Tricritical phenomena in asphaltene/aromatic hydrocarbon systems

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The calculation of phase behavior performed for asphaltene-micelles systems that assume several forms when they are mixed with petroleum fluid depending on its aromaticity, and on the relative sizes and polarities of the particles present in such fluid mixtures, is extended to tricritical phenomena. Asphaltene monomers form micelles in the presence of excess amounts of aromatic hydrocarbons and polar solvents, and they are dispersed in a petroleum fluid. The coupling between the micellization and phase separation may, in principle, lead to a near-tricritical coexistence of a monomer phase and a micellar phase; however, this tricritical phenomenon has not been experimentally observed. In this report, such tricritical phenomenon for asphaltene / aromatic systems is predicted.

Keywords: Asphaltene–aromatic systems; phase separation; micellar solutions; tricritical points; second order phase transition.

El cálculo de la conducta de fase efectuado para sistemas de micelas de asfaltenos que supone varias formas cuando son mezclados con fluidos petroleros dependientes tanto de su aromaticidad como de los tamaños relativos y de las polaridades de las partículas presentes en tales mezclas de fluidos, es extendido al fenómeno tricrítico. Monómeros de asfaltenos forman micelas en la presencia de cantidades de hidrocarburos aromáticos en exceso y solventes polares, y están dispersados en un fluido petrolero. El acoplamiento entre la micelización y la separación de fase puede, en principio, llevar hacia una coexistencia tricrítica de una fase monómero y una fase micela; sin embargo, el fenómeno tricrítico no ha sido observado experimentalmente en soluciones de asfaltenos. En este reporte, se predice dicho fenómeno tricrítico para sistemas asfalteno / aromático.

Descriptores: Sistemas asfalteno-aromático; separación de fase; soluciones micelares; puntos tricríticos; transiciones de fase de segundo orden.

1. Introduction

Asphaltene is defined as the fraction of carbonaceous fossil energy sources (petroleum crude oil, coal, tar sand and oil shale). It is insoluble in low-boiling paraffin hydrocarbon solvents, such as methane, ethane, propane, etc. and soluble in aromatic hydrocarbons like benzene, toluene, and xylene. Such compounds as asphaltenes and resins are present in petroleum fluids in minute amounts, but in heavy oils and other fossil energy sources in insignificant quantities. In nature, it is hypothesized that asphaltenes are formed as a result of oxidation of natural resins. On the contrary, the hydrogenation of asphaltenic compounds (resins, asphaltenes and asphaltenic acids) may produce heavy hydrocarbon oils which contain polycyclic aromatic or hydroaromatic hydrocarbons. They differ, however, from polycyclic aromatic hydrocarbons due to presence of oxygen and sulfur in their structures in varied amounts [1,2]. On heating above 300-400°C, asphaltenes are not melted, but decompose, forming carbon and volatile products. Asphaltenes react with sulfuric acid forming sulfonic acids, as might be expected on the basis of the polyaromatic structure of these components. The dark-brown color of crude oils and residues is due to the combined effect of neutral resins and asphaltenes. The black color of some crude oils and residues is related to the presence of asphaltenes, which are not properly peptized.

Asphaltene after heating [3] are subdivided in: Non-volatile (heterocyclic N and S species), and, volatile (paraffin + olefins), benzenes, naphtalenes, phenanthrenes, several others). Speight [3] also reports a simplified representation of the separation of petroleum into the following six major fractions: volatile saturates, volatile aromatics, nonvolatile saturates, nonvolatile aromatics, resins and asphaltenes. He also reports arbitrarily defined physical boundaries for petroleum using carbon-number and boiling point. The molecular structures proposed for the asphaltene (heavy organic) molecules [4] includes carbon, hydrogen, oxygen, nitrogen, sulfur as well as polar and non-polar groups see Fig. 1.

It can be said that asphaltene particles are known to be polymeric and polydisperse. They behave lyophobic and steric, and they posses electrostatic and associative forces. Due to polydispersivity of asphaltenes, entropic effects are important in mixtures containing asphaltenes [5].

Asphaltene particles in crude oil assume various forms depending on the oil aromaticity, and on the other compounds present in the oil. Experimental observations have indicated that asphaltene monomers form micelles in the presence of certain concentrations of aromatic hydrocarbons, and the resulting micelles are dispersed in the petroleum fluid [6,7].

The behavior of asphaltenes in presence of excess amount of toluene can be analogous to the behavior of a surfactant in

presence of an oil-water mixture. Pacheco and Mansoori [5] proposed a model for the phase behavior of asphaltenes in aromatic hydrocarbons and could predict the conditions when different kinds of micelles may be formed in such mixtures. In the present paper we report our theoretical studies on the coupling between formation of asphaltene micelles and phase separation which may, in principle, lead to a near-tricritical coexistence of a monomer asphaltene phase and a micellar phase.

2. Background

Dickie and Yen [8], using X-ray diffraction studies on solid asphaltenes, proposed unitary sheets made up a system of highly condensed polinuclear aromatic ring with alkylical chains tied to the ring structure. They also proposed that the asphaltene association takes place through stacking of aromatic sheets due to $\pi - \pi$ interactions. These aggregates or particles were then proposed to associate into what was called micelles.

Several more investigators have established the existence of asphaltene micelles when there is an excess of aromatic hydrocarbons present in a crude oil [7,9-12]. Of course, the well-studied micelles known today are the kind, which are formed between water and oil in the presence of surfactants. Since asphaltene in oil has a large size distribution, investigators have concluded that the asphaltene micellar system is conceptually equivalent to an oil/many-surfactant/water system [13-15].

