the equilibrium condition of the system. The cell is equipped with two sapphire windows (4) to give full visibility of the fluids inside.

The second part involves a high-pressure container in carbon fiber and a high precision balance (9) to weight the gas injected at pressures not exceeding 30 MPa. Finally, a display system allows detection of asphaltenes flocculation onset. This part consists of an analogical camera coupled to an endoscope (5) parallel to cell axis. The cell has two sapphire windows, one of them is for visual inspection by using the endoscope. The other sapphire window, at 90° from the other, is to illuminate inside the cell by a white light source. Additionally, there are two valves (12) connected to the cell for sample and CO_2 gas introduction and removal.

The temperature in the cell was adjusted by a constant recirculating thermostatic bath of ethylene glycol mixture and controlled in a range between 283 to 473 K using a probe (3) (Pt 100, with an accuracy of 0.1 K). The pressures obtained with a Kulite pressure gauge (6) (HEM 375), which operates between 0.1 and 100 MPa.

Sample

The APE study made with a sample from Furrial field (Eastern Venezuelan Basin). This crude oil presents serious problems of asphaltenes precipitation. Furrial crude oil has 4% of asphaltenes and 24°API. The asphaltene sample was obtained by precipitation with *n*-heptane from the crude oil by a well-known method IP-143.[38]

Asphaltenes phase envelope

APE were obtained from asphaltene solution prepared by dissolution in toluene:*n*-heptane mixture (Heptol 4:6). This mixture has a similar Furrial asphaltene flocculation onset (46 wt% of *n*-heptane) and is used like synthetic model oil. The asphaltene concentration was fixed in 0.04 wt%. It was studied the APE at three final concentration of CO_2 added in the pressure cell: 10 wt%, 15 wt% and 20wt%, calculated based on 9g of asphaltene solution. These CO_2 quantities cover a wide range of possibilities; at low concentration there was not

observed a precipitation of particles and a high concentration it was obtained the precipitation.

Experimental procedure

Prior to any experiment, the cell and all the connecting lines was cleaned with toluene and a light suction is applied to dislodge the solvent. For each analysis, 9.0 g of the asphaltene toluene:n-heptane solution was introduced at atmospheric pressure in the cell by using a piston positive displacement. The temperature was raised to the selected work value. Then, the sample is pressurized by a negative (backward direction) piston displacement and it was equilibrated at the temperature of the cell after CO_2 is injected through the valves to the cell at constant pressure. The quantity of CO_2 injected into the pressure cell was determinate by difference of weight of the mini-cylinder of CO_2 with a high precision balance.

Two magnetic bars were used to continuously stir to avoid the asphaltene particles deposition. The pressure was increased to 60 MPa for two hours to complete the fluids dissolution and allow the system to reach to equilibrium state. The latter was considered when the entire sample was dissolved. At this point, a constant negative piston displacement rate of 1.5 MPa min^{-1} was used to decrease the pressure slowly and isothermally up to the desired pressure. After this, the system was in stand by mode for 24h assure the equilibrium state and finally a visual inspection was made through the endoscope. The images from this endoscope permit a resolution in order of microns. Each point at the APE curve was obtained at constant temperature from high to low pressure and it was delimiting the pressure as function on the appearance and disappearance of asphaltene particles (with a precision of +/- 0.5 MPa). In a similar way, the same was applied to the bubble point that corresponds to the pressure in which gas bubbles appear at each selected temperature.

RESULTS AND DISCUSSION

The first part of this study focuses on the selection of the working concentration to obtain the APE, given the complexity and opacity of the asphaltene solutions, as well the limitation of the experimental setup. The concentration was carefully chosen, based in the solution opacity, as the maximum value that allows the visual detection of asphaltene particles using the endoscope and white light illumination. For this, it was tested the pass of the light through the cell having the asphaltene solution ranging from 0.1 to 0.05 wt% in presence of CO_2. It was found that the maximum asphaltene concentration was 0.04 wt%.

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Figure 2 presents APE curves obtained from asphaltene toluene/*n*-heptane solution at three CO_2 concentration (10, 15 and 20%) setting temperatures between 283 to 423 K °C. The continuous curves represent the asphaltene precipitation values and define the stability area. Up to this curve the asphaltene are dissolved in solution and below are precipitated. The dashed curves show the bubble point and define the vapor-liquid equilibrium zone.

Figure 2 also shows that the asphaltenes are more soluble at high pressure for all concentrations of CO_2. For example, in figure 2a, at 14 MPa bar and 313 K (diamond), the asphaltene solution is in stable region. However, if the pressure drops (isothermally) to 8 MPa , asphaltene precipitation onsets are obtained and two phases coexist in the system until the bubble point pressure are obtained (dashed curve, 2 MPa). At this point $CO_2(g)$ starts to break free of the solution.

