http://dx.doi.org/10.5935/0100-4042.20150172 *Quim. Nova,* Vol. 39, No. 1, 26-31, 2016

COMPARISON BETWEEN ASPHALTENES (SUB)FRACTIONS EXTRACTED FROM TWO DIFFERENT ASPHALTIC RESIDUES: CHEMICAL CHARACTERIZATION AND PHASE BEHAVIOR

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Recebido em 02/06/2015; aceito em 14/09/2015; publicado na web em 11/11/2015

Asphaltenes are blamed for various problems in the petroleum industry, especially formation of solid deposits and stabilization of water-in-oil emulsions. Many studies have been conducted to characterize chemical structures of asphaltenes and assess their phase behavior in crude oil or in model-systems of asphaltenes extracted from oil or asphaltic residues from refineries. However, due to the diversity and complexity of these structures, there is still much to be investigated. In this study, asphaltene (sub)fractions were extracted from an asphaltic residue (AR02), characterized by NMR, elemental analysis, X-ray fluorescence and MS-TOF, and compared to asphaltene subfractions obtained from another asphaltic residue (AR01) described in a previous article. The (sub)fractions obtained from the two residues were used to prepare model-systems containing 1 wt% of asphaltenes in toluene and their phase behavior was evaluated by measuring asphaltene precipitation onset using optical microscopy. The results obtained indicated minor differences between the asphaltene fractions obtained from the asphaltic residues of distinct origins, with respect to aromaticity, elemental composition (CHN), presence and content of heteroelements and average molar mass. Regarding stability, minor differences in molecule polarity appear to promote major differences in the phase behavior of each of the asphaltene fractions isolated.

Keywords: asphaltene extraction; asphaltene characterization; asphaltene phase behavior; asphaltene precipitation.

INTRODUCTION

Asphaltenes, together with paraffins with high molar mass, are among the main compounds that cause organic deposits in the oil industry. Unlike paraffins, asphaltenes do not melt, and they can form deposits in rock formation pores, valves, pumps, storage tanks and refinery lines.[1-5] Asphaltenes along with naphthenic acid salts are also blamed for stabilizing water-in-oil emulsions, making the demulsification process more difficult.[6-12]

In general, their complex structures consist in polynuclear aromatic rings with different alkyl branches containing acid and basic groups and some elements such as sulfur, oxygen, nitrogen, vanadium and nickel.[4] Asphaltenes are constituted by a family of molecules with structures that have similar characteristics of molar mass and polarity, when compared with other petroleum components. Besides that, the content and the chemical structure of asphaltenic fractions depend on the source of the crude oil. These molecules tend to autoaggregate in a lamellar way because present interconnected aromatic rings. These interactions generally occur by hydrogen bonds, donor-acceptor electrons in complexes with transition metals and relocation of ϖ electrons in condensed aromatic rings.[9]

Asphaltenes can remain soluble in the oil or can precipitate if the petroleum equilibrium is shifted by changing pressure or oil composition. Asphaltenes stability depends basically on their content and light fractions one in the oil. For instance, aromatic fractions act as solvents for asphaltenes, and, on the other hand, hydrocarbons do not, i.e. any adverse disturbance in the balance between the hydrocarbon and aromatic fractions can lead to the precipitation of asphaltenes.

Because of these problems, many studies have been performed to elucidate various aspects of asphaltenes, such as their chemical composition, chemical structure, phase behavior in crude oil and model systems, and solubility parameters.[4,13-19] However, due to the diversity and complexity of these structures, there is still much to be investigated.

The aim of this study was to extract asphaltene (sub)fractions from an asphaltic residue (AR02), characterize the (sub)fractions by nuclear magnetic resonance (NMR), elemental analysis, X-ray fluorescence and mass spectrometry (MS-TOF), and to compare the results with those for the same types of (sub)fractions extracted from an asphaltic residue (AR01), described in a previous article,[13] in order verify differences in asphaltenes fraction in function of asphaltic residue source. We also evaluated the phase behavior of all these (sub)fractions in model systems containing 1 wt% of asphaltenes in toluene, by monitoring the precipitation onset through optical microscopy, in order to compared phase behaviors and try to correlate that with characterization data.

