



Study of the interaction between asphaltenes and resins by microcalorimetry and ultraviolet–visible spectroscopy



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HIGHLIGHTS

- We study the interaction between asphaltenes and resins.
- The resins are able reduce asphaltenes' precipitation.
- The solubility parameter of asphaltenes was modified by resins' presence.
- There is an optimal concentration for the interaction between these fractions.

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ABSTRACT

Precipitation of asphaltenes causes large losses to the petroleum industry. Therefore, dispersant additives are generally used to prevent this precipitation. On the other hand, some studies indicate that asphaltenes can be stabilized by the presence of resins, but the mechanism by which asphaltenes are stabilized by resins or dispersant additives is not fully understood. The objective of this paper was study the interaction between asphaltenes and resins. For this, the solubility parameter range of the resins with or without the presence of asphaltenes was determined by ultraviolet–visible spectrometry. By microcalorimetry, the interaction enthalpies between resins and asphaltenes were determined, as well as it were studied the interaction heats of two dispersant agents and asphaltenes mixtures. The results showed that the resins tested were able to stabilize the asphaltenes by interacting strongly with them and modifying their solubility parameters. Furthermore, the most effective stabilizing additive presented an exothermic interaction with asphaltenes.

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1. Introduction

Asphaltenes are by definition the crude oil fractions that are insoluble in light hydrocarbons (pentane, heptane) but soluble in benzene and toluene [1]. Asphaltenes have been extensively studied due to their tendency to precipitate, even at low concentrations, generating losses during oil production and refining, as well as for their emulsification power, which hampers the separation of water and oil, causing various other problems for the petroleum industry [2–4]. The precipitation of asphaltenes depends on temperature and pressure [5]. Hamadou et al. indicate that they precipitate along with resins and although carry out the treatment of the damaged cores using a good solvent, a amount of asphalt-

enes and resins are still retained in the core [6]. The constituent fractions of resins have also been widely studied, and theories have been developed according to which they are responsible for stabilizing asphaltenes and thus influencing the behavior of these components [7–9].

Despite having been studied for decades, questions about asphaltenes and resins fractions still have not been fully clarified. Asphaltenes are composed of very complex molecules, prompting recent studies of their deposition [10] and structure [11]. Regarding the influence of resins on the behavior of asphaltenes, Marques et al. found results that contradict the suggestion made by other authors since the 1940s that resins can stabilize asphaltenes [12]. However, this study was performed with resin concentrations of at most 1%, so the authors suggested further research with higher concentrations, although stressing that good stabilizers work even at low concentrations. Rahimi et al. also indicated lower stabilization efficiency of resins in relation to synthetic stabilizers [13], but demonstrated the efficacy of stabilization by resins and indicated

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the action mechanism was that suggested by León et al. In this model, the resins are initially adsorbed on the surface of the asphaltenes, then penetrate the micropores in the asphaltene structure, rupturing them to allow the diffusion of asphaltene–resin particles in the solvent [14].

Despite this proposed model, there is still no consensus on the stabilization of asphaltenes by resins. For example, another study shows the possibility of adsorption of multiple resin layers on the surface of asphaltenes [15].

Spiecker et al. [16] showed that the addition of resins can reduce the precipitation of asphaltenes by between 10% and 50%, also diminishing the size of the aggregates in solution. Besides these findings, the authors suggested that resins can form small aggregates similar to those of asphaltenes and that resins from different crude oils can present similar efficiencies to solvate asphaltenes from a determined source.

Many substances have been tested to stabilize asphaltenes to prevent them from precipitating in production lines [17]. Additionally, many studies have been carried out to shed more light on the mechanism by which asphaltenes can be stabilized or to find an equation to predict precipitation of asphaltenes [18].

These substances, called dispersants, should reduce or retard the precipitation of asphaltenes or diminish the tendency of aggregates to build up on surfaces [19]. Good dispersants also should reproduce the interactions that occur between asphaltenes, i.e., be capable of π – π interactions and hydrogen bonding. For this purpose, they need to have Lewis acid or Lewis base reactions, depending on whether the asphaltenes are carried positively or negatively [17,20].

Chang and Fogler [21] concluded that good dispersants should have an aromatic ring with a polar group and an aliphatic chain. Linear alkyl benzene sulfonic acid and 4-n-octyl benzoic acid are compounds that meet these requirements and are already used in the petroleum industry [22].

Despite many years of study, the mechanism relating the interactions of asphaltenes, resins and additives is not fully understood, requiring more research. One such study [23] determined the solubility parameters of asphaltenes and crude oils using a principle similar to that for determining the solubility parameters of polymers, but applying the microcalorimetry and ultraviolet techniques (UV–Vis). In that study, the authors found microcalorimetry to be effective to measure the heat generated by the interaction between substances, and both techniques to be effective to determine the solubility parameter range of asphaltenes and crude oil [23].