The existence of asphaltene micelles is confirmed by measurements of surface tension [6,15] and viscosity [7]. The data were also used to show that below the critical micelle concentration (*cmc*) with small concentrations, the as-
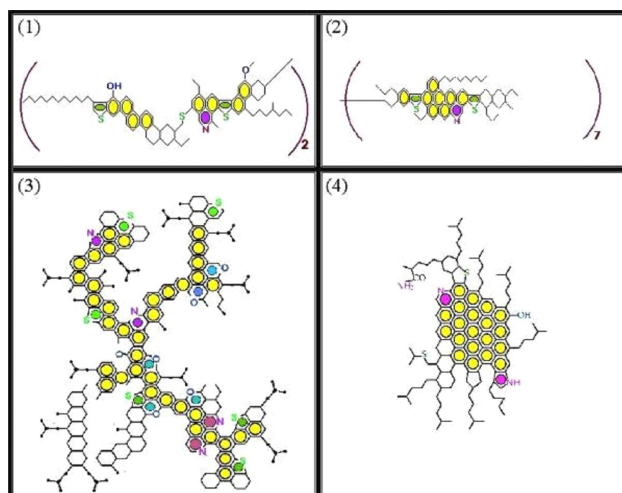

FIGURE 1. Molecular structures of asphaltenes derived from various sources. The asphaltene structures shown here are separated from asphaltene deposits consisting of asphaltene steric colloid flocs and encapsulated in them other compounds [4]. Benzene rings are represented with double bonds, and ciclohexane rings with single bond.
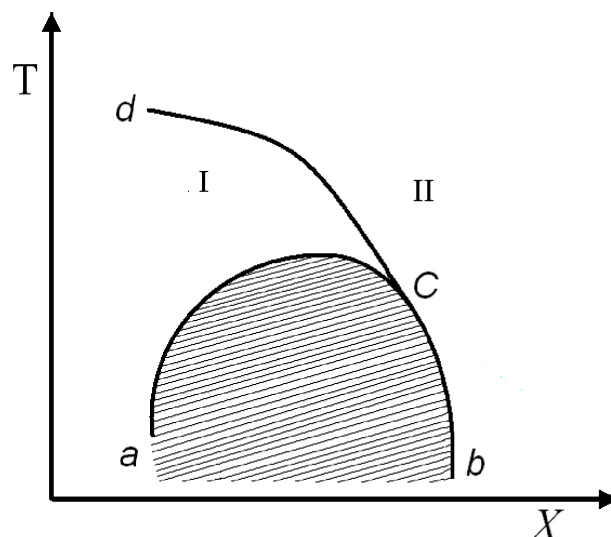

FIGURE 2. Lambda "λ" form of the coexistence curve showing tricritical phenomenon, because line *aCb* is first order and line *dC* is second order.

phaltenes in the solution are in a molecular state, while, above the *cmc*, asphaltene micelle formation will occur, in a manner similar to that in oil/surfactant/water micellar systems while surfactant monomers are much uniform in their structure and less polydisperse. Experimental measurements for the phase diagram of asphaltene micelle formation were performed by Rogacheva O. V. *et. al.* [6] and Priyanto *et al.* [7].

Blankschtein *et. al.* [16] developed the thermodynamic method of phase separations in micellar solutions. Pacheco and Mansoori [5] used their method to propose the phase behavior of asphaltene in aromatic systems. Experimental studies by various investigators have indicated that the solute asphaltene molecule (amphiphile or monomer) forms micelles in the presence of aromatic hydrocarbon solvents [6,7,11,15].

Landau and Lifshitz [17] briefly discussed the critical point for second-order phase transitions in mixtures of two substances. It can be shown that the state diagram near such a point takes the λ-form observed in Fig. 2. As abscissa it is plotted the concentration X of the mixture, and as ordinate, the temperature. The curves *Ca* and *Cb* are first-order phase transition boundaries and *Cd* is a curve for the second-order phase transition. The dashed area *aCb* is the region split into two phases of which phase I is the less symmetrical and phase II the more symmetrical. The point C is the critical point; the curve *bC* joins smoothly onto *Cd*. One more thing is that at the critical point the specific heat C_p of the mixture undergoes a finite discontinuity.

According to Uzunov [18] in binary alloys as FeAl and, especially, in ternary and quaternary fluid mixtures (See Griffiths [19]) critical points, which have no analogue in simple fluids, can be observed. These are the *tricritical points*- critical points where three phases co-exist and have identical compositions. The experiments on systems which possess tricritical points show that at such points the first-order phase transition line in the thermodynamics 3D space of fields (T,

P, μ) changes to a line of critical points (second-order transition) as shown in Fig. 2 where *Cd* is a line of critical points.

At a pure-substance critical point, densities of the two coexisting fluid phases become identical and the meniscus between them disappear. In principle, at a tricritical point, densities of the three coexisting phases simultaneously become identical. Knobler and Scott [20] performed experimental studies for multicritical points in fluid mixtures. They concluded that the disappearance of the meniscus at an ordinary critical point could be observed in the laboratory by heating (or sometimes cooling) the system in a sealed tube. However, the analogous experiment cannot be performed for a fluid mixture at a tricritical point: for fluid mixtures, there is no closed-system path along which three visually distinct phases can be observed going into one.

Knobler and Scott [20] also commented that the first experimental discovery of a tricritical point has been attributed to Efremova by her coworkers Krichevskii *et al.* Efremova and Prianikova found upper and lower critical end-points in the ternary system n-C_4H_{10}+ CH_3COOH + H_2O. In a more detailed study in collaboration with Krichevskii *et al.*, they observed a separation of only $0.3°C$ between the critical end-points. At both critical end-points (189.2 and 189.5°C) and in the intervening three-phase region, all three phases showed near-critical opalescence. The third-order critical point was estimated to lie at 190°C. One year prior to the publication of the study on the ternary system, Radyshevskaya *et al.* reported experiments on phase behavior in the system water + ammonium sulfate + ethanol + benzene as a function of temperature at fixed (atmospheric) pressure. They described a "triple critical point", which they estimated to exist at 49°C.