EXPERIMENTAL

Materials

n-Decane P.A., 99.5% n-heptane, 99.0% n-nonane, n-octane P.A. and 99.0% n-pentane were acquired from Vetec Química Fina (Xerém, RJ, Brazil) and used as received. Commercial toluene obtained from the same supplier was used after distillation and drying in alumina. Deuterated chloroform, from Cambridge Isotopic Laboratory (Tewksbury), was also used as received. The asphaltic residue from unit 1790 of the Duque de Caxias Refinery (REDUC)

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(Duque de Caxias, RJ, Brazil), sampled on August 18, 2010, was donated by the Petrobras Research Center (CENPES), here called AR02. Asphaltene (sub)fractions,[13] obtained from another asphaltic residue from the same unit and refinery, sampled on February 1, 2008 and called AR01, were used for comparison.

Methods

Extraction of asphaltene fractions from asphaltic residue AR02

Two fractions were separated from asphaltic residue AR02 by extraction with n-pentane: resins C5S and asphaltenes C5I. For this purpose, about 30 g of asphaltic residue was ground and left under the action of 1 L of a paraffinic solvent (n-pentane) to precipitate for 24 hours under stirring. Then the material was filtered through filter paper at room temperature (25 °C), to obtain two fractions: the resins soluble in the paraffinic solvent and the precipitated asphaltenes caught in the filter paper. This precipitate was placed in a Whatman cartridge (internal diameter: 94 mm) and submitted to extraction in a Soxhlet extractor to separate and dissolve the resin residues still adsorbed to the asphaltenes. In a round-bottom beaker n-pentane was added in a volume related to 1:35 (g of asphaltic residue/mL of n-pentane). The extraction process was continued until the solvent appeared clear in the upper part of the extractor. The resins dissolved in the beaker were added to the previously obtained solution and recovered after evaporation of the solvent in an IKA RV 05 basic rotary evaporator coupled to vacuum pump, under reduced pressure at 50 °C.

The asphaltenes that remained precipitated in the filter within the cartridge were then submitted to reflux with dry toluene (aromatic solvent), at a ratio of 1:35 (g of asphaltic residue/mL of solvent) until the solvent in the upper part of the extractor was clear. The dissolved asphaltenes were recovered after toluene evaporation in rotary evaporator, under reduced pressure at a temperature of 80 °C. The asphaltenes and resins obtained in the evaporator were placed in a Pyrex jar (wrapped with aluminum foil to prevent contact with light). The jar was then placed inside an exhaust hood for evaporation of the residual solvent for approximately 3 days. Finally, these fractions were placed separately in closed flasks covered with aluminum foil to prevent their oxidation by the action of light.

Starting from asphaltenes C5I, the asphaltenes C5I-C6 and asphaltenes C6 were obtained by using n-hexane. From asphaltenes C6, it was obtained C6I-C7 and C7 using n-heptane. And by a sequence of similar extractions using n-octane, n-nonane and n-decane, it was obtained asphaltenes C7I-C8, C8I-C9 and C9I-C10, respectively. The last extraction procedure produced also asphaltenes C10I. The separation method used with the asphaltic residue AR02 was the same as employed in a previous study[13] for separation of asphaltenes from asphaltic residue AR01; in such reference there is also a scheme explaining all the procedure.

Characterization of asphaltene fractions

The asphaltene (sub)fractions were analyzed by X-ray fluorescence in a Rigaku 3100 EDX-720 energy dispersive spectrometer equipped with an Rh tube. This device comes with six analyzers: RIX 35, RIX 60, LiF 200, LiF 220, Ge and PET. The samples were submitted to a vacuum on the order of 10^{-5} Pa and the data were processed with the SmartLab Guidance software.

To characterize the content of aromatic and aliphatic hydrogen, nuclear magnetic resonance (NMR) experiments were performed with a Varian Mercury 300. Hydrogen spectra were obtained at 300 MHz with 0.1% wt v^{-1}. The integration of spectra was carried out with Mestrenova® program. To characterize the content of mono- and diaromatic hydrogen, and α, β and γ saturared hydrogens, NMR experiments were performed with a Varian Inova 300 spectrometer, at 300 MHz with a 5% wt v^{-1} sample dissolved in a 1:1 mixture of deuteriochloroform and tetrachloroethylene at room temperature, using 4.9-microsecond (45-degree) pulses and 128 transients. The integration of the spectra was done with the MestRec® program.

