



UNIVERSIDADE ESTADUAL DE CAMPINAS
SISTEMA DE BIBLIOTECAS DA UNICAMP
REPOSITÓRIO DA PRODUÇÃO CIENTÍFICA E INTELLECTUAL DA UNICAMP

Versão do arquivo anexado / Version of attached file:

Versão do Editor / Published Version

Mais informações no site da editora / Further information on publisher's website:

<https://pubs.acs.org/doi/10.1021/ef501488d>

DOI: 10.1021/ef501488d

Direitos autorais / Publisher's copyright statement:

©2014 by American Chemical Society. All rights reserved.

DIRETORIA DE TRATAMENTO DA INFORMAÇÃO

Cidade Universitária Zeferino Vaz Barão Geraldo

CEP 13083-970 – Campinas SP

Fone: (19) 3521-6493

<http://www.repositorio.unicamp.br>

CO₂ and Temperature Effects on the Asphaltene Phase Envelope As Determined by a Quartz Crystal Resonator

F. M. R. Cardoso,^{*,†,‡,§} H. Carrier,[†] J.-L. Daridon,[†] J. Pauly,[†] and P. T. V. Rosa[‡]

[†]Laboratoire des Fluides Complexes et Leurs Réservoirs, UMR 5150, Université de Pau et des Pays de l'Adour, Pau, France

[‡]Instituto de Química, Universidade Estadual de Campinas, Campinas, Brazil

[§]Centro de Pesquisas e Desenvolvimento Leopoldo Américo Miguez de Mello, PETROBRAS/CENPES, Rio de Janeiro, Brazil

ABSTRACT: Knowledge of the asphaltene phase envelope (APE) is crucial for oil companies, especially when enhanced oil recovery is applied. An innovative quartz crystal resonator (QCR) technique was employed to assess the phase behavior of asphaltene under reservoir conditions. The effect of CO₂ injection coupled to temperature changes on the APE of a recombined oil with a very low asphaltene content (0.235% w/w of C7 asphaltene in dead oil) are reported. It has been shown that QCR is an appropriate and highly sensitive nondestructive experimental technique for detecting asphaltene flocculation. Pressure onsets were found to be dependent on the depressurization rate.

■ INTRODUCTION

The International Energy Agency has indicated that 53.7% of the world energy matrix in 2011 came from the use of oil and natural gas.¹ The growing demand for these fluids requires the incorporation of new reserves situated in increasingly remote locations. In addition to the discovery of new reserves, in order to meet oil demand it is essential to ensure operational continuity of its production.

In view of the fact that oil composition is very complex,² the complete determination of its constituents is virtually impossible. Therefore, compositional characterization is conducted by fractionation of oil in predefined chemical families. The most widely applied method is SARA fractionation, which consists of separating the oil into four fractions, namely, saturates, aromatics, resins, and asphaltenes.³ The fractions of saturated and aromatic compounds have well-defined chemical structures. The distinction between resins and asphaltenes comes from the difference in their solubilities in certain solvents. The fraction of resins is soluble in light alkanes such as pentane and heptane. Asphaltenes are defined as the fraction that is insoluble in light aliphatics such as pentane and heptane but soluble in aromatic solvents such as toluene.⁴

The complex structure of asphaltenes allows the existence of intra- and intermolecular interactions that can result in aggregate formation. The interactions between asphaltene molecules occur mainly through π - π stacking, which can cause asphaltene destabilization and consequently particle formation.⁵

From the perspective of oil production, two main factors destabilize the asphaltenic fraction: (i) the depressurization that occurs during the production of fluids and (ii) the injection of gas for enhanced oil recovery purposes.⁶ Under reservoir conditions, the various fractions that compose the fluid are in thermodynamic equilibrium. As oil is lifted from the reservoir to the surface, the pressure and temperature decrease. These changes disrupt the equilibrium between the fractions present in the fluid. Solid phases can appear, and deposition might

happen in the pores of the reservoir, in the well, in the pipelines, or in surface equipment, decreasing oil production.⁷

The oil depressurization during the lift process from the reservoir to the surface may cause destabilization of the previously stable asphaltene and consequently its precipitation and deposition. This destabilization might occur because of the increment of the molar volume of oil light fractions,⁸ which are more compressible than the others. The increased ratio of volume occupied by light fractions can be high enough to reduce the solvency of the oil toward the asphaltenes, destabilizing them.⁹ The injection of carbon dioxide^{10–12} or natural gas into the reservoir to enhance oil recovery can destabilize the asphaltenes as a result of the increasing molar fraction of lightweight components in the oil, which also minimizes the oil solvency toward the asphaltenic fraction.

To ensure oil production, it is of paramount importance to understand the phase behavior of produced fluids with the intention of predicting and preventing deposition of solids. Knowledge of the asphaltene phase envelope (APE) is crucial for oil companies in order to avoid flow assurance problems, especially when enhanced oil recovery is applied. As reported in the open literature, asphaltene deposition and flow restrictions are often observed in fields producing light oils with a low asphaltene content.^{7,13} In such cases, the small amount of particles to be detected, the complexity of asphaltene flocculation phenomena, and the high-pressure conditions make determination of the APE very challenging.

In this context, the aim of the present work was to better understand the phase behavior of these complex systems under conditions representative of those encountered in reservoirs, as assessed by an innovative quartz crystal resonator (QCR) technique, since it has been recently reported¹⁴ to be very sensitive for the detection of asphaltene flocculation under atmospheric conditions. Quartz-crystal-based techniques have