In case of binary systems, upper and lower critical solution points (UCST, LCSP) have been known since 1800 [21] and it is reported in every solution thermodynamic book [22]. In this case, when the components are reasonably similar, *e.g.* n-hexane + methanol, the system comes first to a liquid-liquid critical point (UCST=34°C). When the components are dissimilar, *e.g.*, n-hexane + water, however, the system comes first to a critical point between the gas, *i.e.*, the mixed vapors, and the liquid phase rich in hexane (T_c=210°C).

Finally, in the asphaltene case, Tran [23] measured heat capacity of athabasca bitumen asphaltenes using differential scanning calorimetry (DSC) and temperature modulated differential scanning calorimetry (TMDSC), founding a second order phase transition. We must stress that Pacheco-Sánchez [24] predicted a second order phase transition in asphaltenes-micellar solutions. Now, we will explain tricritical points in this work, as part of second order phase transition of asphaltene-micellar solutions.

3. Asphaltene Micellization Theory

We will theoretically consider asphaltene micellization (micelle formation) in this section. In a theory of phase separation in asphaltenes-micellar solutions, Pacheco-Sánchez [24] developed an advance of the behavior of phase separation for

asphaltene-micelles in petroleum fluids proposed by Pacheco and Mansoori [5]. In here, it is now extended to the prediction of tricritical points.

We consider that micelles can exchange asphaltene amphiphile molecules. This exchange is represented as a multiple chemical equilibrium among the members of the micelle distribution as follows:

$$\mu_n = n\mu_1 \qquad n = 1, 2, 3, \ldots \qquad (1)$$

where the chemical potential per asphaltene amphiphile molecule must be the same in all the micelles.

In the thermodynamics of micelle formation is postulated that the interactions between asphaltene amphiphile molecules which result in micelle formation are mainly due to the following three effects: a) *Kinetic effect* due to collisions between molecules into micellar solutions, which cause synergetic phenomena, molecular interactions are present. b) *Polar effects* in the form of electrostatic interactions present between asphaltene amphiphiles, which are responsible for the polar heads in the asphaltene amphiphiles. All of this is reflected in the entropy of mixing of the formed micelles. c) *Asphaltene amphiphile effects* due to association present in micellar solutions of asphaltene amphiphiles and aromatic solvents known as micellar interactions.

Based on the above three postulates it is possible to write the equation for the total Gibbs free energy $G = G_a + G_b + G_c$ for a system of N_{ar} aromatic solvent molecules and N_{as} asphaltene amphiphile molecules at temperature T and pressure P. Asphaltene amphiphile micellization in this system produces a distribution $\{N_n\}$, where N_n is the number of micelles having n asphaltene amphiphile in their structure. Then, the most important equations in this theory are:

i The chemical potential of aromatic solvent in a micellar solution:

$$\mu_{ar} = \mu_{ar}^0 + kT[\ln(X_{ar}) + X_{as} - \Sigma_n X_n]$$
$$+ C\gamma X_{as}^2/\{2[1 + (\gamma - 1)X_{as}]^2\} \qquad (2)$$

where μ_{ar}^0(T,P) is the pure state chemical potential of an aromatic solvent molecule, k is the Boltzmann constant, T is the absolute temperature,

$$X_{as} = \frac{N_{as}}{(N_{as} + N_{ar})}$$

and

$$X_{ar} = \frac{N_{ar}}{(N_{ar} + N_{as})}$$

are the mole fraction of asphaltene amphiphile molecules and aromatic solvent molecules in the solution, respectively, such that

$$X_{ar} + X_{as} = 1 \qquad X_n = \frac{N_n}{(N_{as} + N_{ar})}$$

is the mole fraction of micelles (each consisting of n molecules of asphaltene amphiphiles), $\Sigma_n X_n$ is defined according to the theory of moments: $M_\alpha(X_{as}, T, P) = \Sigma_n n^\alpha X_n$, $C = U(T, P)/\Omega_{as}$ where U(T,P) is the magnitude of the potential energy, and $\gamma = \Omega_{as}/\Omega_{ar}$ where Ω_{as} is the volume of an individual asphaltene amphiphile molecule and Ω_{ar} is the volume of an aromatic solvent molecule.

ii By using the Gibbs-Duhem equation ($N_{ar}d\mu_{ar} + \Sigma_n X_n d\mu_n = 0$) it is possible to obtain an expression for the chemical potential of micelles in the solution

$$\mu_n = \mu_n^{*0} + kT[\ln(X_n) + n(X_{as} - \Sigma_n X_n - 1)]$$
$$+ \frac{nC}{2}\left\{\frac{(1-X_{as})^2}{[1+(\gamma-1)X_{as}]^2} - 1\right\} \tag{3}$$

where $\mu_n^{*0} \equiv \mu_n^0 + kT$ and μ_n^0 is the hypothetical pure micelle chemical potential at the same temperature and pressure as the mixture.

iii The distribution of micelles is given by

$$X_n = X_1^n \exp[-\beta(\mu_n^{*0} - n\mu_1^{*0})]$$
$$\times \exp[(\beta U(T, P)/\Omega)\Sigma_j f_{nj}N_j], \tag{4}$$

where $\beta = 1/kT$, $\{X_n\}$ is the distribution of micelles containing n asphaltene-amphiphile-monomer, X_1^n represents the likelihood that n molecules will be localized in the same region of space, $\exp[-\beta(\mu_n^{*0} - n\mu_1^{*0})]$ is the Boltzmann factor which represents the enhancement of the micellar configuration due to the chemical potential difference ($\mu_n^{*0} - n\mu_1^{*0}$) arising upon assembling of n dissolved molecules into a single micelle. In fact, the sequence of the chemical potential differences can be represented as a spectrum of energy levels [5], the last term $\exp[(\beta U(T, P)/\Omega)\Sigma_j f_{nj}N_j]$ is equal to unity. The conservation of asphaltene amphiphile mass implies the following normalization condition:

$$X_{as} = \Sigma_n n X_n \tag{5}$$

The separation of the micellar solution into two coexisting phases having different total concentrations Y_{as} and Z_{as} of asphaltene amphiphile will be developed in the following section.