This article reports experiments employing these same techniques to study the interaction of asphaltenes and resins. For this purpose, we ran precipitation tests of asphaltenes with resins and commercial dispersants at different concentrations using UV–Vis spectroscopy. We also used this technique to assess whether the resins could alter the solubility parameter range of the asphaltenes. Finally, we used microcalorimetry to determine the enthalpy of interaction of the asphaltene–resin or asphaltene–dispersant mixtures, to verify how the resins can be interacting with the asphaltenes.

2. Materials and methods

An asphaltic residue sample, called AR, was donated by Petrobras, Brazil. The solvents n-hexane, n-heptane, ethanol and toluene, all with P.A. purity, were supplied by Vetec Química Fina, Brazil. The solubility parameters (in $\text{MPa}^{1/2}$) of Hildebrand and Hansen (cited in brackets) of these solvents are, respectively [24], 14.9 ($\delta_d = 14.9$, $\delta_p = 0$, $\delta_h = 0$), 15.3 ($\delta_d = 15.3$, $\delta_p = 0$, $\delta_h = 0$), 26.2 ($\delta_d = 15.8$, $\delta_p = 8.8$, $\delta_h = 19.4$) and 18.2 ($\delta_d = 18.2$, $\delta_p = 1.4$, $\delta_h = 2.0$)

$\text{MPa}^{1/2}$. The dispersant additives used were linear alkyl benzene sulfonic acid (purity grade $\geq 95\%$) and 4-n-octyl benzoic acid (purity grade $\geq 99\%$), supplied by Sigma–Aldrich, USA.

2.1. Extraction of asphaltenes and resins from the asphaltic residue

An asphaltenes fraction (called asphaltenes–C7AR) and a resins fraction (called resins–C7AR) were extracted from the asphaltic residue. The asphaltenes were separated from the crude oil by the IP 143 method [25], in which the asphaltenes were isolated from the asphaltic residue by precipitation induced by the addition of a flocculant (n-heptane) in a Soxhlet extractor, with reflux of 1 h or until the reflux solvent was clean. In this way, we obtained a solution of resins in the paraffinic solvent (n-heptane) and asphaltenes as a precipitate in filter paper. We considered the resins to be the fraction of the asphaltic residue not soluble in n-heptane. Then we extracted the asphaltenes contained in the precipitate with toluene. The asphaltenes and resins were recovered after evaporation of the solvents toluene and n-heptane, respectively.

2.2. Characterization of the extracted substances

To characterize the asphaltenes–C7AR and resins–C7AR fractions, we determined the concentration of carbon, hydrogen, nitrogen and oxygen (CHNO) with a Thermo Finnigan Flash EA 1112 CHN elemental analyzer. This analysis is based on the ASTM D 5291-01 method [26]. The sulfur content was determined indirectly, by subtracting the sum of the contents of C, H, N and O from 100%.

2.3. Precipitation tests

The flocculation or dispersion of the asphaltenes was assessed using the asphaltenes precipitation test [27]. This test is based on causing the destabilization of the asphaltenes dispersed in a mixture of solvents. When varied quantities of n-heptane are added to the asphaltene–toluene system, for example, the previously stabilized asphaltenes can precipitate out of solution. The concentration of the remaining asphaltenes in solution can be obtained by measuring the absorbance in an ultraviolet–visible spectrophotometer, by comparison against a standard curve [27].

For these tests we used a Varian Cary 50 UV–Vis spectrophotometer, equipped with an external probe with optical path of 2 mm. The standard curve of absorption intensity versus asphaltene concentration was performed by preparing a stock asphaltene–C7AR solution (0.2% w/v in toluene, from which solutions with different concentrations were obtained by successive dilutions. The absorbance values of the solutions were obtained at a wavelength of 850 nm. This wavelength had already been selected in previous works [23,27,28].

To perform the asphaltene precipitation tests, solutions of the resins (5.0% w/v or 2.5% w/w) containing asphaltenes (1.0% w/v) were first prepared. These solutions were left at rest for 24 h to promote complete solubilization of the sample. Then nine aliquots of 1 mL were taken from these solutions and distributed in nine test tubes, after which 9 mL of a mixture of solvents containing toluene and n-heptane, in varied proportions, was added to each tube, so as to obtain mixtures of 15, 30, 40, 50, 60, 70, 80 and 90% v/v of n-heptane in relation to total volume. A blank test, without adding any stabilizer, was also carried out. Therefore, the results of this test refer to the mixtures containing 0% (blank test), 0.5% w/v and 0.25% of resins, each one containing 0.1% w/v of asphaltenes.

All the prepared samples were left at rest for 24 h and then centrifuged at 30,000 rpm for 30 min. Details of the estimation of the

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