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Thermodynamics of Interactions at Infinite Dilution between Asphaltenes and a Surfactant or Crude Oil Resins

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We present a thermodynamic study of the interactions between asphaltenes and a surfactant and between asphaltenes and resins of crude oil at 303.15 K in toluene solution, using a recent thermodynamic scheme, which allows the study of multicomponent systems at infinite dilution. The specific partial volumes and the specific partial adiabatic compressibility coefficients at infinite dilution were calculated from the experimental measurements of densities using vibrating tube instruments and of speeds of sound. Systems containing asphaltenes and the surfactant tert-octylphenol in solution in toluene behave in the same way as systems containing noncharged polymeric particles and a cationic surfactant in water. Therefore, it can be concluded that the main interactions in these systems are the solvophobic interactions and that these interactions only affect the surface of the asphaltene aggregates. To study the interactions between asphaltenes and resins, we developed an alternative method to separate the resins fractions. This method is quicker, cheaper, and more accurate than the usual method based on chromatography columns. Systems composed of asphaltenes and resins in solution in toluene present a similar sequence of interactions as systems composed of a protein and a ionic surfactant in solution in water.

Introduction

The instability of a petroleum system[1] is usually associated with fractions that are not mutually soluble. In particular, the molecular structure and physicochemical properties of the asphaltene fraction have been shown to have significant influence on the stability of crude oils and related materials. Asphaltenes were identified[2] by Boussingault in 1837 from an ether-insoluble fraction of asphalt, and they are considered an important factor that causes hindrance in many petroleum operations—productions, transportation, refining, even wax crystallization, crude oil emulsification, and de-emulsification. Under certain conditions,[3] asphaltenes can flocculate in the crude causing the formation of heavy deposits. Various reasons, such as the injection of CO_2, N_2, or methane, mixing of different oils in oil storage, pressure change, etc., can cause the asphaltene dropout. Although many of these claims are not fully proven

or understood,[2] asphaltenes do have a negative effect on many of the above operations and it is natural to attribute these negative impacts to their particular molecular and thermodynamic properties. From a scientific point of view, asphaltenes are a solubility class of compounds found in crude oil[4] and they are defined by their insolubility in *n*-alkane solvents and their solubility in aromatic solvents, such as toluene. Therefore,[5] it is difficult to assign them in a proper chemical classification because any property of an asphaltene sample, as molecular weight or size, is very polydispersed. Nevertheless, as in the case of the definition of the critical micelle concentration, one can use the well-suited quotation of Charles Tanford:[6] "The concept of asphaltenes as a solubility class is inexact but convenient". That is, this definition of asphaltenes provides[5] sufficient chemical restriction to be useful in both a chemical and an operational sense.

The chemical composition of crude oil is extremely complex because it may contain a very large number of chemical species. However, using the criterion of groups of similar structure and common solubility, it is possible to distinguish four major fractions because they are deduced by the thin-layer chromatography technique: saturates, aromatics, resins, and asphaltenes (SARA) fractions. It is common practice to first separate the

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asphaltenes fraction by precipitation. The deasphalted oil, the maltene fraction, is subdivided by adsorption chromatography. In this procedure, saturates and aromatics elute with a nonpolar solvent and the resins remain on the adsorbent until desorbed by a polar solvent.[7]

Several analytical procedures for asphaltenes precipitation are known.[8−13] Among these techniques, ASTM D2007 involves the method for fractionating the deasphalted oil into saturates, aromatics, and resins using clay-gel adsorption chromatography. Although clay-gel chromatography (ASTM D2007) is more tedious and time-consuming than high-performance liquid chromatography (HPLC),[14] it has been extensively used because the technique is not destructive and the procedure is standardized.

Accordingly to our experience, resins separation based on the column chromatography technique is very slow and expensive and the separated amount is small. Consequently, the experiments are usually carried out with a limited number of measurements, which reduce the number of experimental data and increase the experimental uncertainty. Therefore, it is necessary to design a quick, efficient, and more economic method for fractionating the deasphalted oil into the polar (resins) and nonpolar (saturates and aromatics) fractions. In this work, crude oil was first divided into the asphaltenic and maltenic fractions. Then, the Soxhlet extraction procedure was used for the separation of the resins fraction. A major advantage of this procedure is that it can be used to separate large quantities of narrow, deep cuts of resins in a short period of time for characterization. Additionally, the solvents consumption is low, and the equipment is inexpensive.

In the early states of understanding asphaltene behavior, two structural models[15] were considered for crude oil involving the aggregation of asphaltenes in their natural medium. The idea of asphaltene colloidal particles stabilized by resins was first introduced by Nellensteyn[16] in 1928. This concept was then refined by Pfeiffer and Saal. In Pfeiffer and Saal's peptization model,[17] asphaltenes form the center of some micellar entities surrounded and stabilized by resins and then by other constituents. In this way, a nearly continuous transition exists from the most polar entities, asphaltenes, at the center of the micelles, to the less polar, aliphatic, entities forming the surrounding medium. Wherever a shortage of resins occurs, attractive forces can be created to give rise to the association between micelles, ultimately leading to an extended gel-type structure. Yen's model[18] depicts the asphaltenes in their natural medium as being gathered in oil-external or reversed micelles, with the centers of the micelles being composed of polar groups associated by hydrogen bonds or charge-transfer interactions. Oil-external micelles can revert to oil-internal ones depending upon the surrounding medium properties. Aggregation of several micelles can form supermicelles, and further aggregation can develop into giant supermicelles or liquid crystal structures. While colloidal models of asphaltenes were extremely beneficial in

the early stages of understanding asphaltene behavior, these analogies are often overused.[19,20] There are other theories based on solubility models that question the existence of micelles,[21−24] and it has even shown that asphaltenes do not form micelles but are soluble maltenes.[25] Solutions of asphaltenes in toluene constitute a simplification of the problem and thus can provide information about the behavior of asphaltenes in their natural medium. It is well-known[15] that molecules of asphaltenes are composed of planar sheets of aromatic rings with some alkyl and/or aromatic tails. The study of the core aggregation with average molecule models has shown that the sheets lie parallel by attractive $\pi-\pi$ bonds, while the steric interactions because of their tails act as an aggregation impediment. The existence of aggregates of asphaltenes was determined by high-Q ultrasonic spectroscopy,[26,27] nuclear magnetic resonance (NMR) diffusion,[28] and conductivity[29] measurements. The size and shape of aggregates were studied by neutron scattering and small-angle X-ray scattering. Disks,[30−32] oblate ellipsoids,[33] spheres,[33] and cylinders[34] were reported depending upon the solvent, temperature, and concentration, and micellar[35−39] or micellar-like[5,40] pictures were proposed as parts of the mechanism of aggregation. Recently, it was reported[41] that the aggregation process of asphaltenes is reversible above 300 K, but it becomes fractal-like at low temperatures.

The crucial role of the resins fraction in the stabilization of asphaltenes was highlighted by the fact that, once resins are removed from the crude oil by chromatography, the remaining

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crude oil can no longer stabilize the asphaltenes.[42,43] Using titration microcalorimetry and inverse chromatography,[44] the mechanism by which the asphaltene aggregates are formed in the presence of *n*-alkanes, leading to flocculation, was elucidated. The exothermic heat effect observed upon mixing *n*-heptanes with a crude oil was interpreted in terms of the decrease of the mobility of *n*-alkane molecules engaged in the interactions with the asphaltene alkyl chains. The latter effect was used to prove the interactions between the alkyl chains of the asphaltenes. On the basis of the results obtained, it was proposed that the van der Waals interactions as well as induced conformational changes and molecular orientations between adjacent chains of both *n*-alkanes and asphaltenes are the main driving forces responsible for the self-assembling of asphaltenes into flat sheets. However, considering that behenic acid[44] can be considered as a model of resin, the *n*-heptane added to the behenic acid or resin-rich oils does not interact with the asphaltenes, which are shielded by a protective molecular layer. In the absence of such a protective layer, the *n*-heptane could interact with the lateral chains of the asphaltenes.