4. Phase Coexistence

In general, in the absence of any external field, the thermodynamic state of a one-component system of fixed size is determined by specifying two variables as the independent variables. Two-component systems require the specification of a third independent variable. Three-component systems require the specification of four independent variables, and

so on. For practical purposes for a c-component system the usual choice for the independent variables are temperature, pressure, and $c - 1$ mole-fractions (or other forms of composition variables).

This choice of independent variables is by no means unique and separates the variables in the sense that temperature and pressure are "field variables" while the composition variables represent "densities". A "field variable" is a quantity, sometimes called a "potential variable", which has the same value in all the coexisting phases at equilibrium, while a "density variable" is a quantity that can have, and normally does have, different values in each of the coexisting phases. For each generalized density variable, there is a corresponding conjugate field variable, as can be seen by writing any general thermodynamic equation, as for example, the generalized Gibbs-Duhem equation: $S_m dT - V_m dP + x_1 d\mu_1 + x_2 d\mu_2 + ...$ where the temperature is the field conjugate to molar entropy, the pressure to molar volume, and the chemical potential of a component to its corresponding mole fraction.

In the system used in this report, the components are asphaltene and toluene, and the variables are temperature, pressure and mole-fraction in each phase. For all the calculations reported here we assume normal pressure.

According to the Gibbs phase rule [20], a system of c-components and p-phases has F = C + 2-p degrees of freedom. At a critical point however, the requirement that two phases become just identical introduces a further constraint and reduces F by one. At an nth-order critical point, where n of the p phases become identical, there are $n - 1$ such additional constraints and the Gibbs phase rule must be written as

$$F = c + 2 - p - (n - 1) = c + 3 - p - n \tag{6}$$

Since $F \geq 0$ and $p \geq n$, it follows that an nth-order critical point requires a minimum of $2n - 3$ components.
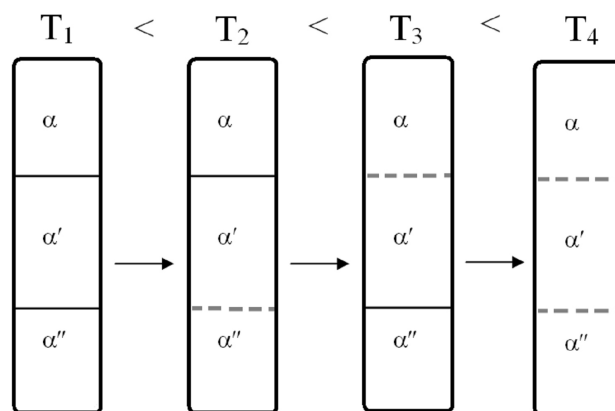

FIGURE 3. Schematic representation about the phase behavior, in a closed binary system near the tricritical point. While solid line indicates separation of two different phases, dashed line indicates that the phase separation is vanishing, consequently two phases become identical.

Thus, one component suffices for an ordinary critical point (in this sense, second order or $n = 2$), three components are necessary for a tricritical ($n = 3$) point, and five components for a tetracritical point ($n = 4$) point, etc. Therefore $c+3-p-3 = c-p \geq 0$ or $c \geq p$. For a two-component three phases in equilibrium Fig. 3 represents the general schematic transition of the phases near a tricritical point [19]. As the temperature is raised the system goes from three phases ($\alpha + \alpha' + \alpha''$) to two phases ($\alpha + \alpha' \equiv \alpha''$) to two phases ($\alpha \equiv \alpha' + \alpha''$) to one phase ($\alpha \equiv \alpha' \equiv \alpha''$). The latter is the tricritical point in which three phases become identical. The dashed line in Fig. 3 is the critical interface [20].

In this particular case, asphaltene-monomers dissolved in an aromatic solvent self-associate. This resulting association is called micelle which will constitute a new phase. Therefore, this system can be considered as a two-component three-phase (α, α' and α'') system, where:

α is the monomer phase.

$\alpha\prime$ is the micellar phase

α is the liquid phase due to the solvent.

As it was mentioned before $c \geq p$, so, it is not possible to get more phases than components in a system. Nevertheless, starting on the case in which there are three phases and three components in equilibrium

$$\mu_\alpha^\ell = \mu_\alpha^{\ell'} = \mu_\alpha^{\ell''}$$
$$\mu_{\alpha'}^\ell = \mu_{\alpha'}^{\ell'} = \mu_{\alpha'}^{\ell''} \qquad (7)$$
$$\mu_{\alpha''}^\ell = \mu_{\alpha''}^{\ell'} = \mu_{\alpha''}^{\ell''}$$

where ℓ, ℓ', ℓ'', are asphaltene-monomer, asphaltene micellar and aromatic components respectively. Specifically: μ_α^ℓ is the asphaltene chemical potential in a monomer phase, $\mu_\alpha^{\ell'}$ is the micelle chemical potential in a monomer phase, and $\mu_\alpha^{\ell''}$ is the solvent chemical potential in a monomer phase, $\mu_{\alpha'}^\ell$ is the asphaltene chemical potential in a micellar phase, and so on. The equilibrium system represented by Eqs. 7 has an algebraic system of six equations, in spite of that, there are only two significant equations in view of the equilibrium condition of Stigter [25] -Tanford [26]: $\mu_n = n\mu_1$. On the other hand, it is well known that [27]

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (8)$$

where a_i is the activity of the component i, and μ_i^0 is the standard chemical potential of the component i. Equations 7 can then be referred to as the system of equality of activities

$$a_\alpha^\ell = a_\alpha^{\ell'} = a_\alpha^{\ell''}$$
$$a_{\alpha'}^\ell = a_{\alpha'}^{\ell'} = a_{\alpha'}^{\ell''} \qquad (9)$$
$$a_{\alpha''}^\ell = a_{\alpha''}^{\ell'} = a_{\alpha''}^{\ell''}.$$

