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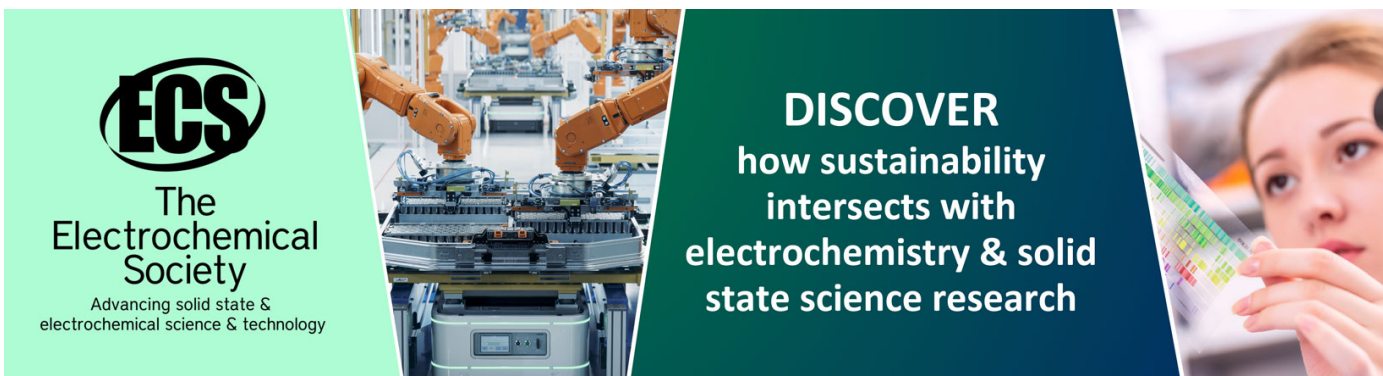
Effect of solvent polarity during electrodeposition of asphaltenes from a Colombian oil in the presence of a magnetic field and magnetic nanoparticles

To cite this article: M Roa *et al* 2020 *J. Phys.: Conf. Ser.* **1587** 012003

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Effect of solvent polarity during electrodeposition of asphaltenes from a Colombian oil in the presence of a magnetic field and magnetic nanoparticles

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Abstract. This work focuses on analyzing the electrokinetic behavior of asphaltenes of extra heavy oil. For this, electrodepositions were carried out in asphaltene solutions (4 %w/w) with two solvents of different polarities: toluene and chloroform. In addition, we worked with different magnetic fields, and the effect of adding 1% w/w of magnetic nanoparticles was analyzed. The asphaltenes were extracted with heptane and were characterized by infrared and ultraviolet visible spectroscopy. In the case of toluene, the initial adsorption (without fields) was 4 mg in both anode and cathode. By using an electric field (100 V/m) the deposits increased to 6 mg (anode) and 5 mg (cathode). However, when using a static magnetic field of 0.1 mT, no changes were observed. But, by modifying said field by a dynamic one (0.1 mT and 60 Hz), 15 mg (anode) and 19 mg (cathode) were obtained. Moreover, the addition of nanoparticles (previously characterized by scanning electron microscopy and X ray diffraction) changed the behavior, worsening in the absence of fields, and improving only in the presence of the dynamic field (104 mg, 26 mg in anode and cathode, respectively). Similar results were obtained when using chloroform. Thus, the best performance was obtained by using a dynamic magnetic field. By not considering the nanoparticles, total deposits increased more than 14 times (102 mg versus 7 mg). However, considering them, the increase was greater than 30 times (302 mg versus 10 mg). Therefore, we consider that adding nanoparticles, and supporting the electrodeposition process with a dynamic magnetic field, is an alternative that must be included to improve process performance.