A better understanding of the properties of asphaltenes and their interactions with the other constituents of oils or residues, such as resins, is highly desirable because it may help in explaining the difficulties encountered and then proposing new solutions to the problems of the petroleum industry.[15] In addition, to tackle such important problems of the petroleum industry, various methods have been proposed, such as physical removal or solvent soakings with aromatic solvents blended in some cases with dispersants. The technological objective is to find additives that prevent or delay the asphaltenes deposition. These inhibitors of asphaltenes deposition are supposed to act similarly to resins by having peptizing capabilities. For these reasons, the interaction between asphaltenes and surfactants has been subjected to intensive research efforts.[43,45–50]

The purpose of this work is to study the interactions between asphaltenes and a surfactant and asphaltenes and resins in toluene solution. The densimetry by mechanical oscillation and the measurement of the speed of sound were the experimental techniques employed. Specific volumes and specific adiabatic compressibility coefficients were calculated from the density and the speed of sound data. We developed the thermodynamic approach in previous studies on the swelling of functionalized polymer particles[51] and the interactions between noncharged polymer particles and surfactant and between proteins and surfactant.[52] It is then possible to calculate the thermodynamic partial properties at infinite dilution in multicomponent systems; accordingly, it allows the study of interactions between two components, while a third component is acting as solution

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medium. The partial properties are discussed in terms of their respective contributions. The specific partial volume is assumed to include a specific volume and a specific volume of solvation. The specific adiabatic compressibility coefficient is assumed to contain an internal cavity contribution and a solvation term.

In a previous work,[52] we have shown that the binding type between two components is related to the behavior of their partial properties at infinite dilution; consequently, the behavior of partial properties permits the identification of the binding type present in the system. Accordingly, the identification of the interaction types occurring in the present systems will be conducted in the same way, comparing the behavior of partial properties to those of systems studied previously. In the asphaltenes−surfactant interactions, we have found that there is an adsorption isotherm, the adsorbed surfactant is on the surface of the asphaltenes aggregates, and this solvophobic interaction does not involve changes in the interior of the asphaltene aggregates. As concerns asphaltenes−resins interactions, there is also an adsorption isotherm that is more complex because it involves a sequence of binding types. At very low concentrations of resins, the first binding type takes place; it is a specific interaction with high affinity and electrostatic in origin. The second binding type takes place at larger resins concentrations. In this domain of concentrations, the resins molecules penetrate into the interior of the asphaltene aggregates, producing the separation of asphaltene molecules and allowing then the entry of solvent molecules into the interior of the aggregates, inducing the aggregates to swell. At much higher concentrations of resins, the interactions have the same characteristics as the interactions between asphaltenes and surfactant. That is, the resins molecules are located on the surface of the swelled aggregates until they eventually encapsulate the aggregates.

Thermodynamics

In a three-component system at constant temperature (T) and pressure (P), an extensive thermodynamic property J can be expressed as $J = J(m_1, m_2, m_3)$, where m_1, m_2, and m_3 are, respectively, the masses of components 1, 2, and 3. In this work, J stands for the volume V and for the adiabatic compressibility coefficient $K = -(\partial V/\partial P)_S$, with S being the entropy. The partial property of component 3, in the presence of components 1 and 2, is defined as

$$j_{3;1,2}(t_2, t_3) = \left(\frac{\partial J(m_1, m_2, m_3)}{\partial m_3}\right)_{m_1, m_2} \quad (1)$$

where t_2 and t_3 are the mass fractions of components 2 and 3. The partial property of component 1 in the presence of components 2 and 3 ($j_{1;2,3}$) and that of component 2 in the presence of the components 1 and 3 ($j_{2;1,3}$) are defined in an analogous way by eq 1. A fraction of the system, F, is defined as a thermodynamic entity with an internal composition that groups several components. The property J can be expressed in terms of component 1 and a fraction F, composed of components 2 and 3, as $J = J(m_1, m_F, t_{f3})$, where $m_F = m_2 + m_3$ and $t_{f3} = m_3/(m_2 + m_3)$. In this way, the partial property of fraction F in the presence of the component 1 is

$$j_{F;1}(t_F, t_{f3}) = \left(\frac{\partial J(m_1, m_F, t_{f3})}{\partial m_F}\right)_{m_1, t_{f3}} \quad (2)$$

where t_F is the mass fraction of fraction F in the system ($t_F = m_F/(m_1 + m_F)$). In a previous work,[52] it was established that

$$j_{F;1} = t_{f2}j_{2;1,3} + t_{f3}j_{3;1,2} \tag{3}$$

where $t_{f2} = 1 - t_{f3}$. The limit of the partial property of F at infinite dilution is defined in the same way as for a two-component system

$$\lim_{\substack{t_F \to 0 \\ t_{f3} \text{ constant}}} j_{F;1}(t_F, t_{f3}) = j_{F;1}(0, t_{f3}) \equiv j^{\circ}_{F;1}(t_{f3}) \tag{4}$$

For components 2 and 3, this limit is defined as

$$\lim_{\substack{t_F \to 0 \\ t_{f3} \text{ constant}}} j_{2;1,3}(t_F, t_{f3}) = j_{2;1,3}(0, t_{f3}) \equiv j^{\Delta}_{2;1,3}(t_{f3}) \tag{5}$$

$$\lim_{\substack{t_F \to 0 \\ t_{f3} \text{ constant}}} j_{3;1,2}(t_F, t_{f3}) = j_{3;1,2}(0, t_{f3}) \equiv j^{\Delta}_{3;1,2}(t_{f3}) \tag{6}$$

Taking the limit of infinite dilution on both sides of eq 3 and substituting eqs 4−6

$$j^{\circ}_{F;1} = t_{f2}j^{\Delta}_{2;1,3} + t_{f3}j^{\Delta}_{3;1,2} \tag{7}$$

In our previous work, it was shown that

$$t_{f2}\frac{dj^{\Delta}_{2;1,3}}{dt_{f3}} + t_{f3}\frac{dj^{\Delta}_{3;1,2}}{dt_{f3}} = 0 \tag{8}$$

Equation 8 is referred, by similarity (see previous work[52]), as a Gibbs−Duhem-type equation. The main difference with the usual Gibbs−Duhem equation is that it cannot be obtained from the arguments that lead to the usual Gibbs−Duhem equation. The Appendix shows in detail this fact. This equation establishes the way along which the three components are interacting at the infinite dilution limit. Because the derivatives of the equation are coupled, the behavior of 2 affects that of 3 and vice versa. On the other hand, because $dj^{\Delta}_{1;2,3}/dt_{f3}$ does not appear in eq 8, the behavior of 1 is not affected by the interaction between 2 and 3. In addition, because the interaction is at infinite dilution, 1 is in its pure state. That is, 1 is acting as a medium in which the interactions between 2 and 3 take place.

Differentiating in eq 7 and using eqs 7 and 8 yields

$$\begin{cases} j^{\Delta}_{2;1,3} = j^{\circ}_{F;1} - \left(\frac{dj^{\circ}_{F;1}}{dt_{f3}}\right)t_{f3} \\ j^{\Delta}_{3;1,2} = j^{\circ}_{F;1} + \left(\frac{dj^{\circ}_{F;1}}{dt_{f3}}\right)(1 - t_{f3}) \end{cases} \tag{9}$$

Using eq 9, it is possible to calculate the partial properties $j^{\Delta}_{2;1,3}$ and $j^{\Delta}_{3;1,2}$, where $dj^{\circ}_{F;1}/dt_{f3}$ is evaluated from plots of $j^{\circ}_{F;1}$ against t_{f3}.