When a component i is absent in a phase, its activity is unity, *i.e.*

$$a_i = 1$$

In the tricritical case the equilibrium condition $\mu_n = n\mu_1$ makes the activities in the monomer phase $a_\alpha^\ell = a_\alpha^{\ell'} = a_\alpha^{\ell''} = 1$ and also activities corresponding to the asphaltene-monomer component $a_{\alpha'}^\ell = a_{\alpha''}^\ell = 1$. Therefore, this system of Eqs. (9) reduces to the following system of equations

$$1 = 1 = 1$$
$$1 = a_{\alpha'}^{\ell'} = a_{\alpha'}^{\ell''} \qquad (10)$$
$$1 = a_{\alpha''}^{\ell'} = a_{\alpha''}^{\ell''}$$

This system is equivalent to the one obtained for phase separation in asphaltene/toluene solutions [5], because it can be reduced to:

$$1 = 1 = 1$$
$$1 = \mu_n \left(Y_{as}, T, P\right) = \mu_n \left(Z_{as}, T, P\right) \qquad (11)$$
$$1 = \mu_{ar} \left(Y_{as}, T, P\right) = \mu_{ar} \left(Z_{as}, T, P\right)$$

In general, when a triple point is reached as the temperature is raised, the compositions of the three phases become more nearly identical, and the α/α' and α'/α'' interfaces may be observed to vanish simultaneously as the tricritical temperature is attained. However, when a tricritical point is reached one of the interfaces α/α' or α'/α'' may never vanish, provided that the overall composition is adjusted so that at least one interface could remain present. i) In an excess of aromatic there are no monomer phase. ii) In a scarcity of aromatic there is no micellar phase.

5. Tricritical Phenomena

The separation of the micellar solution into two coexisting phases having different total concentrations Y_{as} and Z_{as} of asphaltene amphiphile requires the thermodynamic equilibrium condition between the phases given by Eqs. (11):

$$\mu_n(Y_{as}, T, P) = \mu_n(Z_{as}, T, P)$$
$$\mu_{ar}(Y_{as}, T, P) = \mu_{ar}(Z_{as}, T, P)$$

Using the later conditions, and after some mathematical manipulations, the coexistence condition between the phases in equilibrium reduces to the following two coupled equations:

$$\frac{\sqrt{Z_{as}} - \sqrt{Y_{as}}}{\sqrt{K}} = (Z_{as} - Y_{as}) + \ln\left(\frac{1 - Z_{as}}{1 - Y_{as}}\right) + \frac{1}{2}\beta\gamma C\left[\frac{Z_{as}^2}{(1 + (\gamma - 1)Z_{as})^2} - \frac{Y_{as}^2}{(1 + (\gamma - 1)Y_{as})^2}\right], \quad (12)$$

$$\frac{1}{\sqrt{K}}\left(\frac{1}{\sqrt{Z_{as}}} - \frac{1}{\sqrt{Y_{as}}}\right) + \frac{\sqrt{Z_{as}} - \sqrt{Y_{as}}}{\sqrt{K}} = Z_{as} - Y_{as} + \frac{1}{2}\beta C\left[\frac{(1 - Z_{as})^2}{(1 + (\gamma - 1)Z_{as})^2} - \frac{(1 - Y_{as})^2}{(1 + (\gamma - 1)Y_{as})^2}\right]. \quad (13)$$

The above two equations depend on the interaction βC and on the growth K parameters, the concentrations Y_{as} and Z_{as} correspond to the monomer phase and micellar phase, respectively. Parameters βC and K are arbitrary positive values which depend on temperature and pressure, however, explicit $\beta C(P)$ or $K(T,P)$ functions have not been proposed until now, which means the proposition of new equations of state is required. On the other hand, parameter βC of interaction energy can be expressed as

$$\beta C(T) = \frac{T_c}{\gamma T} \quad (14)$$

A wider explanation can be found in the Ref. 24 where the corresponding spinodal line is calculated. In that reference, βC values of four different fractions of crude oil were also calculated, where was $\gamma = \Omega_{as}/\Omega_{ar}$ obtained directly from the properties and characteristics of the crude oil, density and molecular weight basically. In practice, to solve the dependence on the critical temperature (T_c), we considered that this corresponds to every point in *cmc* line experimentally measured. The later is allowed by the knowledge that *cmc* is the critical line. The growth parameter K can be expressed as

$$k(T, P) \equiv \exp[\beta(\mu_{n_0}^{*0} - n_0\mu^{*0})] \quad (15)$$

where n_0 is the minimum number of amphiphiles in the micelle. Assuming a spherocylinder form of the asphaltene-amphiphile micelle, $\mu_{n_0}^{*0}$ is the reference chemical potential per asphaltene amphiphile monomer associated to the end region, and μ^{*0} is the reference chemical potential per asphaltene amphiphile monomer associated to the cylindrical region. The corresponding sequence of chemical potential levels is $\mu_n^{*0} = \mu_{n_0}^{*0} + (n - n_0)\mu^{*0}$, for $n \geq n_0$. In general, parameter K is responsible for the form of each micelle. Assuming spherocylinder form for micelles, K can assume the following values:

0<K<1: If $\mu_{n_0}^{*0} < \mu^{*0}$ *then asphaltene* amphiphiles are distributed in the cylindrical region of the micelles being formed, *i.e.*, asphaltene amphiphile micelles form is disk-like. This is the normal flat form of asphaltenes and graphite.

K=1: If $\mu_{n_0}^{*0} = n_0\mu^{*0}$ *then* asphaltene amphiphiles are proportionally distributed in both cylindrical and end regions of the micelles being formed, *i.e.*, asphaltene amphiphile micelles form is sphere-like. This is the form of fullerenes.