The above described behavior was observed in all the temperature range studied and for 15 and 20 % of CO_2 mixtures (figures 2b and 2c). Thus, it is possible to conclude that an increase in pressure enhances the asphaltenes stability, by increasing the solubility of the medium. This trend is in agreement with literature,[31,34,35,39,40] and it can be explained by changes in density and solubility parameters of all the components of mixture during the process.[39,41] To illustrate this, figure 3 shows the changes of solubility parameter (δ) calculated for toluene, *n*-heptane and CO_2 with pressure at 303 K. The δ was calculated using the cubic equation of state of Peng-Robinson (1).[42] The values to feed the equation at different pressures and temperature were obtained from National Institute of Standard Technology (NIST).[43]

$$\delta^2 = \frac{\sqrt{2}}{4b}\left(a - T\frac{da}{dT}\right)\left[ln\left(\frac{V(T,P)+b(\sqrt{2}+1)}{V(T,P)+b(\sqrt{2}-1)}\right)\right]\left(\frac{1}{V(T,P)}\right) \quad (1)$$

It can be appreciated not significant variations of solubility parameter (δ) for toluene and *n*-heptane with pressure, in contrast, δ of CO_2 increases proportionally with pressure. Accordingly, this component of the mixture is responsible for the variations in the solubility parameter of the complete system toluene/*n*-heptane/CO_2, particularly at pressure below 15 MPa. The solubility parameter of the mixture follows the rule of mixture in volume [34,44,45] and this is in agreement with equation 2, this is, when the CO_2 is present, the solubility parameter of the mixture decreases the asphaltene solubility giving that the solubility parameter reported for Furrial asphaltenes is about 18 $MPa^{1/2}$.[9] This effect is more significant when the pressure drop in the system.

$$\delta_{mezcla} = \varphi_{C_7}\delta_{C_7} + \varphi_{Tol}\delta_{Tol} + \varphi_{CO_2}\delta_{CO_2} \quad (2)$$

The effect of the temperature in the APE is really complex, in contrast to the results with pressure. The experimental values showed an increase of asphaltenes solubility for pressure values above bubble point for temperature up to 353 K. Over this point, the asphaltenes solubility started to diminish in all CO_2 concentrations. This tendency cannot be explained based only by the solubility parameter of the mixture. Trying to explain this behavior, Figure 4 shown the variation of solubility parameter calculated for CO_2 and asphaltene solutions, at different pressures, as a function of temperature. It can be noted that solubility parameter curve for CO_2 never intercept to asphaltene curve.

Generally, asphaltenes precipitation curves at high pressure presented in the open literature are simulated values of crude oils solutions using equations of state, such as PC-SAFT. According to these models, the solubility parameter of CO_2 (δ_{CO2}) below the threshold temperature, is greater than the solubility parameter of crude oil, $\delta_{crude\ oil}$. Therefore, CO_2 addition under pressure increases the solubility parameter of the mixture so asphaltenes solubility also increases. At higher temperature, $\delta_{crude\ oil}$ decreases with the addition of CO_2 and the asphaltenes solubility declines leading to precipitation.[35,40] It is evident that experimental results do not match this computer-generated data.

The presence of critical temperature may be explained by taking into account the following aspects: a) An increase in temperature improves the miscibility in absence of specific intermolecular forces. Two fluids can be mixed easily at high temperature due to the contribution of entropy of mixture in the Gibbs energy; b) In contrast, an increase in temperature also causes a decrease in the density (and viscosity) of the liquids and fluid solubility parameter reduces the efficient solvency. At constant temperature, asphaltenes solubility decreases with the density of the solvent. As conclusion, the observed solubility behavior is the result of the competition between two opposite phenomena: changes in entropy and density. The former effects may predominate at temperatures below 80 °C and the latter controls the system at higher values.

Recent study reported by Acevedo et al. [10,36] and Zanganeh et al.,[21] contributes also to clarify the effect of the temperature in the high pressure and temperature system. Our results are in agreement with the solubility differences reported for the asphaltene sub-fractions A1 and A2, hence molecular structure differences.[21] The first group of authors demonstrate that these asphaltene sub-fractions have notable solubility differences. These sub-fractions are stable in solution, but any change in the solubility parameter of the media may induce the destabilization of the system. In this connection, our experimental APE behavior suggest that solubility of A2 sub-fraction increase with temperature, causing that A2 drop out from the periphery of particle to solution and consequently a decrease of

asphaltene aggregate size. At higher temperatures, the low solution viscosity and high entropy of the system promotes collisions between particles rich in A1 which are devoid of A2, allowing effective particles interactions between A1 sub-fraction low solubility type molecules, increasing the aggregation. The differences in asphaltene molecular structures could promotes the attraction and interaction between molecules and increase the aggregation, flocculation and deposition of asphaltene.[21]

CONCLUSIONS

For the first time an APE curve were constructed from direct experimental data. A high-pressure cell to study the effects of temperature (up to 423 K) and pressure (up to 55 MPa) in presence of CO_2 was used and a novel methodology was developed to detect the phase change. An increase in the pressure at constant temperature always leads to increase asphaltenes solubility and stability in the fluid. It was observed critical asphaltene solubility and aggregation behaviors with temperature over bubble point at constant pressure. This tendency can be explained by changes in viscosity and density with temperature that may alter the asphaltene aggregates composition, mixture miscibility and the entropy of the system. Also, the differences between A1 and A2 sub-fractions solubility suggest that aggregates present in solution are constituted by A1 so asphaltenes stability in solution decreased when temperatures over 353 K.