Elemental analysis was used to determine the composition of the fractions in terms of % weight of hydrogen, carbon and nitrogen. The sample was subjected to thermal oxidation at a temperature of 975 °C under an oxygen atmosphere, leading to total and quantitative conversion of the components in CO_2 (for quantification of carbon), H_2O (quantification of hydrogen) and NO_2 (quantification of nitrogen), under controlled pressure, temperature and volume conditions. In this procedure, the gaseous products are carried to the separation module in which selective separation occurs. Copper and silver columns are used for separation of CO_2 and H_2O, respectively. Once separated, the gases are detected in function of their thermal conductivities, with N_2 being the first to be detected because it is not retained. Next the CO_2 and last the H_2O are thermally desorbed. This analysis enables determination of the H/C or C/H ratio, which provides the unsaturation degree of the sample.[20] The elemental analysis was performed with a Perkin-Elmer CHN 2400 analyzer to measure the percentages of carbon, hydrogen and nitrogen present in the samples.

The matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF) spectrometry technique was used to measure the molar masses of the asphaltene fractions and subfractions. The samples' spectra were obtained with a Shimadzu AXIMA Confidence mass spectrometer. The TOF linear mode was used with positive ionization and an N_2 laser, operating at 200 Hz. Fifty microliters of THF was employed to prepare a solution of about 2 μg mL^{-1}, which was deposited on the support for analysis and evaporated at room temperature. In these assays, no matrix was used for ionization. The data were processed with the software that comes with the instrument.

Determination of asphaltene precipitation onset

Initially model systems of asphaltenes in toluene at 1 wt% were prepared. The titration with n-heptane is usually monitored by using near infrared (NIR) spectrometry at 1600 nm.[21] However in this work we have used optical microscopy to determine the precipitation onset of the asphaltenes (sub)fractions. For this purpose, each model system was mixed with n-heptane and after adding every 0.1 mL, the system was analyzed under an Olympus BX50 optical microscope with an Uplanfl 20x/0.5PH1 lens.

RESULTS AND DISCUSSION

Extraction and characterization of asphaltene samples

We extracted asphaltene fractions and subfractions C5I, C5I-C6, C6I-C7, C7I-C8, C8I-C9, C9I-C10 and C10I from an asphaltic residue sample (AR02). The residue and its fractions were characterized and compared against the results previously obtained with (sub)fractions extracted from another asphaltic residue (AR01),[13] to elucidate possible differences in the molecules obtained from different sources. Besides this, we also compared the characterization results and phase behavior of these fractions in model systems at 1 wt% in toluene. The type of fractioning carried out permitted obtaining subfractions containing molecules characteristic of a solubility range, unlike conventional fractioning. For example, all the molecules of fraction C10I were found to be present in fraction C5I, which is a broader fraction in terms of solubility parameter range.

Table 1 shows the yield obtained for the fractions C5I and C10I after extraction. Table 2 shows the yield obtained for each fraction after extraction with the different solvents. The portion of material that remained after the separation of fraction C5I from AR02 was called resin C5S. The yield obtained from the fractioning carried out with AR02 in comparison to AR01, obtained by Honse *et al.*,[13] showed that the percentage of fraction C5I obtained was very similar between the two sources, as was the percentage of fraction C10I. However, differences were observed in the quantities of material distributed in the subfractions. For example, the percentage by mass of subfraction C5I-C6 obtained from residue AR02 was only half that of the same subfraction obtained from residue AR01,[13] meaning the presence of a lower number of these more stable asphaltene molecules. These differences can be related to the nature and predominance of the types of structures present in the two types of asphaltic residue and their relative solubilities during fractioning, indicating the variations of asphaltenic structures (type and content) that can be found in different types of crude oil.

Each of these (sub)fractions obtained along with the asphaltic residue sample was characterized by means of X-ray fluorescence, NMR, elemental analysis and mass spectrometry.