We are interested in the case where component 3 is absorbed on component 2 while a particular adsorption isotherm is held, then the partial property of 3 can be written as[52]

$$j^{\Delta}_{3;1,2} = t_{3a}j^{\Delta}_{3a;1,2} + t_{3s}j^{\circ}_{3;1} \tag{10}$$

where $j^{\Delta}_{3a;1,2}$ and $j^{\circ}_{3;1}$ are, respectively, the partial properties of component 3 adsorbed and component 3 free in solution and t_{3a} and t_{3s} are, respectively, the ratios of the mass fractions of both species. These ratios $t_{3a} = t_{3a}(t_{f3})$ and $t_{3s} = t_{3s}(t_{f3})$, are related to the adsorption isotherm. Substituting eq 10 in eq 8 gives[52]

$$t_{f2}\frac{dj^{\Delta}_{2;1,3}}{dt_{f3}} + t_{f3}(j^{\Delta}_{3a;1,2} - j^{\circ}_{3;1})\frac{dt_{3a}}{dt_{f3}} + t_{f3}t_{3a}\frac{dj^{\Delta}_{3a;1,2}}{dt_{f3}} = 0 \quad (11)$$

Equation 11 relates the behavior of the partial properties to the adsorption isotherm (by the term $t_{3a} = t_{3a}(t_{f3})$) and to its shape (by the term dt_{3a}/dt_{f3}). With regard to the interactions between proteins

and surfactants, it is well-know[53] that the shape of the binding isotherm is related to the type of interaction. For this reason, eq 11 is interesting because it establishes the possibility to identify interaction types from the behavior of partial properties.

Substituting eq 10 in eq 7 yields

$$j^{\circ}_{F;1} = \underbrace{t_{f2}v^{\Delta}_{2;1,3} + t_{f3}t_{3a}v^{\Delta}_{3a;1,2}}_{\substack{\text{Contribution of the cluster} \\ \text{composed of component 2 and} \\ \text{component 3 adsorbed}}} + \underbrace{t_{f3}t_{3s}v^{\circ}_{3;1}}_{\substack{\text{Contribution of} \\ \text{component 3} \\ \text{free in solution}}} \tag{12}$$

In this way, the contributions to the partial property of fraction F at infinite dilution are due to the cluster composed of component 2 and the adsorbed part of component 3 and to the part of 3 free in solution.

The specific partial volume of component 2 and, similarly, of component 3 will be expressed as follows:[52,54−58]

$$v^{\Delta}_{2;1,3} = v^{\Delta}_{2;1,3/M} + \Delta v^{\Delta}_{2;1,3/h} \tag{13}$$

where $v^{\Delta}_{2;1,3/M}$ is the specific intrinsic volume of component 2 and $\Delta v^{\Delta}_{2;1,3/h}$ is the specific volume of solvation. The specific intrinsic volume corresponds to the solute domain into which the solvent molecules cannot penetrate. The specific volume of solvation is the solute-induced change in the solvent volume. The contribution $v^{\Delta}_{2;1,3/M}$ is positive, and the contribution $\Delta v^{\Delta}_{2;1,3/h}$ is negative. The specific intrinsic volume has two contributions

$$v^{\Delta}_{2;1,3/M} = v^{\Delta}_{2;1,3/c} + v^{\Delta}_{2;1,3/cav} \tag{14}$$

where $v^{\Delta}_{2;1,3/c}$ is the specific constitutive atomic volume and $v^{\Delta}_{2;1,3/cav}$ results from imperfect atomic packing.

The specific partial adiabatic compressibility coefficient of component 2 at infinite dilution, $k^{\Delta}_{S\,2;1,3}$, can be written as[52,55,58−60]

$$k^{\Delta}_{S\,2;1,3} = -\left(\frac{\partial v^{\Delta}_{2;1,3}}{\partial P}\right)_S = k^{\Delta}_{S\,2;1,3/cav} + \Delta k^{\Delta}_{S\,2;1,3/h} \tag{15}$$

where $k^{\Delta}_{S2;1,3/cav} = -(\partial v^{\Delta}_{2;1,3/cav}/\partial P)_S$ is the cavity adiabatic compressibility coefficient and $\Delta k^{\Delta}_{S2;1,3/h} = -(\partial \Delta v^{\Delta}_{2;1,3/h}/\partial P)_S$ is the solvation adiabatic compressibility coefficient. In eq 15, the effect of pressure on the atomic volume was neglected.

Materials and Methods

Chemicals and Solvents. 4-tert-Octylphenol, TOP, 90% (Fluka); acetone, 99.5%; ethanol, 99.7%; toluene, 99.5%; and *n*-heptane, 99.0% (Chemical Products of Monterrey) were used as received. Silica gel 60 for chromatography, 70-230 mesh (Merck). For the measurement of the density and speed of sound, toluene was dried and distilled from sodium.

Separation of Asphaltenes and Resins. A crude oil sample was first deasphalted. A total of 40 g of material was added to 2 L of *n*-heptane in a flask, stirred for 24 h, and left to settle overnight. The black precipitate was filtered using a Whatman filter paper number 42. The solid was mixed with 500 mL of *n*-heptane, and

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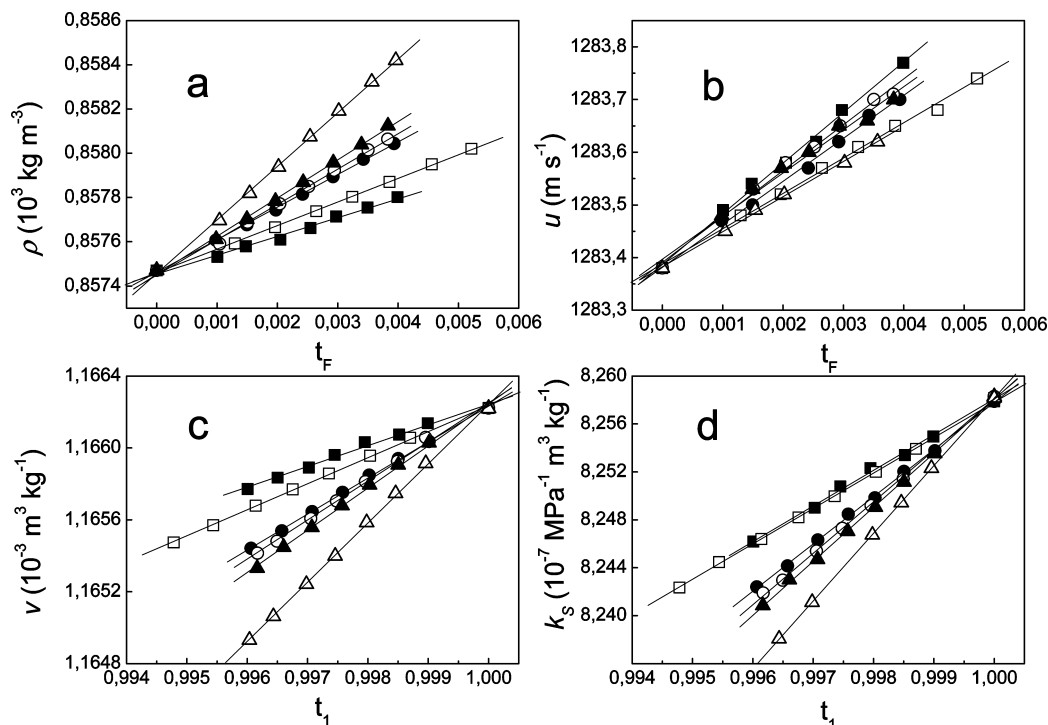
Figure 1. System composed of asphaltenes and surfactant TOP at 303.150 K. Only some values of t_{f3} are shown for clarity: (■) $t_{f3} = 0$, (□) $t_{f3} = 0.245$, (○) $t_{f3} = 0.406$, (●) $t_{f3} = 0.506$, (▲) $t_{f3} = 0.596$, and (△) $t_{f3} = 1$. (a) Density as a function of t_F. (b) Sound speed against t_F. (c) Specific volume as a function of t_1. (d) Specific adiabatic compressibility coefficient against t_1.

stirring and filtering were repeated to ensure the complete removal of maltenes (saturate, aromatic, and resins compounds). Then, the asphaltenes were dried at 45 °C under vacuum for 3 h. After filtration, the maltenes were recovered by evaporating the solvent using a rotary evaporator and then placed in a vacuum oven at 45 °C for 24 h until there was no change in their weight with time.