Received: July 3, 2014

Revised: October 17, 2014

Published: October 21, 2014



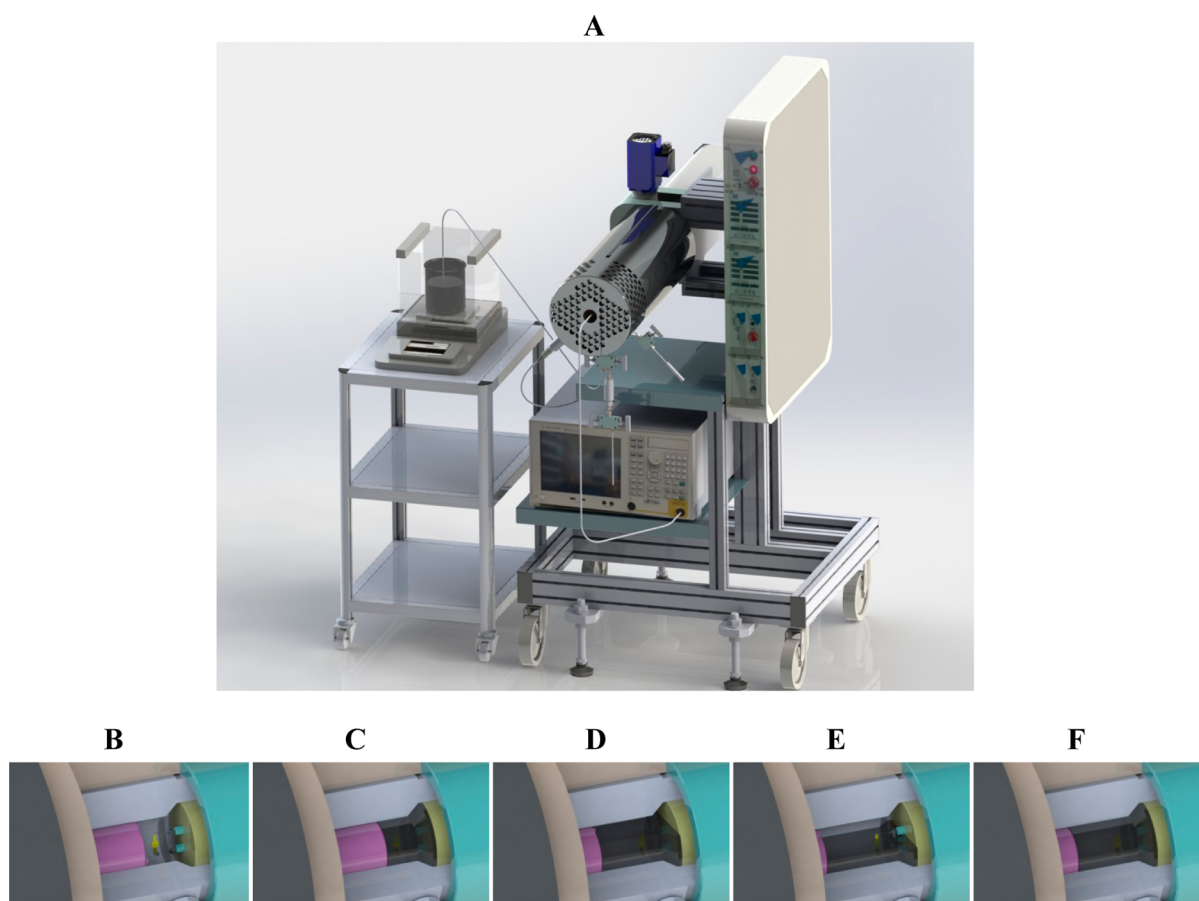


Figure 1. Schematic of the experimental setup to perform QCR experiments. (A) Full view showing the pump, network analyzer, and analytical balance. (B–F) Internal views of the pump showing (B) vacuum, (C) oil transfer by the gravitational effect, (D) injection of methane, (E) injection of carbon dioxide, and (F) the monophasic system pressurized at 70.0 MPa.

been widely applied to study the adsorption, precipitation, and deposition of asphaltenes, especially under ordinary conditions. Using a quartz crystal microbalance with dissipation (QCM-D), Abudu and Goual¹⁵ found that asphaltenes adsorb onto the surface of a QCR even in toluene solutions, suggesting that this sensor is sensitive to asphaltene detection. Farooq et al.¹⁶ studied the desorption of asphaltenes from silica-coated quartz crystal surfaces using saline aqueous solutions. They noticed that desorption from the sensor occurred in solutions with high ionic strength because of repulsion between negatively charged sites acquired at the silica and at the asphaltenes. Tavakkoli et al.¹⁷ carried out QCM-D experiments to evaluate asphaltene deposition in different depositing environments using model oil systems and varying the solvent, temperature, surface, and flow rate, showing several possibilities to apply the QCM-D or QCR technique in order to study asphaltenes. In this work, the innovative developed QCR technique was applied to determine the effect of CO₂ injection onto the APE of a recombined oil, a dead oil with 51.0 mol % CH₄ and 8.0 mol % CO₂ containing a very low asphaltene amount (0.235% w/w C7 asphaltenes in dead oil).

EXPERIMENTAL SECTION

Sample Preparation. The samples were prepared from a Brazilian dead oil (DO). Methane (Linde) and carbon dioxide (Messer) having 99.9995% and 99.99% purity, respectively, were used in the experiments.

All of the samples evaluated were prepared directly inside the syringe pump employed in the tests (Sanchez Technologies, Stigma 300) (Figure 1A). The pump had a work volume of 300 mL and was able to reach a pressure of 100 MPa. Heating was carried out by electrical resistance. A resistive sensor (Pt 100) was in contact with the metallic body of the pump, allowing temperature control during the experiments. The piston of the pump contained a stirring system that allowed the samples to be prepared inside the pump, as described by the following procedure:

- (i) The pressure inside the pump was reduced (Figure 1B) with the aid of a vacuum pump.
- (ii) Oil was injected into the pump (Figure 1C) by the effect of gravity. The mass of transferred dead oil was measured by difference with an analytical balance (Mettler Toledo XP5003S).
- (iii) Transfer of methane (Figure 1D) and carbon dioxide (Figure 1E) inside the syringe pump was carried out by injection of the gases, which were confined in 1 L pressurized bottles. The mass of the gas injected was measured by difference using an analytical balance (Mettler Toledo XP5003S).
- (iv) The system was pressurized to 70.0 MPa (Figure 1F), and the temperature was adjusted to 353.15 K. Before the tests were started, the mixture was kept stirring at 1600 rpm for 24 h.
- (v) The prepared single-phase samples were used in experiments to determine the asphaltene onset.

In order to ensure that samples were prepared as single-phase ones and to check for the absence of solids, an isobaric filtration at the sample preparation pressure was carried out after 24 h of homogenization. To check for complete gas solubilization, during the depressurization process the pressure-versus-volume curve for the

system was evaluated, and a fluid with low compressibility was observed.