X-ray fluorescence analysis permits identifying and quantifying the individual elements (in percentage terms) contained in a sample, from sodium to uranium (periodic table).[22] The different asphaltene fractions were analyzed by this technique to better understand the differences in chemical composition of these molecules. The results are reported in Table 3. In all cases of the subfractions obtained from AR02, the most prevalent element detected (86 to 96%) was sulfur. Similar results were obtained for the subfractions from AR01, where the sulfur content varied from 83 to 95%.[13] The elements calcium (Ca), copper (Cu), iron (Fe), nickel (Ni), phosphorous (P), silicon (Si) and vanadium (V) were detected at much lower levels that sulfur (S), in the range from 0.03 to 7.45%. Cobalt (Co), chromium (Cr), erbium (Er) and thulium (Tm) were not detected in AR02. Similar results were obtained for the subfractions obtained from AR01,[13] evidencing that these elements do not make a significant contribution to the possible differences of behavior between the fractions from the different sources.

Characterization by H^1-NMR was only performed for the asphaltene subfractions from AR01. The subfractions from AR02 and resins C5S were not analyzed by this technique. As expected, the spectra of all the samples presented peaks related to aromatic and aliphatic hydrogen, from which we calculated the relative percentages of these two hydrogen types. The results are given in Table 4. Although the literature suggests that the polarity of asphaltene molecules increases with rising aromaticity,[4,23] we did not observe a significant difference of the aromatic/aliphatic hydrogen ratios, which varied randomly from 0.28 to 0.31. All the fractions obtained from residue AR02 showed solubility differences, but these must be attributed to other factors (such as molar mass), or the differences between H_{aro} and H_{ali} are so small that the resonance technique is unable to detect them. While for the subfractions from AR01[13] it was possible to detect a slight tendency for increase of aromatic hydrogen in relation to aliphatic hydrogen in the more polar fractions, the results obtained for the

Table 1. Mass of samples extracted from asphaltic residues AR01[13] and AR02

Samples	AR01[13] (150g)			AR02 (150g)		
	Resins C5S	Asphaltenes C5I	Asphaltenes C10I	Resins C5S	Asphaltenes C5I	Asphaltenes C10I
Mass (g)	121.5	28.5	18.56	122	28	20.32
Mass (%)	-	100	65.1	-	100	72.6

Table 2. Yield of the asphaltenes subfractions obtained from C5I AR01[13] and C5I AR02

	Yield of (sub)fractions (%)					
	C5I-C6	C6I-C7	C7I-C8	C8I-C9	C9I-C10	C10I
From C5I AR01[13]	3.48	1.01	0.72	1.15	0.27	13.02
From C5I AR02	1.87	0.83	1.55	0.31	0.55	13.53

Table 3. Elements (from sodium to uranium) detected in the samples AR01[13], AR02 and theirs asphaltenes fractions

Elements	AR01[13]				AR02			
	Residue (%)	Resin C5S (%)	Asphaltenes C5I (%)	Asphaltenes C10I (%)	Residue (%)	Resin C5S (%)	Asphaltenes C5I (%)	Asphaltenes C10I (%)
Ca	0	3.992	0.768	0	0.479	3.393	0.295	0
Co	0	0	0.273	0	0	0	0	0
Cu	0.356	0.120	0.284	0	0.412	0.293	0	0.040
K	0	0	0	0	0.104	0	0	0
Fe	0.813	0.332	0.735	1.193	0.243	0.282	0.168	0.182
Ni	1.178	0.185	1.607	2.772	1.203	0.287	0.292	0.281
P	0	0	3.331	3.533	3.454	2.865	2.812	2.932
S	88.841	95.332	85.941	83.187	85.721	91.095	95.275	95.266
Si	7.290	0	4.326	5.971	7.45	1.452	0	0
V	1.522	0.039	2.733	3.345	0.934	0.333	1.158	1.241
Zn	0	0	0	0	0	0	0	0.058
Total	100	100	100	100	100	100	100	100

subfractions from AR02 indicated an absence of this relationship for the fractions analyzed. Other studies involving more precise analysis[16,24] by resonance have indicated greater presence of condensed aromatic (diaromatic) rings than monoaromatic rings in asphaltenes' structure (Table 5). However, our results did not show an increase in diaromatic and a decrease in monoaromatic hydrogen with increased polarity of the sample.