The Soxhlet extraction technique has been previously used for asphaltene fractionation with good results.[61] In this work, as an alternative application of this technique, Soxhlet extraction was used for the separation of the resins fraction. Other authors used Soxhlet extraction for the separation of the resins fraction previously.[62] The difference with our method is that they used chloroform as a solvent and we used a mixture of acetone and ethanol. In addition to this, they did not specified the type of support employed. We used silica gel, and it is well-known[63] that the type of support determines the type of obtained product. The silica gel was activated for 24 h at 120 °C under vacuum. A total of 1 g of maltenes was dissolved in 100 mL of *n*-heptane. A mixture of silica gel (40 g) in *n*-heptane (100 mL) was added, and this was stirred for 30 min. The solvent was removed at 80 °C using a rotary evaporator. The maltenes adsorbed onto silica gel were subjected to Soxhlet extraction with 250 mL of toluene for 2 h and at the boiling point of the solvent. The extraction was interrupted, and the resins fraction adsorbed onto silica gel was then removed using 200 mL of a solvent mixture of acetone and ethanol (90/10 respective concentrations) and filtered. The resins were recovered by evaporating the solvents at 60 °C, using a rotary evaporator, and then placed in vacuum at 45 °C for 24 h until there was no change in weight with time.

Sample Preparation. Toluene was considered as component 1; asphaltenes were considered as component 2; and surfactant (TOP) or resins were considered as component 3. The fraction F was considered as composed of 2 and 3 as follows: $t_F = (m_2 + m_3)/(m_1 + m_2 + m_3)$, $t_1 = t_F - 1$, and $t_{f3} = m_3/(m_2 + m_3)$.

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Measurements of Density and Speed of Sound. Measurements of density and speed of sound were carried out using a DSA 5000 (Anton Paar density and speed of sound analyzer) at a work temperature of 303.150 ± 0.005 K. The uncertainty in the density measurement is 5×10^{-3} kg m^{-3}, and the uncertainty in the sound measurement is 5×10^{-2} m s^{-1}.

Parts a and b of Figure 1 show respectively the density and sound speed for the system composed of toluene, asphaltenes, and surfactant as functions of t_F for some values of t_{f3}. For clarity, some values of t_{f3} were omitted. The experimental concentration ranges of t_F were established to obtain a linear behavior of the measured specific properties with respect to t_F (high dilution region[51,52]). With regard to TOP, its micellar behavior in toluene solution had not been previously reported in the literature. For each value of t_{f3}, in the system composed of asphaltenes and surfactant, eight concentrations were chosen from $t_F = 0$ to 0.004 and, for the system composed of asphaltenes and resins, seven concentrations where chosen from $t_F = 0$ to 0.003, also at regular intervals. All samples were heated at 303.1 ± 0.1 K for 24 h in a water bath.

Calculation of the Partial Properties. The specific volume v and the specific adiabatic compressibility coefficient k_S were calculated by

$$v = \frac{1}{\rho} \tag{16}$$

$$k_S = \left[\frac{1}{\rho u}\right]^2 \tag{17}$$

where ρ is the density and u is the speed of sound. Parts c and d of Figure 1 show the specific volume and specific adiabatic compressibility coefficient as functions of $t_1 = 1 - t_F$ at different values of t_{f3}, where for clarity some values of t_{f3} were omitted. For each value of t_{f3}, the specific volume and the specific adiabatic compressibility coefficient were fitted with the following smoothing functions:

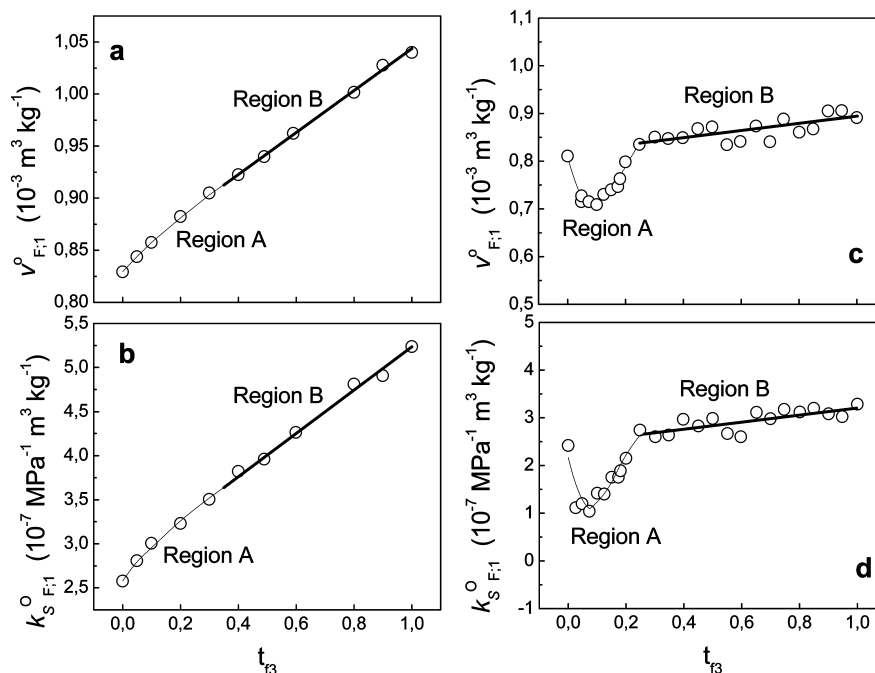$$j = j^\circ_{F;1} + (j_1 - j^\circ_{F;1})t_1 \tag{18}$$

Figure 2. (a) Specific partial volume at infinite dilution, $v_{F;1}^{\circ}$, of fraction F in toluene at 303.15 K as a function of the composition of the fraction. Fraction F is composed of asphaltenes and the surfactant TOP. (b) Specific partial adiabatic compressibility coefficient at infinite dilution, $k_{SF;1}^{\circ}$, of fraction F in toluene at 303.15 K as a function of t_{f3}. (c) Specific partial volume at infinite dilution, $v_{F;1}^{\circ}$, of fraction F (composed of asphaltenes and resins) in toluene at 303.15 K as a function of the composition of the fraction. (d) Specific partial adiabatic compressibility coefficient at infinite dilution, $k_{SF;1}^{\circ}$, of the fraction composed of asphaltenes and resins in toluene at 303.15 K as a function of t_{f3}.

where j stands, respectively, for v and k_S, $j_{F;1}^{\circ}$ stands for $v_{F;1}^{\circ}$ and $k_{SF;1}^{\circ}$, and j_1 stands for v_1 (specific volume of pure toluene) and k_{S1} (specific adiabatic compressibility coefficient of pure toluene). Parts a and b of Figure 2 show, respectively, $v_{F;1}^{\circ}$ and $k_{SF;1}^{\circ}$ as functions of the composition of fraction F for the system composed of asphaltenes and surfactant. In parts c and d of Figure 2, these partial properties are shown when fraction F is composed of asphaltenes and resins. The partial properties $j_{2;1,3}^{\Delta}$ and $j_{3;1,2}^{\Delta}$ (Figures 3 and 4) were calculated using eq 9. The values of the derivatives $dj_{F;1}^{\circ}/dt_{f3}$ were obtained by polynomial or linear fits from the plots in Figure 2.

Results and Discussion

Interactions between Asphaltenes and Surfactant. Parts a and b of Figure 2 show, respectively, $v_{F;1}^{\circ}$ and $k_{SF;1}^{\circ}$ as functions of t_{f3} when fraction F is composed of asphaltenes (component 2) and surfactant (component 3). In both figures, there is a first nonlinear region (region A) and a second linear region (region B). The transition between these two regions is between $t_{f3} =$ 0.3 and 0.4. In our previous work,[52] it was demonstrated that, if the plot of $j_{F;1}^{\circ}$ is linear from $t_{f3} = 0$ to 1, then the components of fraction F are not interacting. A pseudo-component was defined as a fraction with constant composition. As a consequence, if $j_{F;1}^{\circ}$ is linear only in a interval (t_{f3}, 1), this means that a pseudo-component, composed of the whole of component 2 and a part of component 3, was formed in region B and that this pseudo-component does not interact with the other part of component 3. This can be ascribed to the saturation of the interaction because the maximum of the interaction is reached between the components of fraction F. For this reason, it is possible to conclude that the maximum of the interaction (or saturation) between asphaltenes and the surfactant TOP occurs between $t_{f3} = 0.3$ and 0.4 according to parts a and b of Figure 2.