Four distinct sample compositions were obtained from DO. A recombined oil was prepared with well-defined chemical composition: 51.0 mol % methane, 41.0 mol % DO (molecular weight depicted in Table 1), and 8.0 mol % carbon dioxide. From the recombined oil,

Table 1. Physicochemical Properties of Brazilian Dead Oil (DO) Sample: Degassed Oil (Dead Oil) and Its Related Bottomhole Sample (Live Oil)

component	dead oil (mol %)	live oil (mol %)
sample content (mol %)		
CO ₂	–	8.24
N ₂	–	0.37
CH ₄	–	51.29
C ₂ H ₆	–	7.07
C ₃ H ₈	0.73	4.87
<i>i</i> -C ₄ H ₁₀	0.37	0.90
<i>n</i> -C ₄ H ₁₀	1.11	1.79
<i>i</i> -C ₅ H ₁₂	0.89	0.59
<i>n</i> -C ₅ H ₁₂	1.56	0.86
C ₆₊	95.34	24.02
molecular weight (g mol ⁻¹)	268	85
API	27.69	–
asphaltene content (% w/w)	0.235	–

other three samples were obtained by keeping the DO/CH₄ molar ratio constant and varying the amount of CO₂ injected into the mixture. This procedure aimed to evaluate the effect of adding carbon dioxide on the stability of the asphaltenic fraction under conditions similar to those found during oil production.

Asphaltene Onset Determination. Tests carried out with the QCR aimed to determine the thermodynamic conditions under which spontaneous asphaltene precipitation occurs at constant temperature during a rate-controlled depressurization ramp.

The QCR technique requires monitoring of the resonance frequency (f_n) and bandwidth ($2\Gamma_n$)¹⁸ of a quartz crystal resonator immersed in the sample. For such investigations, a new experimental device was specially designed and built. It consisted of an automatic variable-volume high-pressure pump in which a quartz crystal was placed vertically (Figure 1A). The sensor was a polished 13 mm diameter AT-cut quartz crystal resonator plate with a fundamental resonance frequency of 3 MHz (International Crystal Manufacturing Co.) on which electrodes were assembled by gold coating on both sides. The electrical responses of the QCR were collected using a network analyzer (Agilent E5071C) during rate-controlled isothermal depressurizations. For each odd overtone n of the resonator, the network analyzer processed 1601 points, allowing the determination of the maximum frequency (f_n) and the bandwidth ($2\Gamma_n$) of the oscillation peak. The vertical division of the oscillation peak into two parts through its maximum provided, at half-height, the parameters named left dissipation or left half-band half-width ($\Gamma_{n,left}$) and right dissipation or right half-band half-width ($\Gamma_{n,right}$).

The first test with the QCR was performed with a reference oil whose asphaltenic behavior was previously studied by isobaric filtration. This test was carried out by logging both f_n and $\Gamma_{n,left}$ of the quartz crystal odd overtones from the fundamental to the seventh one during a rate-controlled depressurization. The test with the reference oil was conducted at 333.15 K over the pressure range of 10.0 to 40.0 MPa using depressurization rate of -0.100 MPa·min⁻¹.

For the samples prepared from DO, the initial pressure of all tests was 70.0 MPa. The final pressure depended on the bubble point of the system. At least two tests were performed at constant temperature using a depressurization rate of -0.100 MPa·min⁻¹. The pressurization or depressurization of the fluid was achieved by positive or negative displacement of the piston, in which a mechanical stirrer was inserted

to ensure fluid homogenization. All of the tests were carried out using a stirring speed of 1600 rpm.

Furthermore, to assess the effect of the depressurization rate of the fluid on the asphaltene onset value, some tests were performed at 318.15 K with the fluid containing 31.0 mol % CO₂. The evaluated rates were -0.025 , -0.050 , -0.100 , -0.200 , and -0.500 MPa·min⁻¹.

At the end of depressurization, the system was repressurized to 70.0 MPa at the same temperature of evaluation and kept under these conditions for 24 h to ensure gas and asphaltene redissolution. During sample restoration, f_n and $\Gamma_{n,left}$ for the third harmonic were monitored until they reached the same initial values presented before performing depressurization tests. It was found that 24 h was enough for both f_n and $\Gamma_{n,left}$ to reach their initial values. After the sample restoration, a new depressurization ramp was restarted.

Isobaric Filtration. In order to check that the QCR technique was assessing asphaltene onset pressures in a reliable way, isobaric filtrations¹⁹ were carried out with the fluid containing 31.0 mol % CO₂ at 331.85 K simultaneously to QCR asphaltene onset evaluation.

Before the isobaric filtrations were performed, the entire system outside of the syringe pump was pressurized with N₂ (Linde, 99.995%). A manual pump was employed for nitrogen pressurization. To prevent nitrogen injection into the evaluated sample, a small pressure difference (around 0.5 MPa) between the fluid in the syringe pump and the N₂ was employed. Under isobaric conditions, 1.5 mL of the aforementioned sample was filtered through a sintered stainless steel filter element (SWAGelok, SS-2F-K4-05) with a nominal pore size of 0.5 μm. After the filtering process, the filter element was disconnected and submitted to visual evaluation.

An initial isobaric filtration was performed at 70.0 MPa in order to check that no solids were previously precipitated in the sample. Two other pressures were evaluated. The first one was the same pressure that QCR signaled as the asphaltene onset. The following filtration was performed 4.0 MPa below the former, a thermodynamic condition expected to be more severe to asphaltene precipitation than the previous one. In the case of the latter, isobaric filtrations were carried out at time intervals of 3 h.

RESULTS AND DISCUSSION

Fluid Characterization. The amounts of methane and carbon dioxide injected in order to obtain the four different samples were calculated on the basis of the DO composition obtained from the physicochemical properties of the degassed fluid (dead oil) and its related monophasic sample (live oil), as shown in Table 1.

The samples were prepared from DO to emulate the physicochemical properties of its related bottomhole samples by incorporation of carbon dioxide and methane to the former. The other lightweight components (C₂H₆, C₃H₈, *i*-C₄H₁₀, and *n*-C₄H₁₀) were not added in the recombination procedure, as the intention was just to work with pressurized samples. In the four different samples prepared from DO (Table 2) the DO/methane molar ratio was kept constant while only the molar concentration of carbon dioxide was varied. The sample named “recombined oil” mimics the related DO live oil. The other three samples emulated the influence of carbon dioxide

Table 2. Four Different Samples Prepared from a Brazilian Dead Oil (DO)

sample name	molar composition (mol %)		
	DO	CH ₄	CO ₂
Recombined Oil	41.0	51.0	8.0
Excess of 10.0% of CO ₂	36.9	45.9	17.2
Excess of 20.0% of CO ₂	32.8	40.8	26.4
Excess of 25.0% of CO ₂	30.7	38.3	31.0

injection into live oil and its effects on asphaltene phase behavior.