The concentrations of carbon, nitrogen and hydrogen were determined in a CHN analyzer and the results are presented in Table 6. Comparison of the (sub)fractions obtained shows that the carbon contents are practically equal, and for the most polar fraction (C10I), the hydrogen content is smaller and the nitrogen higher than for the other fractions. The fact that the total contents do not reach 100% is coherent with the X-ray fluorescence technique, which mainly reveals the presence of sulfur, while oxygen can also be present. The variation of nitrogen was, in some extension, confirmed by the fact that it was not possible to determine asphaltenes precipitation onset of these subfractions by near infrared spectroscopy at 1600 nm, which enables detecting the N-H bonds of the asphaltenes without interference from the vibrations related to the bonds present in the solvents.[25] The same tendency for variation of nitrogen content of the subfractions extracted from residue AR01[13] was observed, although the percentage obtained for the fractions extracted from AR01 are slightly higher than those obtained for the fractions extracted from AR02. However, the results reported by Speight[19] indicate that the ratio between these elements does not differ significantly in asphaltenes. Therefore, we can suggest that the molecules that compose the asphaltenic fraction can vary in composition and composition distribution, so that solubility differences can be caused by one or another factor, such as aromaticity, molar mass, presence of the elements O, S and others, or type of chemical group formed by the arrangement of these elements.

Table 4. Percentage of aromatic and aliphatic hydrogens at the asphaltenes C5I and asphaltenes C10I extracted from asphaltic residues AR01[13] and AR02

	AR01[13]			AR02		
	$H_{\text{aromáticos}}$ (%)	$H_{\text{alifáticos}}$ (%)	$H_{\text{aro}}/H_{\text{ali}}$	$H_{\text{aromáticos}}$ (%)	$H_{\text{alifáticos}}$ (%)	$H_{\text{aro}}/H_{\text{ali}}$
C5I	15.2	84.8	0.18	13.8	86.2	0.16
C5I – C6	14.0	86.0	0.16	12.5	87.5	0.14
C6I – C7	17.5	82.5	0.21	14.5	85.5	0.17
C7I – C8	18.5	81.5	0.23	13.8	86.2	0.16
C8I – C9	18.3	81.7	0.22	16.0	84.0	0.19
C9I – C10	17.6	82.4	0.21	15.6	84.4	0.18
C10I	22.0	78.0	0.28	13.0	87.0	0.15

Table 5. Percentage of diaromatic, monoaromatic and aliphatic hydrogens at the asphaltenes fractions and subfractions extracted from asphaltic residue AR 02

Hydrogen types	Asf. C5I	Asf. C5I – C6	Asf. C6I – C7	Asf. C7I – C8	Asf. C8I – C9	Asf. C9I – C10	Asf. C10I
Di Aromatic	17.43	16.80	18.29	17.86	17.51	15.72	15.97
Mono Aromatic	6.03	4.86	5.35	5.64	5.73	5.70	6.39
α	19.31	22.15	21.05	20.32	24.35	16.54	19.51
β	36.78	41.28	37.39	37.53	41.08	38.51	36.55
γ	20.44	14.90	17.92	18.65	11.33	23.54	21.58
Total Aromatics (%)	23.47	21.67	23.64	23.50	23.25	21.42	22.37
Total Saturates (%)	76.53	78.33	76.36	76.50	76.75	78.58	77.63
$H_{\text{ARO}}/H_{\text{ALI}}$	0.31	0.28	0.31	0.31	0.31	0.27	0.29

Table 6. Content of carbon, hydrogen and nitrogen of asphaltenes fractions extracted from asphaltic residues AR01[13] and AR02

Asphaltenes	Residue	C	H	N	Total	H/C	N/C
C5I	AR01[13]	86.72	8.35	1.76	96.83	0.096	0.020
C5I – C6		86.40	10.53	1.55	98.48	0.122	0.018
C8I – C9		86.35	8.96	1.60	96.91	0.104	0.019
C10I		81.16	7.93	1.69	91.05	0.098	0.021
C5I	AR02	84.48	5.68	1.24	91.40	0.067	0.015
C5I – C6		83.50	9.74	0.61	93.85	0.117	0.007
C6I – C7		83.88	9.27	0.91	94.06	0.111	0.011
C7I – C8		83.36	8.11	0.91	92.38	0.097	0.011
C8I – C9		83.43	8.59	0.93	92.95	0.103	0.011
C10I		83.00	7.46	1.14	91.60	0.090	0.014

* Analyses error: 0.3 % of the obtained value.