To calculate the derivative $dj_{F;1}^{\circ}/dt_{f3}$, data of region A were fitted to a fourth-order polynomial and data of region B were fitted to a straight line.

Parts a and b of Figure 3 show the specific partial volumes of asphaltenes and surfactant, respectively, as functions of t_{f3}. In our previous work,[52] we studied the interaction between noncharged polymer particles and a surfactant. This system was chosen because the main interaction is hydrophobic. The specific partial volumes of polymer particles and surfactant are shown in Figure 3a, and the specific partial adiabatic compressibility coefficients are shown in Figure 3b. Interestingly, one observes that the particular behavior of this system is very similar to that of the interaction between asphaltenes and surfactant (parts c and d of Figure 3).

The partial properties of the polymer particles (parts a and b of Figure 3) increase until they reach a constant limiting value. The increase is interpreted in terms of dehydration because of the location of surfactant molecules on the particle surface. When the surface of particles is saturated with surfactant molecules, the constant value is then reached. The partial properties of the surfactant (parts a and b of Figure 3) decrease until they reach a constant value, which can be interpreted in terms of a simple model. By derivation of eq 10 with respect to t_{f3}, supposing $j_{3a;1,2}^{\Delta}$ is constant and bearing in mind that $t_{3a} + t_{3S} = 1$

$$\frac{dj_{3;1,2}^{\Delta}}{dt_{f3}} = -[j_{3a;1,2}^{\Delta} - j_{3;1}^{\circ}]\frac{dt_{3s}}{dt_{f3}} \tag{19}$$

From parts a and b of Figure 3, at very small values of t_{f3}, the slope of $j_{3;1,2}^{\Delta}$ is negative and then $dj_{3;1,2}^{\Delta}/dt_{f3}$ is negative. Surfactant free in solution is more hydrated than surfactant adsorbed to the particle, and then by virtue of eqs 13 and 15, ($j_{3a;1,2}^{\Delta} - j_{3;1}^{\circ}$) is positive. Therefore, dt_{3a}/dt_{f3} must be positive, indicating an increase of free surfactant in solution.

In our previous work,[52] it was concluded that the particular behavior of the interactions between the noncharged polymer particles and surfactant is characteristic of an hydrophobic
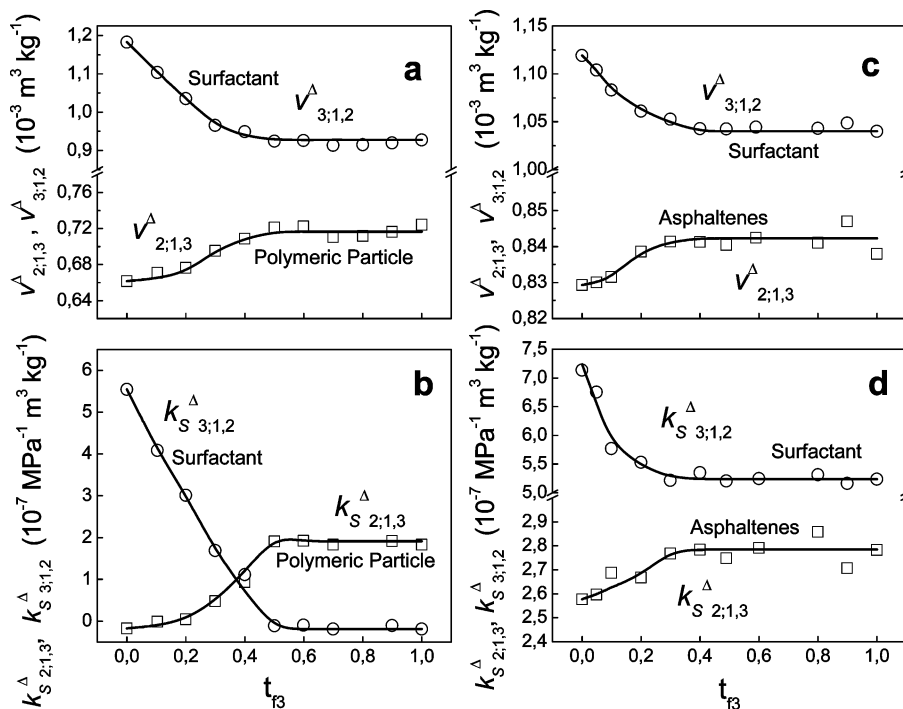
Figure 3. (a) Specific partial volumes at infinite dilution of noncharged polymer particles $v_{2;1,3}^{\Delta}$ and an ionic surfactant $v_{3;1,2}^{\Delta}$ in water solution at 303.15 K as a function of t_{f3}. Data were taken from ref 52. (b) Specific partial adiabatic compressibility coefficients at infinite dilution of noncharged polymeric particles, $k_{S2;1,3}^{\Delta}$, and an ionic surfactant, $k_{S3;1,2}^{\Delta}$, in water solution at 303.15 K as a function of t_{f3}. Data were taken from ref 52. (c) Specific partial volumes at infinite dilution of asphaltenes $v_{2;1,3}^{\Delta}$ and the surfactant TOP $v_{3;1,2}^{\Delta}$ in toluene solution at 303.15 K as a function of t_{f3}. (d) Specific partial adiabatic compressibility coefficients at infinite dilution of asphaltenes, $k_{S2;1,3}^{\Delta}$, and the surfactant TOP, $k_{S3;1,2}^{\Delta}$, in toluene solution at 303.15 K as a function of t_{f3}.
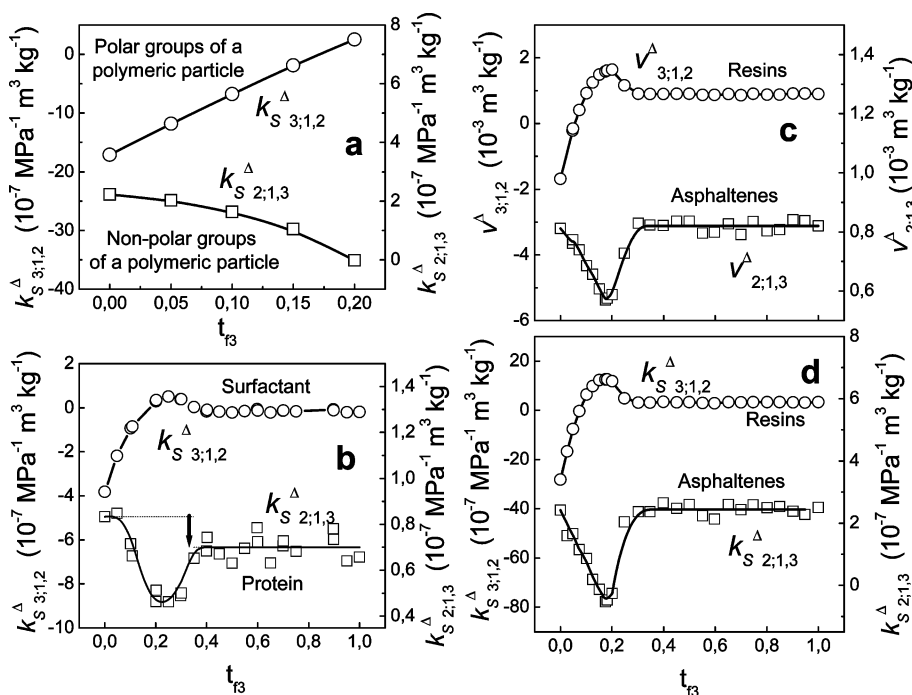