Tests with a Reference Oil. Scanning tests to determine f_n and $\Gamma_{n,\text{left}}$ were carried out from the fundamental up to the seventh oscillation overtone during a depressurization of a reference oil (Table 3).

Table 3. Properties of the Reference Oil

API gravity	saturates (wt %)	aromatics (wt %)	resins (wt %)	asphaltenes (wt %)
21	42	34	18	7

Preliminary studies using a mixture of the reference oil with 19.0 wt % CO₂, conducted by isobaric filtrations, showed that asphaltene onset at 333.15 K would take place around 22.0 MPa.²⁰ Two types of depressurization experiments were conducted with the reference oil. The first one was carried out with the pure reference oil. The second type was performed with a mixture of the reference oil and CO₂. The results of both tests with the reference oil are summarized in Figure 2.

As depicted in Figure 2, for the curves obtained from the mixture containing the reference oil and CO₂ compared with the curves for the pure reference oil, it was observed that both f_n and $\Gamma_{n,\text{left}}$ experienced deviations well above 22.0 MPa (negative slope for f_n and positive for $\Gamma_{n,\text{left}}$), suggesting a previously underestimated onset value obtained by the isobaric filtration technique.²⁰ As expected,^{15,21} precipitated asphaltenes adsorbed onto the gold surface coating the quartz crystal, causing f_n shifts. This observation is consistent with the idea that the QCR technique is sensitive to asphaltene precipitation,

considering that the formation of asphaltene particles from a sample previously evaluated by isobaric filtrations was also assessed by this technique. For the tests with the pure reference oil, a linear approximation can fit very well the decrease in f_n as a function of pressure (Figure 2A,C,E). For Newtonian fluids, at a constant temperature and moderate pressures (25.0–100.0 MPa), the viscosity–density product has a linear dependence on pressure, as verified for some aliphatic hydrocarbons such as pentane, hexane, and heptane.²² The linear approximation observed in Figure 2A,C,E is explained by the Kanazawa–Gordon equation,²³ which assumes that for a Newtonian fluid the shift in the resonance frequency of a quartz crystal is directly proportional to the fluid density (ρ_{fluid}) and viscosity (η_{fluid}), as shown in eq 1:

$$\Delta f_n = -\sqrt{n} \frac{f_0^{3/2}}{\sqrt{\pi\mu_q\rho_q}} \cdot \sqrt{\rho_{\text{fluid}}\eta_{\text{fluid}}} \quad (1)$$

where f_0 is the fundamental resonance frequency of the quartz resonator under vacuum, ρ_q and μ_q are the density and the shear modulus of quartz, respectively, and n is the overtone number under evaluation. The pressure variation of the parameters μ_q and ρ_q may be neglected.¹⁸

As depicted in Figure 2B,D,F, for the pure oil, which might behave as a Newtonian fluid, it is possible to verify that $\Gamma_{n,\text{left}}$ increased linearly as a function of pressure, as described by eq 2:²⁴

$$\Delta\Gamma_n = +\sqrt{n} \frac{f_0^{3/2}}{\sqrt{\pi\mu_q\rho_q}} \cdot \sqrt{\rho_{\text{fluid}}\eta_{\text{fluid}}} \quad (2)$$

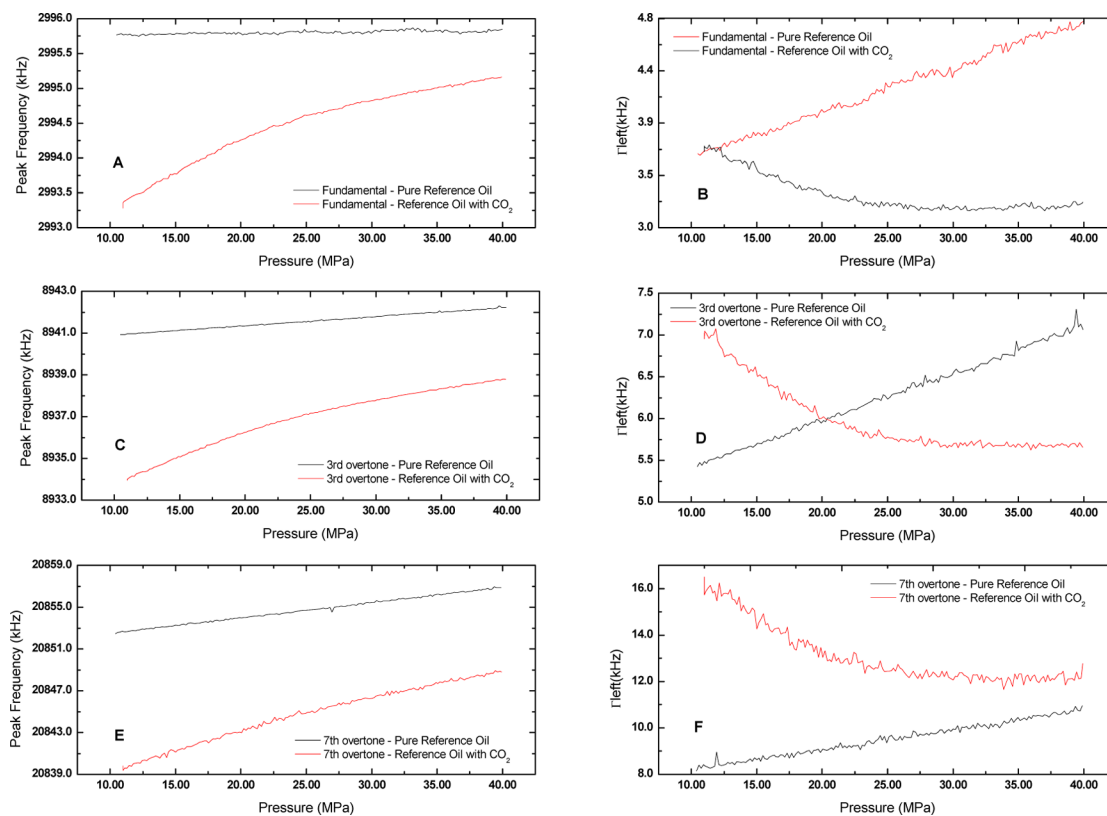


Figure 2. QCR responses during depressurization of pure reference oil and its mixture with 19.0 wt % CO₂ at 333.15 K. Shown are (A, C, E) peak frequencies and (B, D, F) left half-band half-widths from (A, B) the fundamental, (C, D) the third overtone, and (E, F) the seventh overtone.