K>1: If $\mu_{n_0}^{*0} > \mu^{*0}$ *then* asphaltene amphiphiles are distributed in the end region of the micelles in formation, *i.e.*, asphaltene amphiphile micelles form is cylinder-like. This is the form of nanotubes.

It has to be mentioned that Ravey *et al.* [28] found these three geometrical forms of aggregated asphaltenes by using Small Angle X-Ray Diffraction, and more recently, fullerenes were found by Camacho-Bragado *et al.* [29] using both High Resolution Transmision Electron Microscopy and Energy Dispersion Spectrometry in a study of asphaltene separated from resins. During their observation in the microscope they saw fullerene formation in structures such as Onions and $C_{240}@C_{60}$. Furthermore, using asphaltenes Wang *et al.* [30] synthesized carbon microspheres using Chemical Vapor Deposition, and characterizing by X-Ray Diffraction, Scanning Electron Microscopy, High Resolution Transmision Electron Microscopy and Raman Spectroscopy. Their results indicate that the monodisperse spheres are graphitic curved structures with diameters: 300 - 400 nm. Asphaltene used consisted in metastable structures at higher temperatures. The aromatic carbon rings promoted the formation of graphitic structures of closed cage. Finally, Velasco *et al.* [31] found nanotubes in crude oil naturally processed.

The system of Eqs. (12) and (13) can be solved simultaneously for calculating Y_{as} and Z_{as} numerically by the Newton-Raphson iterative method, which for a general concentration is expressed as:

$$X_{n+1} = X_n - \frac{f(X_n)}{f'(X_n)}. \quad (16)$$

To accomplish this calculation we assume Eq. (12) is solved by the Newton-Raphson method for one of the variables (either Y_{as} or Z_{as}) assigning an initial value to the other variable. Then Eq. (13) is also solved by the Newton-Raphson method using the solution to the Eq. (12) as the initial value. This iterative procedure converges for

$$\varepsilon = |X_i - X_{i-1}| \ll 1. \quad (17)$$

This iterative solution will provide us Y_{as} and Z_{as} which are used for producing the theoretical coexistence curve for a micellar solution of asphaltene in toluene. To speed up the convergence in the Newton-Raphson iterations we use

the following functionality $f\left((KX)^{1/2}\right) \cong f(K)$ and $f\left(K^{1/2}X^{-1/2}\right) \cong f(1)$ which means that when K<0 the solution goes to imaginary numbers; however, when K>0 a convergent solution in real numbers is obtained. Then K is always positive.

Three asphaltene fractions of Kotur-Tepinsk crude oil and one asphaltene fraction of Arlan crude oil were used to test different values of βC and K of this model by Pacheco-Sanchez [24]. For tar asphaltene fraction of crude oil Kotur-Tepinsk, the following cases were analyzed. One case was for βC=314.45/(γT) considered, in which K=0.5,0.7071,1,10,100 in one graph and K=0.1,0.5,0.7,1,10,100,1000 in the other graph, where the coexistence curves show lambda form; and in the other case βC=380/(γT) for K=0.003,0.01,0.1,1,50,280 in two graphs, where the coexistence curves were closed without showing any lambda form as expected because βC value is above *cmc*. In principle, this model will take us to get tricritical points by solving the set of Eqs. (12) and (13) for particular values of parameters βC and K as we will see in the results, over all when βC is around room temperature and K is lower than 1 as expected for asphaltene.

6. Results

This part of the analysis will be done by choosing γ=10.4038, βC = 314.45/(γT) and different positive values of the parameter K, which reflects the tendency of asphaltene monomers to their aggregation in the form of spherocylinder micelles. The Rogacheva *et al.* [6] experimental points of *cmc* for tar asphaltene fraction of crude oil Kotur-Tepinsk were assigned as the initial values in Newton-Raphson iterative calculations. A graph for a superposition of coexistence curves when K = 100, 10, 1, 0.7071 and 0.5 was calculated by Pacheco-Sanchez [24]. Using these values of K we solve the system of Eqs. (12) and (13). When K=100 and the temperature is greater than 320 K all the experimental points are almost reproduced without region of two coexisting phases. This means that the two-phase region is quite thin. When K = 10 the two-phase region is wider than for K=100. The two-phase region is more and more open as the value of K is decreasing. The widest open two-phases region is shown for K = 0.5. The later K-value is in the disk-like form of the micelle, which corresponds to planar asphaltenes. It has to be mentioned that asphaltenes were found in both planar and curved forms using molecular dynamics simulations [32]. Curved forms of asphaltenes are consistent with several facts: i) reversed micelles [33], ii) existence of nanotubes and fullerenes [28-31], iii) activated carbons containing pentagonal to heptagonal rings, which adopt curved forms [34]. To these activated carbons we could call them asphaltene-blankets whether the asphaltenes grew extensively.

Fixing the parameter βC = 314.45/(γT) and allowing the variation of parameter K, Pacheco-Sanchez [24] shows that there are some differences when we use as initial values ei-
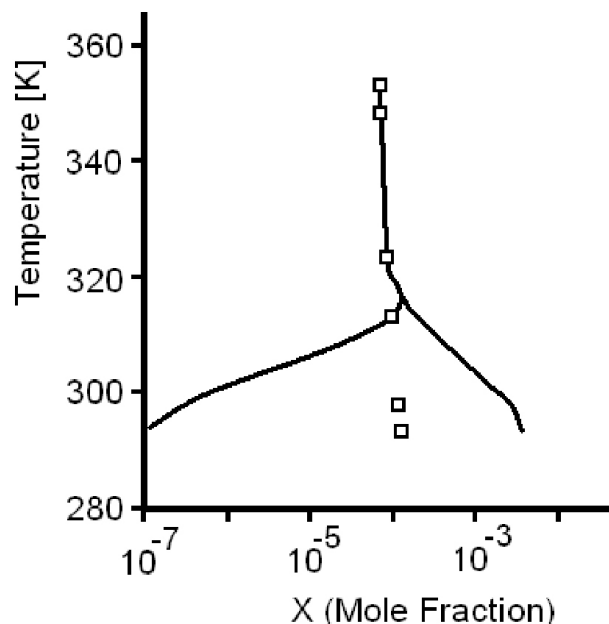