Table 7. Average molar masses of asphaltenes fractions extracted from asphaltic residues AR01[13] and AR02

Sources of asphaltenes	Molar masses (Da)						
	C5I	C5I-C6	C6I-C7	C7I-C8	C8I-C9	C9I-C10	C10I
AR01[13]	350	-	-	-	-	-	440
AR02	340	340	325	375	355	365	445

There has been a good deal of discrepancy in the findings regarding the molar mass of asphaltenes in recent years due to different sample preparation methods and measurement techniques. Size exclusion chromatography (SEC), vapor pressure osmometry, viscosimetry, fluorescence correlation spectroscopy (FCS) and mass spectrometry are among the techniques used to determine the molar mass of asphaltenes. The values reported vary from 500 to 40,000 g/mol.[4,26-30] Among these techniques, mass spectrometry (MS) has been gaining wider acceptance and the most recent values observed are substantially lower than those reported in previous decades (300 to 1,400 g mol^{-1}).[31-33] The average molar mass values found by MS for the asphaltenes (sub)fractions are presented in Table 7. These show a trend for increased molar mass with greater polarity of the asphaltenic fraction, with higher average values for fraction C10I (445 Da) than C5I (340 Da).[4] This order of size is consistent with the values obtained by MS by other authors, while the differences between fractions C5I and C10I are in line with the values obtained previously for the fractions obtained from the other asphaltic residue (RA01) applying the same separation method used in this study.

Evaluation of phase behavior of asphaltenes in toluene model systems

Precipitation of asphaltenes can be induced by adding a flocculant solvent. Light n-alkanes, such as n-pentane and n-heptane, fit in this category, because asphaltenes are insoluble in this type of compound.[34,35] A variety of techniques can be applied to measure the onset of asphaltene precipitation in petroleum.[36] Despite near--infrared (NIR) spectrometry is more applied, in this study we used optical microscopy (OM), since no characteristic profiles of absorption against volume of n-heptane could be obtained at 1600 nm. It can be associated to the relative low nitrogen content in some of the subfraction. For optical microscopy, the model system is maintained under stirring and after the addition of each aliquot of n-heptane, a very small quantity is examined under the microscope until asphaltene particles can be observed.

The asphaltene precipitation onset results of the model systems prepared with fractions C5I and C10I and subfractions C5I-C6, C6I-C7, C7I-C8 and C8I-C9, obtained from asphaltic residues AR01 and AR02, are reported in Table 8.

By comparing fractions C5I and C10I, it should be noted that they contain the same more polar molecules, which tend to precipitate first as the solubility parameter of the solvent medium declines due to the addition of n-heptane to toluene.[4,37] According to Aguiar *et al.*,[17] asphaltene fractions C5I and C10I, from a certain crude oil, present solubility parameter ranges from 17.9 to 23.8 MPa$^{1/2}$ and 19.1 to 23.8 MPa$^{1/2}$, respectively. As expected,[15] fraction C5I proved to be more stable than C10I, because the precipitation of the C5I asphaltenes required a larger volume of n-heptane than the volume of that solvent necessary to induce precipitation of the C10I asphaltenes. This results from the fact that fraction C5I contains less polar asphaltenes molecules than does C10I, giving greater stability to the more polar molecules. The same behavior was observed in comparing the results for the same asphaltene fractions extracted from distinct residues (AR01 and AR02) (Table 8), that is, the stability decreases from subfraction C5I-C6 to C8I-C9, which is in accordance with the fact that these fractions were obtained under the same solubility conditions. However, the values obtained differ significantly for the subfractions obtained from different residues, probable because of: (i) differences in polarity of the molecules due to the distinct sources and/or (ii) differences in the relative quantities of each "class" of molecules within the same fraction, as discussed in the preceding item. In the first case (i), it is possible that the asphaltene fractions extracted from different sources contain more polar molecules with different solubility parameters in each system. Indeed, the results showed in Table 3 indicate that fractions extracted from AR01 have structures with higher aromatic/aliphatic and, so, more polar and more unstable. This is also confirmed by elemental analyzes results (Table 4). Other authors have also suggested that the chemical composition affects the aggregation of asphaltenes.[38] The second case (ii) is based on the differences of the yields distribution obtained for every subfractions from different residues. But, the influence of such distribution is hard to observe since the so obtained subfractions represent a very low percentage (Table 2) of the total amount of molecules which constitute fraction C5I.