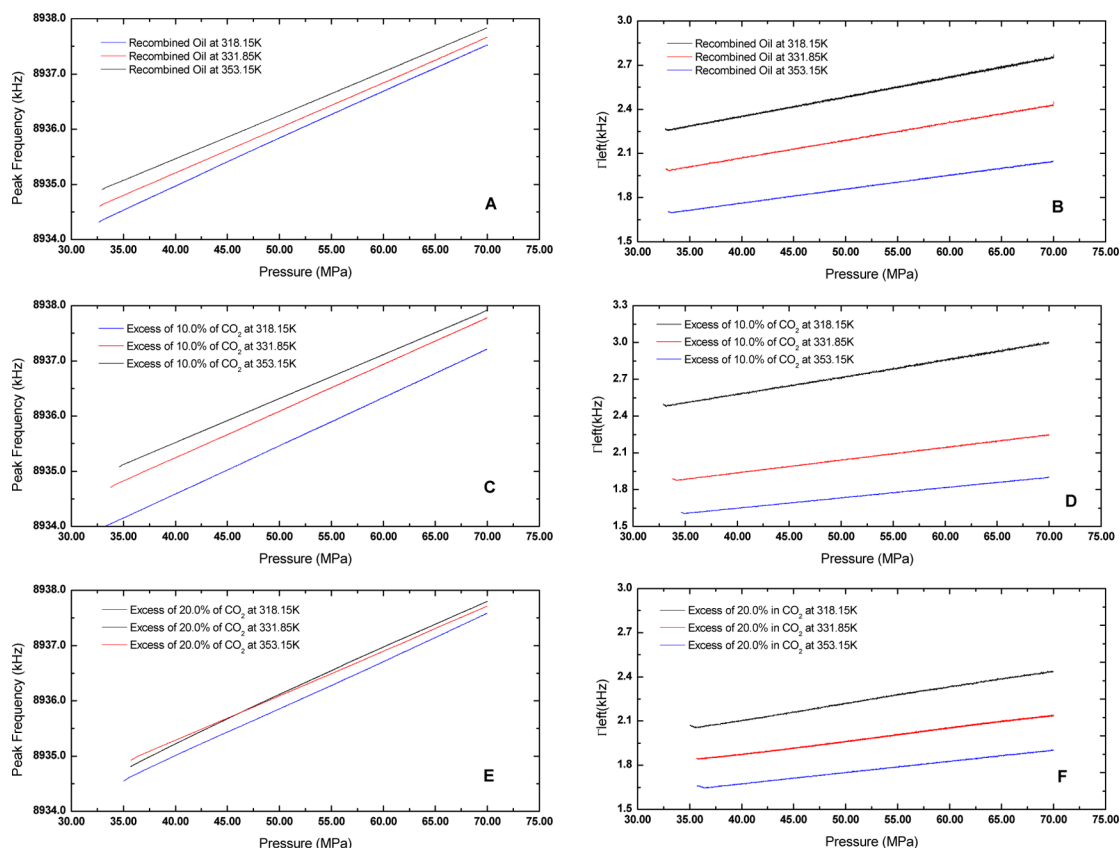


Figure 3. QCR third overtone responses obtained during isothermal depressurizations of three different samples. Shown are (A, C, E) peak frequencies and (B, D, F) left half-band half-widths from the following samples: (A, B) Recombined Oil, (C, D) Excess of 10.0% of CO_2 , and (E, F) Excess of 20.0% of CO_2 .

It was observed that a deviation from Newtonian behavior occurred around expected onset value for the reference oil. This suggested that solid adsorption onto the quartz crystal and rheological changes in the fluid were suitable to cause deviations in both f_n and $\Gamma_{n,\text{left}}$, allowing the piezoelectric sensor to assess asphaltene precipitation. Daridon et al.¹⁸ showed that f_n changes during asphaltene onset determination by titration of dead oils are due to both a significant change in solution viscosity and an adsorption increase, while $\Gamma_{n,\text{left}}$ changes are related only to increases in the solution's viscosity. The first results were analyzed, and it was found that the acquisition of the parameters f_n and $\Gamma_{n,\text{left}}$ for the third overtone were sufficient to determine the asphaltene onset. $\Gamma_{n,\text{left}}$ evaluation was more accurate to detect this onset, taking into account the fact that asphaltene adsorption does not change $\Gamma_{n,\text{left}}$ values. It is important to note that wax precipitation can also lead to an erroneous evaluation of asphaltene onset, since the viscosity of the system increases a lot when waxes are formed. For this reason, conditions near the wax appearance temperature were avoided for both oils studied.

Tests with Samples Prepared from DO. The following results are related to the tests carried out with the four samples obtained from DO, as described in Table 2. In contrast to the reference oil, DO presents a lower asphaltene content. The former contains 7.0% w/w asphaltenes, while the latter contains 0.235% w/w.

Figures 3 and 4A show f_n and $\Gamma_{n,\text{left}}$ for the third overtone of the quartz crystal employed in the experiments. These values were obtained during isothermal depressurizations at a rate of $-0.100 \text{ MPa}\cdot\text{min}^{-1}$. The temperatures evaluated for all of the

experiments were 318.15, 331.85, and 353.15 K. The evaluation was extended to 373.15, 393.15, and 413.15 K in the case of the sample containing 31.0 mol % CO_2 . No deviations from Newtonian behavior were observed for the recombined oils with 10.0% excess CO_2 and 20.0% excess CO_2 , according to the graphs plotted in Figure 3. This suggests that asphaltenes in these systems are stable under depressurization using a rate of $-0.100 \text{ MPa}\cdot\text{min}^{-1}$. It is important to mention that during the depressurization, the time for fluid homogenization at a given temperature (T) and pressure (P) was close to zero. However, it was not possible to ensure that no precipitation would occur if the system were allowed to rest at the same P and T conditions for a large period of time.