FIGURE 4. Phase behavior (of asphaltene-toluene systems for γ=10.4038, K = 500 and βC = 314.45/γT) in λ-form as in the Landau theory of tricritical points as reported in Fig. 2. Rogacheva *et al.* [6] *cmc* points were used as initial values in the numerical solution. Horizontal coordinate is the asphaltene mole fraction.

ther *cmc* or arbitrary points, in the Newton-Raphson numerical solution of Eqs. 12 and 13. He exhibits two general graphs on which lambda form of second order phase transition and tricritical points of asphaltene micelar solutions can be inferred. Here we clearly exhibit this idea.

The *cmc* points are used as initial values in the numerical solution on Fig. 4. Such Figure shows a behavior similar to a lambda in a continuous line calculated by this theoretical model. This line approximately coincides within four *cmc* points, however the others *cmc* points remained inside of the two phases region. This is due to the critical temperature used for βC value, which produces a very thin (or, vanished in fact) two phase region for temperatures greater than critical temperature. In principle, *cmc* points are considered as critical points in this way, from which we can take critical temperature. Then, this is not a first order phase transition as that obtained for water (just one component) at a triple point solid liquid and vapor. This is a second order phase transition as that proposed by Landau on certain variation in the symmetry of the body due to a change in its pressure or its temperature or its composition as in the Fig. 2.

The tricritical point in Fig. 4 is such that the three lines are joined as in Fig. 2. Then, below tricritical point it is observed a region of two phases, the monomer phase and the micellar phase of asphaltenes, this might be considered as the flocculation region. Above tricritical point it is just observed separation between monomers and micelles as it was observed by Yudin *et al.* [12] because they detected asphaltene "molecules" (monomers) below *cmc* and micelles above *cmc* by measurements of dynamic light scattering (photon
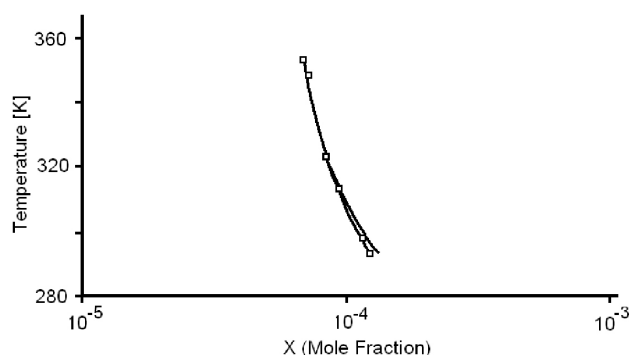
FIGURE 5. The horizontal coordinate corresponds to the mole fraction of asphaltene in toluene. All *cmc* square points of Rogacheva *et al.* [6] were reproduced using $\gamma = 10.4038$, $\beta C = 293/\gamma T$ and $K = 500$). A small improvement of βC or K will provide just one calculated curve.
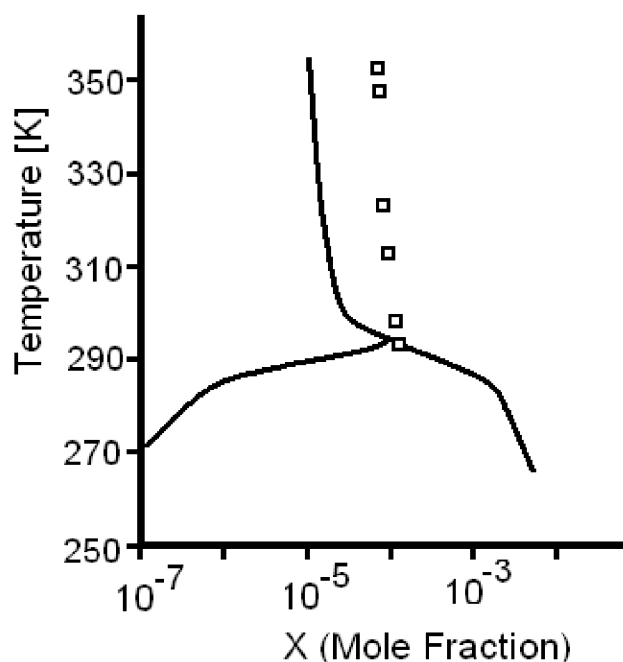

FIGURE 6. Phase behavior (of asphaltene+toluene system for $\gamma=10.4038$, $K = 500$ and $\beta C = 293/\gamma T$) in λ-form as in the Landau theory of tricritical points. Arbitrary initial values to solve equations (18) and (20) were used in our numerical solutions. Horizontal coordinate is the asphaltene mole fraction.

correlation spectroscopy) on asphaltenes in toluene + heptane mixtures.

Three *cmc* points were exactly reproduced in Fig. 4 without region of two phases; however, in Fig. 5 all *cmc* points of Rogacheva *et al.* [6] were reproduced using the following values of the parameters: $\gamma = 10.4038$, $\beta C = 293/\gamma T$ and $K = 500$. This K-value is in the cylinder-like form of the micelle, which corresponds to nanotubes. The *cmc* points used as initial values in this numerical solution are still showing a very tiny lambda form. When arbitrary initial points are used to solve the system of equations by Newton-Raphson method, as the important difference respect to the last one, Fig. 6 was obtained. Two things are observed in this Figure,

one is its lambda form and the other is the line above tricritical point is one order of magnitude parallel to the left of the *cmc* points.