Table 8. Asphaltenes precipitation onset obtained by optical microscopy (OM) for model systems containing 1 wt% of asphaltenes (sub)fractions, extracted from asphaltic residues AR01 and AR02, in toluene

Asphaltenes (sub) fractions	Asphaltenes precipitation onset (mL of n-heptane/mL of model system) ± 0.05	
	AR01	AR02
C5I	1.37	2.05
C5I-C6	7.00	> 20.00
C6I-C7	5.36	20.00
C7I-C8	3.75	5.06
C8I-C9	2.86	3.20
C10I	1.08	0.55

CONCLUSIONS

Comparison of the C5I and C10I fractions, and subfractions extracted from distinct asphaltic residues indicated differences and similarities in function of the origin of the material. The main similarities were the average molar masses of the different fractions (340-350 and 445-450 Da, respectively, for C5I and C10I of distinct origins) and the similar differences in molar mass distribution observed when comparing C5I with C10I. The differences noted were the solubility distribution of the various molecules composing the residue, the presence and content of elements in the range from sodium to uranium, and the aromaticity distribution. However, the differences observed among the (sub)fractions extracted from distinct asphaltic residues are not very emphasized. With respect to stability, the results indicates that slight differences in the polarity of the molecules, which constitute asphaltenes, provokes large differences in the phase behavior of these (sub)fractions.

ACKNOWLEDGEMENTS

We thank CNPq, CAPES, FAPERJ, Nalco Brasil Ltda., ANP and Petrobras for grants and financial support.

REFERENCES

1. Mansoori, G. A.; Jiang, T. S.; Kawanaka, S.; *Arabian J. Sci. Eng.* **1988**, *13*, 7.
2. Hong, E.; Watkinson, P.; *Fuels* **2004**, *83*, 1881.
3. Sousa, M. A.; Oliveira, G. E.; Lucas, E. F.; González, G.; *Prog. Colloid Polym. Sci.* **2004**, *128*, 283.
4. Mullins, O. C.; Sheu, E. Y.; Hammami, A.; Marshall, A. G.; *Asphaltenes, Heavy Oils, and Petroleomics*, Springer: New York, 2007.
5. Henriques, C. B.; Winter, A.; Koroishi, E. T.; Maciel Filho, R.; *Quim. Nova* **2011**, *34*, 424.

Vieira, L. C.; Buchuid, M. B.; Lucas E. F.; *Energy Fuels* **2010**, *24*, 2213.