In Figure 4, related to the tests with the sample containing 31.0 mol % CO_2 , it is possible to note that there were deviations from linearity predicted by eqs 1 and 2. The pressure at which the deviation was observed for the $\Gamma_{3,\text{left}}$ linearity as a function of pressure was determined and taken as the asphaltene onset, as depicted in Figure 4B, for the case of depressurization at 318.15 K. To obtain this pressure, the depressurization curve was plotted using the software Table Curve 2D version 5.01. The curve was smoothed and fitted to a linear equation. A residual graph, constructed with the difference in percentage between experimental values and the values predicted by the linear fitting, was plotted. The first point that reached a residual value of 0.5% was taken as the asphaltene onset. Half-band half-width was preferred to indicate the asphaltene onset as it is pressure- and adsorption-independent while the peak frequency depends on the hydrostatic pressure and also the adsorbed mass.^{25,26} To

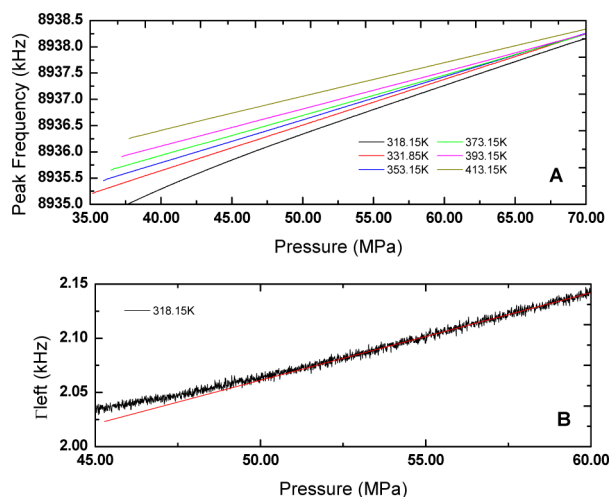


Figure 4. QCR third overtone responses obtained during isothermal depressurizations of the sample Excess of 25.0% of CO₂: (A) peak frequencies at several temperatures; (B) left half-band half-width variation obtained at 318.15 K.

determine the true thermodynamic stability boundary of the asphaltenic fraction, it would be necessary to evaluate the behavior of $\Gamma_{3,\text{left}}$ at a given P and T during a long time, an alternative that was experimentally infeasible.

The data obtained experimentally allowed the construction of the asphaltene phase envelope (Figure 5). Pressure–

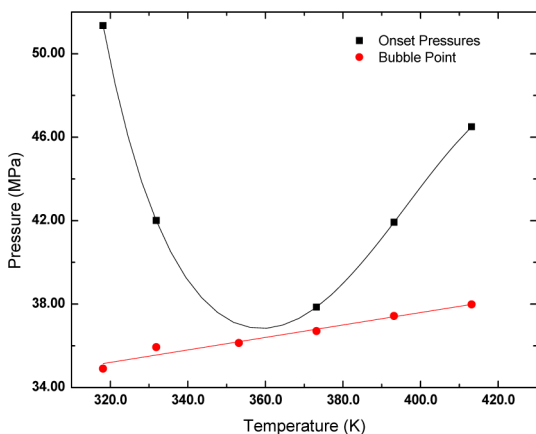


Figure 5. Asphaltene phase envelope obtained with the QCR technique during a $-0.100 \text{ MPa}\cdot\text{min}^{-1}$ depressurization for the mixture containing 31.0 mol % CO₂. Saturation pressures were acquired from the pressure–volume curve obtained during isothermal depressurizations.

temperature (P – T) pairs located above the asphaltene onset curve refer to the thermodynamic conditions under which there is a single-phase fluid. P – T pairs located between the asphaltene onset curve and the bubble point pressures refer to a two-phase region in which the solid fraction that comes out of solution is composed of asphaltenes. The black line drawn in Figure 5 is a hypothetical curve for the asphaltene phase behavior, added just to guide the eyes. No thermodynamic model was applied to obtain it. The curve minimum region might not be the real minimum for the evaluated fluid. When this is taken into account, it should be noted that for the fluid containing 31.0 mol % CO₂, lower temperature leads to a greater asphaltenic instability region, suggesting that under

these conditions there might be a decrease in oil solvency power toward the asphaltene fraction. Additionally, it is interesting to note that for the depressurization rate evaluated, it was not possible to determine the asphaltene onset pressure at 353.15 K. Perhaps its value is very close to the bubble point of the system, resulting in a very short time within the region of instability that was insufficient for growth of asphaltene particles. If qualitative behavior like that shown by the black line is assumed, according to Figure 5 there is an inversion of stability around 360 K. Up to this temperature, heating the system leads to asphaltene stability, similar to the behavior of a polymer solution with an upper critical solution temperature (UCST).²⁷ After 360 K, increasing the temperature leads to asphaltene instability, similar to the behavior of a polymer solution with a lower critical solution temperature (LCST).²⁷ The solvency of the oil toward the asphaltene fraction depends on P and T . When the pressure is kept constant, the system might exhibit a UCST or an LCST, depending on the temperature range.

The QCR technique is also able to assess the amount of asphaltenes adhered to the sensor. With knowledge of the density and the viscosity variation of the fluid, it is possible to apply the same strategy developed by Abudu and Goual.¹⁵ With both pieces of information, a predicted value for f_n can be calculated. Any changes in the predicted oscillation frequency might be associated with asphaltenes adhered to the quartz crystal surface. The sensor oscillates at lower frequencies when asphaltenes adhere to the quartz crystal. In a next step of our work, density and viscosity measurements at high pressure might be performed to obtain the mass of asphaltenes adhered to the piezoelectric sensor.

Isobaric Filtration. The isobaric filtration technique aims to assess asphaltene instability under certain pressure, temperature, and composition conditions by checking for particle formation.¹³ In addition, the instability result is also function of time and particle size. The presence of solids on the filter element indicates that the asphaltenic fraction is unstable within the fluid under the filtration conditions (elapsed time, temperature, pressure, composition, and minimum size of the entrapped particle).