The γ value changes when one of the other *cmc* curves in the same graph of Rogacheva's experimental data is used, however, the general information can hardly increase if it is analyzed another one. Then, it is believed that the analyses done until now are enough to describe tricritical phenomena in asphaltene/aromatic solutions.

7. Discussion

For asphaltene dissolved in toluene, at a certain concentration and temperature asphaltene micelles will be formed. Then self-assembly (coacervation) of asphaltene micelles may take place at higher concentrations and/or lower temperature and around one of the transition points. Of course, micelle coacervates may deposit if the coacervate size exceeds a certain limits, while micelles change to become coacervates due to their growth depending on the concentration of the solution. In these reversible processes asphaltene micelle-coacervates may swell in the presence of a proper solvent. The micellization point starts on the critical micelle concentration (*cmc*), and ends on self-assembly (coacervation) of asphaltene micelles.

In a closed binary system, made up of monomers and micelles in liquid state above *cmc* (below *cmc* micelles do not exist), micelles can coexist in several forms and different (polydisperse) sizes depending on the nature of asphaltene molecule and temperature of the solution. Two phases are expected for micelles: monomer and micellar phases. Monomer phase is due to low aromaticity, and micellar phase is due to high aromaticity of the solution.

In this model the fact experimentally found by Yen [35], about self-association in stacking of two to four asphaltenes is taken as a natural way of the micelle formation. Such asphaltene stacking is emphasized by considerations proposed by Rogel [36,37] using the free energy of Gibbs also for asphaltene micellar considerations. The stacking of 2-4 asphaltenes is a self-associating model which has a strong tendency to be considered as oligomer [38]. Recently, according to the thermodynamic theory of phase separation in self associating micellar solution Huang *et al.* [39] open the possibility that instead of oligomers of asphaltene stacking they might be unimers (subunits of a surfactant micelle, as opposed to monomer, the subunit of a polymer) which is a natural starting for micelle growing in different geometric forms, for which the intermolecular forces allow self associating in micellar phase for planar and curved asphaltene as follows:

i) Disk-like can be considered as planar asphaltene micellar growth toward graphite (which is also stacking of huge planar pentagonal and hexagonal carbon rings)

ii) Sphere-like are considered as curved asphaltene micellar growth to cumulus of spheres aggregates. Each

sphere is made up pentagonal and hexagonal carbon rings. These spheres might be fullerenes.

iii) Cylinder-like are also considered as curved asphaltene micellar growth to cylinder aggregates. Each cylinder is built of pentagonal and hexagonal carbon rings. They might be nanotubes.

Until now, asphaltenes are considered only as planar molecules, according to the Yen *et al.* model [35]; however, asphaltene stacking for planar and curved asphaltenes can be observed in a previous work [32], which reports structure factors agree with Yen *et al.* work [35], and it is nearer to the asphaltene habitat conditions than that proposed by Yen *et al.* [35]. Furthermore, the existence of activated carbons as those proposed by Harris *et al.* [34] gives us confidence about the existence of curved asphaltenes, that might arrive to be nanotubes, or fullerenes according to the conditions as we observed in this work.

In general, the m-phase region (m = 1,2,3,...) is the focus of most SANS investigations since it is the region of micelle formation and micelles are of nanometer size. The m-phase region is rich in mesophases (with various morphologies). It contains spherical, cylindrical and lamellar micelles depending on the temperature range. Structures for these mesophases correspond to cubic (spherical micelles), hexagonal (cylindrical micelles) and lamellar symmetry respectively. Moreover, oil-in-water micelles are obtained at low temperature and "reverse" (water-in-oil) micelles are obtained at high temperatures.

This method can be used as a model of two parameters to be adjusted. The model is good for: i) aqueous solutions, ii) asphaltene in aromatic micellar solutions, iii) asphaltene in chromatographic fractions. In this work, the model has been tested for temperatures among $0 - 80°C$ and concentrations lower than 10^{-2} (mole fraction). The model is still in development to be tested for temperatures $10-400°C$ and higher concentrations of asphaltenes among 0.01-1 (mole fraction) where the aggregated stability of petroleum dispersed systems is a central problem.

Rogacheva *et al.* [6] extended their work in order to find the phase state of asphaltenes in petroleum dispersed systems in the temperature range $10-400°C$ [40], and concentrations 0-40 mass %. Their results are very far of the CMC; however, they affirm that the new measurements are consistent with those previously accomplished by themselves. They used optical density, calorimetry, and surface tension at least for their measurements. A preliminary calculation using our model needs more revision, because at those temperatures they report two concentrations for one temperature value, and we still need to validate the calculation accomplished. Our model works near *cmc* values, the most probable idea is that new considerations have to be taken into account in order to get a successful model.

8. Conclusions

All the experimental *cmc* points were reproduced in Fig. 5 for specific values of the parameters βC and K tuned by *cmc* experimental points. In principle, the model can give an idea of the phase diagram in case one *cmc* point is given, such point will be considered as the tricritical point by this model.

If the *cmc* point were in the top of the phase diagram it will hardly be found a second order phase transition, however, it is expected a limited miscible fluid, this means that asphaltene can stay dispersed in the solution. If the *cmc* point were in the middle of the phase diagram a second order phase transition can be obtained as in the Fig. 4. If the *cmc* point were in the bottom of the phase diagram a second order phase transition can be found as in Fig. 6.

The coupling between the micellization and phase separation may, in principle, lead to a near-tricritical coexistence of a monomer phase and a micellar phase, however, this tricritical phenomenon has not been experimentally observed, nevertheless Fig. 6 is very indicative that this can be a good possibility. Rowlinson gives another good indication of this possibility because he reported tricritical points at 273 K for binary systems, and it can be considered that tricritical point is at 293 K in Fig. 6, which is considered for a binary asphaltene + toluene system. Fig. 5 is also indicative of tricritical points or second order phase transition, because it has a superposition of different K values showing how can be closed that open region in a lambda form as Landau reported.

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