6. McLean, J. D.; Kilpatrick, P. K.; *J. Colloid Interf. Sci.* **1997**, *189*, 242.
7. Kilpatrick, P. K.; Spiecker, P. M.; Gawrys, K. L.; *J. Colloid Interf. Sci.* **2003**, *267*, 178.
8. Yarranton, H. W.; Hussein, H. E.; Masliyah, J. H.; *J. Colloid Interf. Sci.* **2006**, *228*, 52.
9. Ramalho, J. B. V. S.; Lechuga, F. C.; Lucas, E. F.; *Quim. Nova* **2010**, *33*, 1664.
10. Gruber, L. D. A.; Damasceno, F. C.; Caramão, E. B.; Jacques, R. A.; Geller, A. M.; Campos, M. C. V.; *Quim. Nova* **2012**, *35*, 1423.
11. Honse, S. O.; Mansur, C. R. E.; Lucas, E. F.; *J. Braz. Chem. Soc.* **2012**, *23*, 2204.
12. Bertelli, J. N.; Dip, R. M. M.; Pires, R. V.; Albuquerque, F. C.; Lucas, E. F.; *Energy Fuels* **2014**, *28*, 1726.
13. Honse, S. O.; Ferreira, S. R.; Mansur, C. R. E.; Gonzalez, G.; Lucas, E. F.; *Quim. Nova* **2012**, *35*, 1991.
14. Heckmann, J. R.; Landau, L.; Gonçalves, F. T. T.; Pereira, R.; Azevedo D. A.; *Quim. Nova* **2011**, *34*, 1328.
15. Garreto, M. S. E.; Mansur, C. R. E.; Lucas, E. F.; *Fuel* **2013**, *113*, 318.
16. Silva, F. B.; Guimarães, M. J. O. C.; Seidl, P. R.; Garcia, M. E. F.; *Brazilian Journal of Petroleum and Gas* **2013**, *7*, 107.
17. Aguiar, J. I. S.; Garreto, M. S. E.; González, G.; Luca, E. F.; Mansur, C. R. E.; *Energy Fuels* **2014**, *28*, 409.
18. Altoé, R.; Oliveira, M. C. K.; Lopes, H. E.; Teixeira, C.; Cirilo, L. C. M.; Lucas, E. F.; Gonzalez, G.; *Colloids Surf., A* **2014**, *445*, 59.
19. Lucas, E. F.; Ferreira, L. S.; Khalil, C. N. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., ed.; John Wiley & Sons: Hoboken, 2015.
20. Speight, J. G.; *The Chemistry and Technology of Petroleum*, 3rd ed., Marcel Dekker: New York, 1999.
21. Garreto, M. S. E.; Gonzalez, G.; Ramos, A. C.; Lucas, E. F.; *Chem. Chem. Technol.* **2010**, *4*, 317.
22. Jenkins, R.; *X-Ray Fluorescence Spectrometry*, 2nd ed., John Wiley & Sons: New York, 1999.
23. Pacheco, V. F.; Ferreira, L. S.; Lucas, E. F.; Mansur, C. R. E.; *Energy Fuels* **2011**, *5*, 1659.
24. Acevedo, S.; Escobar, G.; Ranaudo, M. A.; Rizzo, A.; *Fuel* **1998**, *8*, 853.
25. Silverstein, R. M.; Bassler, G. C.; Morril, T. C.; *Spectrometric identification of organic compounds*, 5th ed., Wiley: New York, 1991.
26. Yarranton, H. W.; Alboudwarej, H.; Jakher, R.; *Ind. Eng. Chem. Res.* **2000**, *39*, 2916.
27. Buch, L.; Groenzin, H.; Gonzalez, E. B.; Andersen, S. I.; Galeana, C. L.; Mullins, O. C.; *Fuel* **2003**, *82*, 1075.
28. Middea, A.; Monte, M. B. M.; Lucas, E. F.; *Chem. Chem. Technol.* **2008**, *2*, 91.
29. Moura, L. G. M.; Ramos, A. C. S.; *Polímeros* **2009**, *19*, 231.
30. Marques, L. C. C.; Pereira, J. O.; Bueno, A. D.; Marques, V. S.; Lucas, E. F.; Mansur, C. R. E.; Machado, A. L. C.; González, G.; *J. Braz. Chem. Soc.* **2012**, *23*, 1880.
31. Acevedo, S.; Gutierrez, L. B.; Negrin, G.; Pereira, J. C.; Mendez, B.; Delolme, F.; Dessalces, G.; Broseta, D.; *Energy Fuels* **2005**, *19*, 1548.
32. Herod, A. A.; Trejo, F.; Ancheyta, J.; Morgan, T. J.; Kandiyoti, R.; *Energy Fuels* **2007**, *21*, 2121.
33. Morgan, T. J.; George, A.; Alvarez, P.; Herod, A. A.; Millan, M.; Kandiyoti, R.; *Energy Fuels* **2009**, *23*, 6003.
34. Clarke, P. F.; Pruden, B. B.; *Fuel* **1997**, *76*, 607.
35. González, G.; Souza, M. A.; Lucas, E. F.; *Energy Fuels* **2006**, *20*, 2544.
36. Strausz, O. P.; Peng, P.; Murgich, J.; *Energy Fuels* **2002**, *16*, 809.
37. Moura, L. G. M.; Rolemberg, M. P.; Ramos, A. C. S.; Santos, M. F. P.; Zilio, E. L.; *Quim. Nova* **2011**, *34*, 226.
38. Durand, E.; Clemancey, M.; Lancelin, J. M.; Verstraete, J.; Espinat, D.; Quoineaud, A. A.; *Energy Fuels* **2010**, *24*, 1051.