The results obtained from isobaric filtration tests using sintered stainless steel filter elements with a nominal pore size of $0.5 \mu\text{m}$ are summarized in Table 4. According to these

Table 4. Isobaric Filtration with the Fluid Containing 31.0 mol % CO₂

pressure (MPa)	elapsed time (h)	results ^a
70.0	0	stable
42.0	0	stable
38.0	0	stable
38.0	3	stable
38.0	6	unstable

^aTests were performed at 331.85 K.

results, asphaltenes were stable under the initial conditions (70.0 MPa), in agreement with the QCR results. At 331.85 K, the QCR technique detected an asphaltene onset at 42.0 MPa. An isobaric filtration performed at the same pressure did not detect any asphaltene precipitation. It is important to note that filtration was carried out simultaneously with QCR measurements. This suggests that QCR is much more sensitive to asphaltene onset detection than isobaric filtration. As previously

reported by Hoepfner et al.,²⁸ deposition tests such as QCR are much more sensitive to phase separation compared with visual techniques. Techniques that allow detection on the submicron scale are able to assess the destabilization of a small fraction of asphaltenes,²⁹ the highly unstable ones. Another three filtrations were carried out at 38.0 MPa, conditions under which QCR signals suggested reasonable asphaltene precipitation. The first filtration, which was performed promptly after depressurization, and the second one, carried out 3 h after pressure holding, did not show any solid formation. Asphaltenes were detected in the last filtration after 6 h of pressure holding, corroborating that kinetics plays an important role in asphaltene precipitation. To be visually detected, particles with diameter larger than 0.5 μm might be collected in the filter pores, allowing solid layers to build up on the filter surface. These results suggest that QCR is able to detect particles smaller than 0.5 μm , anticipating solid detection during a real-time depressurization.

Effect of Depressurization Rate of the Fluid on the Asphaltene Onset Value. The effect of the depressurization rate on the asphaltene onset value was investigated at 318.15 K with the fluid containing 31.0 mol % CO_2 using the following rates: -0.500 , -0.200 , -0.100 , -0.050 , and -0.025 $\text{MPa}\cdot\text{min}^{-1}$. In order to check the repeatability of the technique, three repetitions at 318.15 K applying a depressurization rate of -0.500 $\text{MPa}\cdot\text{min}^{-1}$ were carried out, in which the onset values found were 46.87, 46.19, and 47.13 MPa.

According to Figure 6, the higher the depressurization rate, the lower the onset value obtained. These results show that

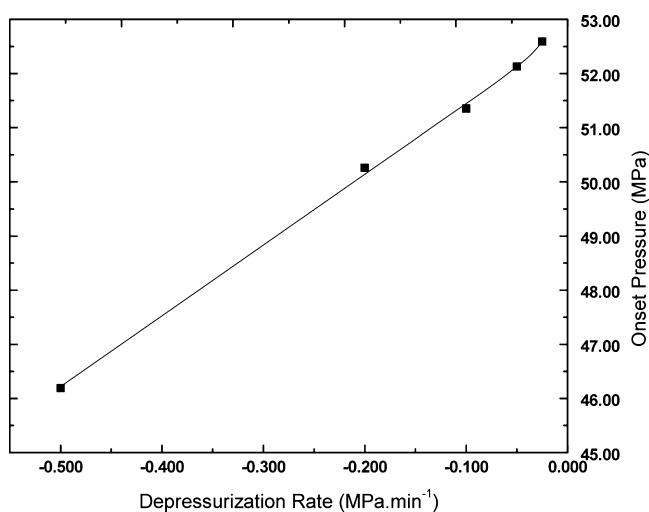


Figure 6. Effect of depressurization rate on asphaltene onset value. All of the data were obtained from the mixture containing 31.0 mol % CO_2 at 318.15 K.

asphaltene precipitation is rate-dependent and consequently time-dependent.³⁰ The asphaltene onset pressure versus depressurization rate curve was well-fit by an exponential function. If the system reaches a metastable condition, the analytical technique employed to determine the onset value will have enough time to detect the particle formation in the case of decreasing depressurization rate. The time between mechanical and thermal stability and particle detection by the experimental method employed is called the induction time.³¹ In this way, keeping the system resting for longer periods at a given P and T in a metastable region might allow the induction time to be

reached, allowing the technique to detect the appearance of particles earlier. Performing asphaltene onset tests at different depressurization rates and subsequent extrapolation to zero would virtually provide to the system an infinite time for particle formation, thus allowing a boundary closer to the true thermodynamic stability to be obtained. The extrapolated asphaltene onset obtained by an exponential approximation was 52.89 MPa, in contrast to the value of 46.19 MPa found during depressurization at -0.500 $\text{MPa}\cdot\text{min}^{-1}$, both at 318.15 K. On the other hand, according to Figure 6, the onset value found at 318.15 K using a depressurization rate of -0.100 $\text{MPa}\cdot\text{min}^{-1}$ was 51.35 MPa, differing from the expected thermodynamic onset by 2.9%. This observation is important to ensure the reliability of the data in Figure 5, in which all the depressurization tests were performed at -0.100 $\text{MPa}\cdot\text{min}^{-1}$.

CONCLUSIONS

It has been shown that QCR is an appropriate and highly sensitive nondestructive experimental technique for detecting asphaltene flocculation. A mixture containing a Brazilian dead oil with 38.3 mol % CH_4 and 31.0 mol % CO_2 showed asphaltene precipitation during depressurization from 70.0 to 42.0 MPa. In the temperature range from 308 to 353 K, the increase in temperature promotes asphaltene stability. On the other hand, the region of asphaltene stability decreases in the temperature range from 360 to 420 K. The pressure onset was found to be dependent on the depressurization rate. Lower depressurization rates resulted in higher asphaltene onset values. The obtained results confirmed that kinetics is a key factor if one wants to provide reliable onset data.

AUTHOR INFORMATION

Corresponding Author

*E-mail: fmauro@petrobras.com.br.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors acknowledge PETROBRAS for providing samples of dead oil.

ABBREVIATIONS

APE = asphaltene phase envelope
 DO = dead oil
 P = pressure
 QCR = quartz crystal resonator
 T = temperature
 w/w = weight/weight

REFERENCES

- (1) International Energy Agency. 2011 Key World Energy Statistics. http://www.iea.org/publications/freepublications/publication/key_world_energy_stats-1.pdf (accessed Aug 27, 2012).
- (2) Speight, J. G. *The Chemistry and Technology of Petroleum*, 3rd ed.; CRC Press: New York, 1999; pp 215–241.
- (3) Fan, T.; Buckley, J. S. Rapid and Accurate SARA Analysis of Medium Gravity Crude Oils. *Energy Fuels* **2002**, *16*, 1571–1575.
- (4) Andersen, S. I.; Speight, J. G. Petroleum resins separation, character, and role in petroleum. *Pet. Sci. Technol.* **2001**, *19*, 1–34.
- (5) Durand, E.; Clemancey, M.; Lancelin, J.-M.; Verstraete, J.; Espinat, D.; Quoineaud, A.-A. Effect of Chemical Composition on Asphaltene Aggregation. *Energy Fuels* **2010**, *24*, 1051–1062.