Figure 4. (a) Specific partial adiabatic compressibility coefficients of nonpolar ($k_{S2;1,3}^{\Delta}$) and polar groups ($k_{S3;1,2}^{\Delta}$) in a swelling process of a functionalized polymeric particle in water solution at 303.15 K as functions of the mass fraction of polar groups. Data were taken from ref 51. (b) Specific partial adiabatic compressibility coefficients at infinite dilution of a protein (lysozyme) and a surfactant, decyltrimethylammonium bromide, ($k_{S2;1,3}^{\Delta}$ and $k_{S3;1,2}^{\Delta}$, respectively) in the process of induced unfolding of the protein by the surfactant in aqueous solution, as functions of t_{f3}. The measurements were made in water solution at 303.15 K. Data were taken from ref 52. (c) Specific partial volumes at infinite dilution of asphaltenes, $v_{2;1,3}^{\Delta}$, and resins, $v_{3;1,2}^{\Delta}$, in toluene solution at 303.15 K as a function of t_{f3}. (d) Specific partial adiabatic compressibility coefficients at infinite dilution of asphaltenes, $k_{S2;1,3}^{\Delta}$, and resins, $k_{S3;1,2}^{\Delta}$, in toluene solution at 303.15 K as a function of t_{f3}.

binding, which only affects the surface of the macromolecules. Because the characteristic behavior of the partial properties of asphaltenes and surfactant is qualitatively identical to that

observed with the system composed of noncharged polymer particles and surfactant; some conclusions can be drawn. First, interactions are solvophobic and only involve the surface of

the asphaltene aggregates without changes at the interior of the aggregates. Second, the behavior of the partial properties of the surfactant infers that an adsorption isotherm exits in concordance with other investigations.[46,48−50]

Interactions between Asphaltenes and Resins. In this case, fraction F is composed of asphaltenes and resins and t_{f3} is the mass fraction of resins in fraction F. Parts c and d of Figure 2 show $v_{F;1}^\circ$ and $k_{SF;1}^\circ$, respectively, as functions of t_{f3}. In both figures, there is a region A (nonlinear) and a region B (linear). The nonlinearity of region A indicates some type of interaction between asphaltenes and resins, which agrees with a previous work using the density functional theory.[64] It was reported that, for the asphaltene−asphaltene, asphaltene−resin, and resin−resin dimers, the preferred configuration corresponds to a face-to-face orientation, with the binding energy for the asphaltene−asphaltene dimers being around 56.5 kJ/mol, the binding energy for asphaltene−resin dimers being around 54.4 kJ/mol, and the binding energy for resin−resin dimers being around 23.8 kJ/mol. We observe that the binding energy for the asphaltene−asphaltene dimer is similar to the asphaltene−resin dimer, and the binding energy of the resin−resin dimer is smaller by at least one-half. On the basis of rigorous quantum calculations,[64] it appears that the resins molecules interact preferentially with the asphaltene aggregates rather than with themselves.

As in the systems investigated above, the linearity of region B in parts c and d of Figure 2 indicates the saturation of the interaction between asphaltenes and resins. To calculate the partial properties of asphaltenes and resins at infinite dilution, data of $v_{F;1}^\circ$ and $k_{SF;1}^\circ$ in region A were fitted to a third-order polynomial, while data of region B were fitted to a straight line.

Parts c and d of Figure 4 show, respectively, the specific partial volume and specific partial adiabatic compressibility coefficients for asphaltenes (component 2) and resins (component 3) at infinite dilution. As in the case of the system composed of asphaltenes and surfactant, this system will be interpreted in comparison to systems previously investigated.[51,52] First, we will examine the swelling process of functionalized polymer particles and then the process of induced unfolding of a protein by an ionic surfactant.

The functionalized polymer particles will be considered as fraction F composed of nonpolar groups (component 2) and polar groups (component 3). Figure 4a shows the specific adiabatic compressibility coefficients of components 2 and 3 as functions of t_{f3}, which represents the mass fraction of polar groups in the particles. At low values of t_{f3}, $k_{S3;1,2}^\Delta$ is negative, indicating that polar groups are largely hydrated, and when t_{f3} increases, $k_{S3;1,2}^\Delta$ becomes positive. At low values of t_{f3}, the polar groups are located on the surface of the particles, which are exposed to the hydration. When t_{f3} increases, the polar groups are located at the interior of the particles where they are less exposed. The specific partial adiabatic compressibility of the nonpolar groups slightly decreases until $t_{f3} = 0.10$. At this concentration, hydrated polar groups migrate into the interior of the particles, causing a slight hydration of the nonpolar groups. At higher values of t_{f3}, $k_{S2;1,3}^\Delta$ decreases faster because of the repulsion between the polar groups of the polymer chains, which leads to the disentanglement and separation of the polymer chains and allows the entrance of a large number of water molecules into the polymer particles.

It is commonly accepted that the interactions between a protein and an ionic surfactant involve a sequence of different types of binding. The first binding type is at low concentrations of surfactant

and takes place on specific sites of the protein. This interaction is electrostatic in origin and involves the entire surfactant molecule. When these binding sites are saturated, the second binding type occurs. The hydrophobic tails of the surfactant penetrate into the hydrophobic domains of the globular molecule to reduce their contacts with water[65] and the unfolding of the protein consequently occurs. This binding type is hydrophobic and cooperative. When the unfolding of the protein is completed, the third binding type takes place with the encapsulation of the protein by the surfactant molecules.[52,65]

In the case of the induced unfolding of the protein, fraction F is composed of the protein (component 2) and the cationic surfactant (component 3). Here, t_{f3} is the mass fraction of the surfactant in fraction F. Figure 4b shows the specific partial adiabatic compressibility of the protein ($k_{S2;1,3}^\Delta$) and the surfactant ($k_{S3;1,2}^\Delta$) as functions of t_{f3} The first binding type occurs from $t_{f3} = 0$ to $t_{f3} \approx 0.05$. At these concentrations, $k_{S3;1,2}^\Delta$ is negative and smaller than $k_{S3;1}^\circ$ (specific partial adiabatic compressibility of the surfactant free in solution). This fact can be explained in terms of the specific interaction with high affinity that involves the whole surfactant molecule.[52,66,67] Bearing in mind the high strength of this interaction, the low value of specific partial adiabatic compressibility coefficient can be explained in terms of a loss of molecular flexibility because of the immobilization of the surfactant molecule on the binding site. In addition, using eq 19 and similar arguments to the system composed of polymer particles and surfactant or asphaltenes and surfactant, one can conclude that $k_{S3;1,2}^\Delta$ first increases in this domain of concentrations because of the presence of free surfactant in solution. Simultaneously, $k_{S2;1,3}^\Delta$ must decrease slightly, according to the Gibbs−Duhem-type equation (eq 8).

The second type of binding occurs from $t_{f3} \approx 0.05$ to $t_{f3} \approx 0.25$. In this region of compositions, $k_{S3;1,2}^\Delta$ reaches positive values, while $k_{S2;1,3}^\Delta$ drops. This behavior is parallel to that of the swelling of the functionalized polymer particles (Figure 4a). The increase of $k_{S3;1,2}^\Delta$ can be interpreted in terms of the introduction of surfactant molecules in the hydrophobic domains of the protein.[65] The quick drop in $k_{S3;1,2}^\Delta$ is interpreted in terms of the exposition of buried amino acid groups to the hydration, resulting from the unfolding of the protein. Interestingly, one observes a sharp transition between the first binding type and the second one.

From $t_{f3} \approx 0.25$ on, the unfolding process is concluded, and up to $t_{f3} \approx 0.40$, a similar qualitative behavior to that of the interaction between polymer particles and surfactant or asphaltenes and surfactant is observed. Therefore, one can conclude that a third binding type takes place, which is hydrophobic and only affects the surface of the unfolded proteins. Other authors interpret this third binding as the encapsulation of the proteins by the surfactant molecules.[65] After $t_{f3} \approx 0.40$, the maximum of the interaction between proteins and the surfactant is reached, while the saturation of the interaction occurs.

Because the behavior of volumes and coefficients of compressibility are very similar in parts c and d of Figure 4, we will discuss only the behavior of compressibility coefficients.