ACKNOWLEDGMENTS

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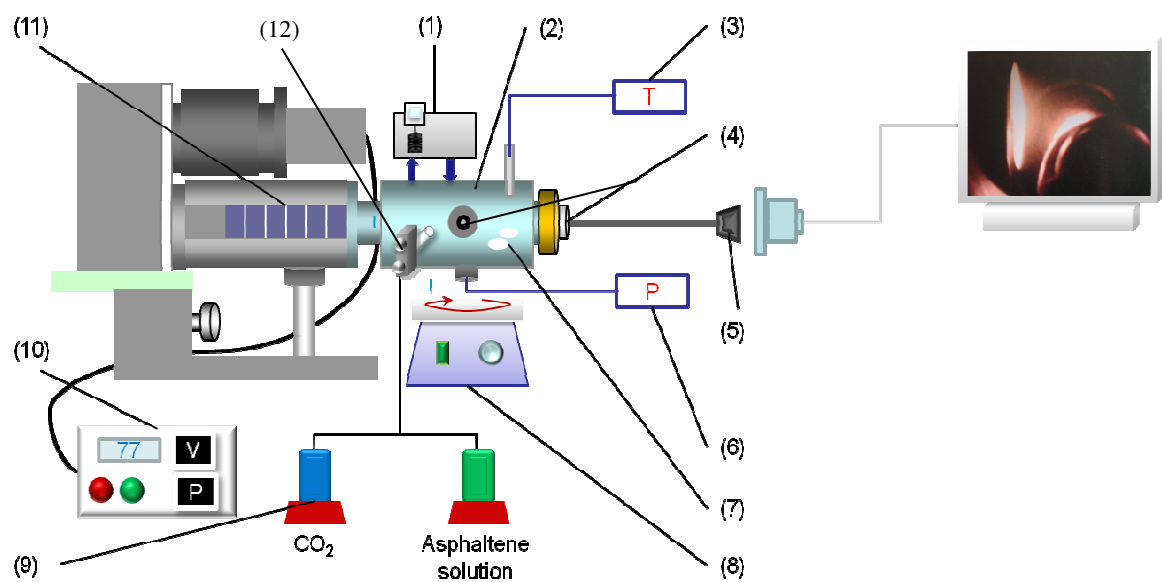41
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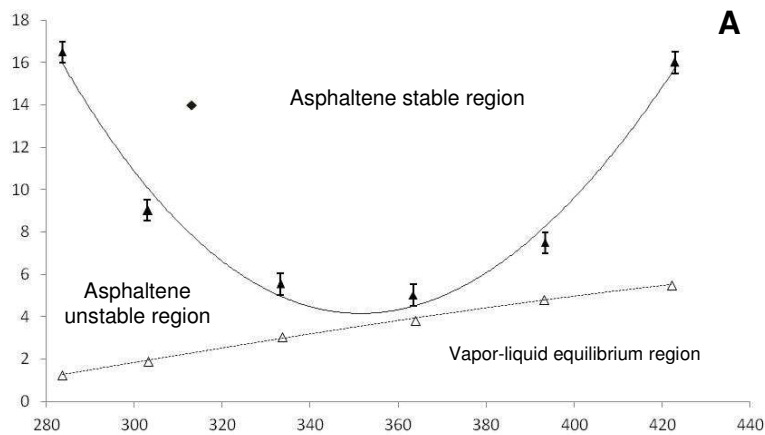51
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Figure Captions

Figure 1. Experimental setup: 1. Thermostat; 2. High-pressure cell; 3. Thermometer; 4. Sapphire windows; 5. Endoscope; 6. Pressure gauge; 7. Magnetic bars; 8. Magnetic stirrer; 9. High precision balance with CO_2 mini-cylinder; 10. Control panel; 11. Mobile piston and 12. Valves.

Figure 2. Asphaltene Phase Envelope (APE) for Furrial asphaltene solution (concentration: 0.04 wt%; solvent: toluene:n-heptane 6:4). Asphaltenes onset points (filled symbols,) and bubble points (open symbols). A) 10 wt% CO_2, B) 15 wt% CO_2 and C) 20 wt% CO_2.

Figure 3. Variation of the solubility parameter of toluene, n-heptane and CO_2 with pressure at 303 K, theoretically calculated using the equation of state of Peng Robinson.

Figure 4. Variation of the solubility parameters of CO_2 and Furrial asphaltenes with temperature using the equation of state of Peng Robinson.

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