- (6) Hammami, A.; Phelps, C. H.; Monger-McClure, T.; Little, T. M. Asphaltene Precipitation from Live Oils: An Experimental Investigation of Onset Conditions and Reversibility. *Energy Fuels* **2000**, *14*, 14–18.
- (7) Guo, B.; Song, S.; Chacko, J.; Ghalambor, A. Flow Assurance. In *Offshore Pipelines*; Gulf Professional Publishing: Burlington, VT, 2005; Chapter 15, pp 169–214.
- (8) Zekri, A. Y.; Almehaideb, R. A. A Novel Technique To Treat Asphaltene Deposition in Carbonate Rocks. *Soc. Pet. Eng. J.* **2001**, DOI: 10.2118/68766-MS.
- (9) Joshi, N. B.; Mullins, O. C.; Jamaluddin, A.; Creek, J.; McFadden, J. Asphaltene Precipitation from Live Crude Oil. *Energy Fuels* **2001**, *15*, 979–986.
- (10) Vargas, F. M.; Gonzalez, D. L.; Hirasaki, G. J.; Chapman, W. G. Modeling Asphaltene Phase Behavior in Crude Oil Systems Using the Perturbed Chain Form of the Statistical Associating Fluid Theory (PC-SAFT) Equation of State. *Energy Fuels* **2009**, *23*, 1140–1146.
- (11) Gonzalez, D. L.; Vargas, F. M.; Hirasaki, G. J.; Chapman, W. G. Modeling of CO₂-induced asphaltene precipitation. *Energy Fuels* **2008**, *22*, 757–762.
- (12) Deo, M.; Parra, M. Characterization of Carbon-Dioxide-Induced Asphaltene Precipitation. *Energy Fuels* **2012**, *26*, 2672–2679.
- (13) Sarma, H. K. Can We Ignore Asphaltene in a Gas Injection Project for Light-Oils? *Soc. Pet. Eng. J.* **2003**, DOI: 10.2118/84877-MS.
- (14) Daridon, J. L.; Cassiède, M.; Nasri, D.; Pauly, J.; Carrier, H. Probing Asphaltene Flocculation by a Quartz Crystal Resonator. *Energy Fuels* **2013**, *27*, 4639–4647.
- (15) Abudu, A.; Goual, L. Adsorption of Crude Oil on Surfaces Using Quartz Crystal Microbalance with Dissipation (QCM-D) under Flow Conditions. *Energy Fuels* **2009**, *23*, 1237–1248.
- (16) Farooq, U.; Sjöblom, J.; Øye, G. Desorption of Asphaltenes from Silica-Coated Quartz Crystal Surfaces in Low Saline Aqueous Solutions. *J. Dispersion Sci. Technol.* **2011**, *32*, 1388–1395.
- (17) Tavakkoli, M.; Panuganti, S. R.; Vargas, F. M.; Taghikhani, V.; Pishvaie, M. R.; Chapman, W. G. Asphaltene Deposition in Different Depositing Environments: Part 1. Model Oil. *Energy Fuels* **2014**, *28*, 1617–1628.
- (18) Daridon, J. L.; Cassiède, M.; Paillol, J. H.; Pauly, J. Viscosity Measurements of Liquids Under Pressure by Using the Quartz Crystal Resonators. *Rev. Sci. Instrum.* **2011**, *82*, No. 095114.
- (19) Verdier, S.; Carrier, H.; Andersen, S. I.; Daridon, J. L. Study of Pressure and Temperature Effects on Asphaltene Stability in Presence of CO₂. *Energy Fuels* **2006**, *20*, 1584–1590.
- (20) Castillo, J.; Canelon, C.; Acevedo, S.; Carrier, H.; Daridon, J. L. Optical Fiber Extrinsic Refractometer to Measure RI of Samples in a High Pressure and Temperature Systems: Application to Wax and Asphaltene Precipitation Measurements. *Fuel* **2006**, *85*, 2220–2228.
- (21) Zahabi, A.; Gray, M. R.; Dabros, T. Kinetics and Properties of Asphaltene Adsorption on Surfaces. *Energy Fuels* **2012**, *26*, 1009–1018.
- (22) NIST Chemistry WebBook. <http://webbook.nist.gov/chemistry> (accessed Aug 27, 2012).
- (23) Kanazawa, K. K.; Gordon, J. G. Frequency of a Quartz Microbalance in Contact with Liquid. *Anal. Chem.* **1985**, *57*, 1770–1771.
- (24) Muramatsu, H.; Tamiya, E.; Karube, I. Computation of Equivalent Circuit Parameters of Quartz Crystals in Contact with Liquids and Study of Liquid Properties. *Anal. Chem.* **1988**, *60*, 2142–2146.
- (25) Cassiède, M.; Daridon, J. L.; Paillol, J. H.; Pauly, J. Impedance analysis for characterizing the influence of hydrostatic pressure on piezoelectric quartz crystal sensors. *J. Appl. Phys.* **2010**, *108*, No. 034505.
- (26) Cassiède, M.; Daridon, J. L.; Paillol, J. H.; Pauly, J. Electrical behavior of a quartz crystal resonator immersed in a pressurized fluid (gas or liquid). *J. Appl. Phys.* **2011**, *109*, No. 074501.
- (27) Freeman, P. L.; Rowlinson, J. S. Lower critical points in polymer solutions. *Polymer* **1960**, *1*, 20–26.
- (28) Hoepfner, M. P.; Limsakoune, V.; Chuenmeechao, V.; Maqbool, T.; Fogler, H. S. A Fundamental Study of Asphaltene Deposition. *Energy Fuels* **2013**, *27*, 725–735.
- (29) Hoepfner, M. P.; Favero, C. V. B.; Haji-Akbari, N.; Fogler, H. S. The Fractal Aggregation of Asphaltenes. *Langmuir* **2013**, *29*, 8799–8808.
- (30) Maqbool, T.; Balgoa, A. T.; Fogler, H. S. Revisiting Asphaltene Precipitation from Crude Oils: A Case of Neglected Kinetic Effects. *Energy Fuels* **2009**, *23*, 3681–3686.
- (31) Kashchiev, D.; Firoozabadi, A. Induction time in crystallization of gas hydrates. *J. Cryst. Growth* **2003**, *250*, 499–515.