Figure 4d shows that, near $t_{f3} = 0.0$, the specific partial adiabatic compressibility coefficient of resins ($k_{S3;1,2}^\Delta$) is smaller than $k_{S3;1}^\circ$ (specific partial adiabatic compressibility coefficient of resins free in toluene solution). As in the case of the interactions between proteins and ionic surfactants, this fact is

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(66) Jones, M. N.; Prieto, G.; del Rio, J. M.; Sarmiento, F. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2805.
(67) Hayashi, K.; Kugimiya, M.; Imoto, T.; Funatsu, M.; Bigelow, C. C. *Biochemisty* **1968**, *7*, 1461.

interpreted in terms of specific interactions with high affinity and strength. This result is in agreement with a previous work[68] using molecular mechanical calculations that showed that resins interact with asphaltenes on specific binding sites at low resins concentrations. In addition, because of the separation process, by which the asphaltenes and resins are obtained from the crude oil, these two fractions are polar fractions and, therefore, it is reasonable to expect some type of electrostatic interactions between them.

In this range of compositions, near $t_{f3} = 0.0$, $k_{S;3;1,2}^{A}$ increases, while $k_{S;2;1,3}^{A}$ decreases. By virtue of eq 19 and in parallel with the interaction between protein and surfactant, the increase in the specific partial adiabatic compressibility coefficient is a consequence of the increase of free resins in solution. The decrease in $k_{S;2;1,3}^{A}$ can be interpreted as the result of a slight solvation because of the reorganization of the asphaltene molecules in the aggregates as a result of these specific and high-affinity interactions with resins.

From near $t_{f3} = 0.0$ to $t_{f3} \approx 0.20$, a second type of interaction is found. In this case, $k_{S;3;1,2}^{A}$ increases until a maximum with positive value is reached, while $k_{S;2;1,3}^{A}$ decreases to a minimum. A similar qualitative behavior was observed in the swelling process of the functionalized polymer particles and in the interactions between proteins and cationic surfactants. In this way, the increase in the specific partial adiabatic compressibility coefficient of the resins ($k_{S;3;1,2}^{A}$) is most likely due to the penetration of resin molecules in the asphaltene aggregates. Simultaneously, this penetration causes the separation of the asphaltene molecules in the aggregates, allowing the entrance of solvent molecules inside the asphaltene aggregates. A second binding type takes place, yielding the swelling of the aggregates. This is an interesting difference between the behavior of asphaltenes and proteins, because the aggregates of asphaltenes swell, whereas the proteins unfold. In addition to this, another interesting difference is the sharp transition from the first interaction type to the second one in the case of the protein and surfactant, which is more diffuse with asphaltenes and resins. With the proteins and surfactant, the native state of the proteins is separated from the ensemble of their denatured states by a highly cooperative transition of the all-or-none type.[69] However, the transition with the asphaltenes and resins is diffuse, because the transition from the first binding type to the second is gradual, as both types of binding coexist.

From $t_{f3} \approx 0.20$ to $t_{f3} \approx 0.35$, the specific partial adiabatic compressibility coefficient of the resins decreases from a positive value to a limiting value, whereas the specific partial adiabatic compressibility coefficient of asphaltenes increases until it reaches a limiting value. A similar behavior was found in systems composed of noncharged polymer particles and a surfactant, asphaltenes and a surfactant, and protein and a surfactant. Therefore, this suggests that a solvophobic interaction exits in which resin molecules are located on the surface of the swelled aggregates. The maximum of the interaction or saturation of the interaction takes place after the aggregates are encapsulated by the resin molecules.

Conclusions

In this work, the systems composed of asphaltenes and a surfactant in toluene solution and asphaltenes and resins in

toluene solution at 303.15 K were investigated at infinite dilution using a thermodynamic method developed by us in a previous work.[52]

In the system composed of asphaltenes and the surfactant TOP in toluene solution, it was shown that the surfactant is located on the surface of the asphaltene aggregates. In the case of the system composed of asphaltenes and resins in toluene solution, it was observed that the interactions take place in a sequence of different types of bindings. The first binding type occurs at very low concentrations of resins and is specific with high affinity. The second type causes the "induced swelling" of the asphatene aggregates by the intrusion of resin molecules. The transition between the first and second type of interactions is diffuse, indicating the coexistence between them. The third interaction type takes place on the surface of the swelled aggregates and eventually ceases with the encapsulation of the aggregates by the resin molecules. These results highlight the important role of solvation effects in interactions that involve asphaltenes. This fact will have consequences when pressure is increased because the structure of the solvent can change and become more like a solvation shell around the solutes.[70]

According to eq 12, the contributions to $j_{F;1}^{o}$ are only due to the clusters and the molecules of component 3 free in solution. That is, $j_{F;1}^{o}$ does not show contributions because of the interaction between clusters or between free molecules of component 3 free in solution. In addition to this, from the Gibbs−Duhem-type equation (eq 8), the two derivatives of $j_{2;1,3}^{A}$ and $j_{3;1,2}^{A}$ with respect to t_{f3} in the Gibbs−Duhem-type equation (eq 8) are mathematically coupled, indicating that the behavior of one affects that of the other. The behavior of component 1 is not affected by the interactions between 2 and 3 because the term $dj_{1;2,3}^{A}/dt_{f3}$ does not appear in the Gibbs−Duhem-type equation. However, the presence of 1 affects the behavior of 2 and 3. Because the interactions occur at infinite dilution, component 1 is practically in the pure state. Accordingly, the Gibbs−Duhem-type equation (eq 8) properly translates the scenario in which components 2 and 3 are interacting together while being immersed in pure component 1, acting as a solution medium. As a consequence, we consider that the thermodynamic results reported in this work can be used to directly compare to computer simulations. If other infinite dilution "limits" are used,[51] the comparisons with computer simulations would not be straightforward.

Finally, we have explored an alternative method to separate the resins fractions from the maltenes using a Soxhlet extraction technique with encouraging results. Under this procedure, it is possible to obtain 1 g of resins in a period of 3 days with no more than 1.5 L of solvent. Thus, this procedure is complimentary to other methods used to separate resins fraction from crude oil.

Appendix

In this Appendix, we show that the Gibbs−Duhem-type equation (eq 8) cannot be directly deduced from the Gibbs−Duhem equation. In a previous paper (see eq 56 of ref 51), we shown that the Gibbs−Duhem equation for a system composed of component 1 and fraction F (composed of components 2 and 3) is

$$m_1 dj_{1;F} + m_F dj_{F;1} = m_F[j_{3;1,2} - j_{2;1,3}]dt_{f3} \qquad (20)$$

Dividing by the total mass of the system, eq 20 takes the form

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(69) Taulier, N.; Chalikian, T. V. *Biochim. Biophys. Acta* **2002**, *1595*, 48.
(70) Chalikian, T. V.; Sarvazyan, A. P.; Funck, T.; Cain, C. A.; Breslauer, K. J. *J. Phys. Chem.* **1994**, *89*, 321.

$$t_1 dj_{1;F} + t_F dj_{F;1} = t_F[j_{3;1,2} - j_{2;1,3}]dt_{f3} \qquad (21)$$

Considering $j_{1;F}$ and $j_{F;1}$ as functions of t_F and t_{f3}, we have

$$dj_{1;F} = \left(\frac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} dt_F + \left(\frac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} dt_{f3}$$

$$dj_{F;1} = \left(\frac{\partial j_{F;1}}{\partial t_F}\right)_{t_{f3}} dt_F + \left(\frac{\partial j_{F;1}}{\partial t_{f3}}\right)_{t_F} dt_{f3} \qquad (22)$$

and substituting eq 22 in eq 21, reorganizing, and bearing in mind that t_F and t_{f3} are independent variables, it yields

$$\begin{cases} t_1\left(\dfrac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} + t_F\left(\dfrac{\partial j_{F;1}}{\partial t_F}\right)_{t_{f3}} = 0 \\[4mm] t_1\left(\dfrac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} + t_F\left(\dfrac{\partial j_{F;1}}{\partial t_{f3}}\right)_{t_F} = t_F[j_{3;1,2} - j_{2;1,3}] \end{cases} \qquad (23)$$

Deriving with respect to t_{f3} in eq 3

$$\left(\frac{\partial j_{F;1}}{\partial t_{f3}}\right)_{t_F} = j_{3;1,2} - j_{2;1,3} + t_{f2}\left(\frac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F} + t_{f3}\left(\frac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F} \qquad (24)$$

and substituting this result in eq 23

$$\underbrace{\underbrace{t_1\left(\frac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} + t_F\left(\frac{\partial j_{F;1}}{\partial t_F}\right)_{t_{f3}}}_{\substack{\text{Interaction between the component 1 and the fraction F}\\ \text{due to the amount of fraction F in the system}}} = 0}_{}$$

$$\underbrace{t_1\left(\frac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} + t_F\underbrace{\left[t_{f2}\left(\frac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F} + t_{f3}\left(\frac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F}\right]}_{\substack{\text{Interaction between the components of the}\\ \text{fraction F in terms of the composition of the fraction}}} = 0}_{\substack{\text{Interaction between the component 1 and the fraction F}\\ \text{due to the composition of the fraction}}} \qquad (25)$$

The first equation in eq 25 describes the effect of the interaction between 1 and fraction F as a result of the concentration of F, without taking into consideration the effects due to the composition of F. The second equation describes the effects of the interactions depending on the composition of F, and considering the effects from the internal interactions in fraction F.

Now, we go to study the Gibbs−Duhem equation (eq 25) at the limit of the infinite dilution of the fraction, considering that the partial property of the solvent (component 1) tends to the specific property of the solvent in pure estate. That is, taking the limit in eq 25 when t_F tends to zero while t_{f3} is kept constant

$$\lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} \left\{ t_1\left(\frac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} + t_F\left(\frac{\partial j_{F;1}}{\partial t_F}\right)_{t_{f3}} \right\} = 0$$

$$\lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} \left\{ t_1\left(\frac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} + t_F\left[t_{f2}\left(\frac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F} + t_{f3}\left(\frac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F}\right] \right\} = 0 \qquad (26)$$

Because $j_{1;F}$ tends to the specific property in pure estate, j_1, and because j_1 does not depend upon either t_F or t_{f3}

$$\lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} t_1\left(\frac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} = \lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} (1-t_F)\left(\frac{\partial j_{1;F}}{\partial t_F}\right)_{t_{f3}} = 0$$

$$\lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} t_1\left(\frac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} = \lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} (1-t_F)\left(\frac{\partial j_{1;F}}{\partial t_{f3}}\right)_{t_F} = 0 \qquad (27)$$

In this way, substituting eq 27 in eq 26 gives

$$\begin{cases} \lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} t_F\left(\dfrac{\partial j_{F;1}}{\partial t_F}\right)_{t_{f3}} = 0 \\[6mm] \lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} t_F\left[t_{f2}\left(\dfrac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F} + t_{f3}\left(\dfrac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F}\right] = 0 \end{cases} \qquad (28)$$

It is very interesting to observe that in the second equation of eq 28

$$\lim_{\substack{t_F \to 0 \\ t_{f3}\text{ constant}}} t_F\left[t_{f2}\left(\frac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F} + t_{f3}\left(\frac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F}\right] = 0 \not\Rightarrow$$

$$\not\Rightarrow t_{f2}\left(\frac{\partial j_{2;1,3}}{\partial t_{f3}}\right)_{t_F=0} + t_{f3}\left(\frac{\partial j_{3;1,2}}{\partial t_{f3}}\right)_{t_F=0} \equiv t_{f2}\frac{dj_{2;1,3}^{\Delta}}{dt_{f3}} + t_{f3}\frac{dj_{3;1,2}^{\Delta}}{dt_{f3}} = 0 \qquad (29)$$

That is to say that the Gibbs−Duhem equation (eq 20, 21, 23, or 25) describes the interactions in the system at finite concentrations. However, at infinite dilution, it does not provide information about the internal interactions of fraction F. For this reason, the Gibbs−Duhem-type equation (eq 8) is a different equation and not a consequence of the Gibbs−Duhem equation.

Nomenclature

J = general notation of an extensive thermodynamic property

m_1 = mass of component 1 (kg)

m_2 = mass of component 2 (kg)

m_3 = mass of component 3 (kg)

$j_{1;2,3}$ = general notation of a specific partial property of component 1 in the presence of components 2 and 3

$j_{2;1,3}$ = general notation of a specific partial property of component 2 in the presence of components 1 and 3

$j_{3;1,2}$ = general notation of a specific partial property of component 3 in the presence of components 1 and 2

F = fraction of the system composed of components 1 and 2

m_F = total mass of fraction F (kg)

t_1 = mass fraction of component 1 in the system

t_F = mass fraction of fraction F in the system

t_{f2} = mass fraction of component 2 in fraction F

t_{f3} = mass fraction of component 3 in fraction F

$j_{1;F}$ = general notation of a specific partial property of component 1 in the presence of fraction F

$j_{F;1}$ = general notation of a specific partial property of fraction F in the presence of component 1

$\Delta j_{F;1}^{\circ}$ = general notation of a specific partial property of fraction F in the presence of component 1 at the infinite dilution of the fraction

$j_{2;1,3}^{\Delta}$ = general notation of a specific partial property at the infinite dilution limit of fraction F of component 2 in the presence of components 1 and 3

$j_{3;1,2}^{\Delta}$ = general notation of a specific partial property at the infinite dilution limit of fraction F of component 3 in the presence of components 1 and 2

t_{3a} = ratio of the mass fraction of component 3 adsorbed on the surface of component 2.

t_{3S} = ratio of mass fraction of component 3 free in solution

$j_{3a;1,2}^{\Delta}$ = general notation of a specific partial property of component 3 adsorbed on the surface of component 2 in the presence of component 1

$j_{3;1}^{\circ}$ = general notation of a specific partial property of component 3 in the presence of component 1

$v_{2;1,3/M}^{\Delta}$ = specific intrinsic volume of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (m^3 kg^{-1})

$\Delta v_{2;1,3/h}^{\Delta}$ = specific volume of solvation of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (m^3 kg^{-1})

$v_{2;1,3/c}^{A}$ = specific constitutive atomic volume of component 2 in the presence of the components 1 and 3 at the infinite dilution limit of fraction F (m^3 kg^{-1})

$v_{2;1,3/cav}^{A}$ = specific cavity volume of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (m^3 kg^{-1})

$k_{S2;1,3}^{A}$ = specific partial adiabatic compressibility coefficient of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (MPa^{-1} m^3 kg^{-1})

$k_{S2;1,3/cav}^{A}$ = specific partial adiabatic compressibility coefficient of the cavity of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (MPa^{-1} m^3 kg^{-1})

$\Delta k_{S2;1,3/h}^{A}$ = specific partial adiabatic compressibility coefficient of solvation of component 2 in the presence of components 1 and 3 at the infinite dilution limit of fraction F (MPa^{-1} m^3 kg^{-1})

ρ = density (m^{-3} kg^1)

u = sound speed (m s^{-1})

v = specific volume (m^3 kg^{-1})

k_S = specific adiabatic compressibility coefficient (MPa^{-1} m^3 kg^{-1})

j = general notation of a specific thermodynamic property

j_i = general notation of the specific property of component 1 in the pure state

v_1 = specific volume of component 1 in the pure state (m^3 kg^{-1})

k_{S1} = specific partial adiabatic coefficient of component 1 in the pure state (MPa^{-1} m^3 kg^{-1})

$v_{F;1}^{\circ}$ = specific partial volume of fraction F in the presence of component 1 at the infinite dilution of fraction F (m^3 kg^{-1})

$k_{SF;1}^{\circ}$ = specific partial adiabatic coefficient of fraction F in the presence of component 1 at the infinite dilution limit of fraction F (MPa^{-1} m^3 kg^{-1})

t_{f3}^{c} = composition of fraction F separating regions A and B