1. Introduction

The electrokinetic behavior of asphaltenes was published by Wright, *et al.* [1], who used solutions made of asphaltene and nitromethane. They evaluated the electrokinetic behavior through electrophoresis tests since the asphaltenes were mainly positively charged [1]. Kokal, *et al.* [2], also used electrophoresis tests with solutions of asphaltene and nitromethane. But they made modifications to the pH of the solution. In the same fashion as the previous experiments, a positive charge for the asphaltenes was achieved. However, the pH affected the charge [2]. The work of Kokal, *et al.*, verifies that asphaltene properties are affected by the chemical environment. Fotland, *et al.*, used Benzene and THF, and found that the asphaltene fraction showed a higher conductivity in THF than in Benzene. This corroborates the influence of solvent polarity in asphaltene conductivity [3].

Gaspar studied the electrokinetic behavior in polar and non-polar media. He found that pH is directly linked to the electrophoretic velocity. Such results correlate with those achieved by Kokal since changes



to pH modify the functional groups of the asphaltene. Therefore, they modify the electric properties and the electrokinetic behavior [4].

This work also analyzes the electrokinetic behavior of asphaltenes. However, our work focuses on electrodeposition processes. For the experiments presented in this manuscript, Colombian extra heavy crude oil (EHCO) was used and considered two solvents, based on previous reports: a polar one (chloroform) and a less polar one (toluene). Aiming at deeply analyzing the electrokinetic behavior of these asphaltenes, was studied the effect of magnetic fields. Was considered both, static and dynamic fields. was studied the effect of adding 1.0% (w/w) magnetite nanoparticles.

2. Materials and methods

As it was mentioned in the introduction, asphaltene was extracted from the EHCO using heptane and following ASTM D6560 [5] procedure. They were then used to set up two solutions, both of them with 4% w/w asphaltenes. The first one used toluene. The second one, chloroform. these solvents were selected because they allow asphaltene solubility and because they exhibit a big difference of electrical conductivity (Chloroform: 0.02 $\mu\text{S}/\text{cm}$; Toluene at 20 °C, 8×10^{-8} $\mu\text{S}/\text{cm}$). Afterward, was added magnetic fields with two different configurations: a static one and a dynamic one. The first one was generated through a traditional transformer (120 V). The second one, through a triple phase stator with 12 poles. In both cases, a magnetic flux density of 0.10 mT and 60 Hz was used. Finally, was repeated the configurations (with and without magnetic field) but adding 1% w/w of magnetite nanoparticles.

2.1. Oil characterization

The first stage was the characterization of EHCO, which was later on used to extract asphaltenes. Was followed norm ASTM D-4124 [6] for the characterization, thus obtaining the saturates, asphaltenes, resins and aromatics (SARA) composition and asphaltene concentration was used norm ASTM 1298 [7] for finding the American Petroleum Institute gravity (API gravity) of the fluid, since it is a feature of heavy oils.

2.2. Extraction and characterization of asphaltenes

Asphaltenes were obtained following norm ASTM D-6560 [5], where the oil is mixed in heptane with a 1:20 relation. Afterward, the mixture is filtered and purified in excess Heptane. The characterization was done with infrared spectroscopy using a Bruker Tensor 27 with attenuated total reflection (ATR) cell spectrophotometer was also used a Shimadzu UV-240 IPC spectrometer for obtaining the ultraviolet or visible light (UV-Vis) spectra.

2.3. Electrodeposition of asphaltenes

Were prepared solutions with 4% w/w asphaltene concentration, in toluene, and in chloroform. Was used each one of them and placed them into an H-type cell, with a 300 ml capacity and a connecting tube 30 cm long. After that, was submerged stainless Steel electrodes (2.5 cm x 2.5 cm) that were previously polished with water sandpaper 400, and without using any kind of electric or magnetic fields. It is worth remarking that the electrodes were also treated with hydrochloric acid and sodium hydroxide and that they were washed with sodium dodecyl sulphate (SDS). After 90 minutes, the electrodes were removed and placed into hot toluene (in excess) to remove all the asphaltenic material. Later on, toluene was evaporated to concentrate the deposit. Excess heptane was then used to generate an asphaltenic precipitate from the deposit, passing it through filter paper (pore size: 0.45 micrometers). Since the filter was weighed before and after using it, was determined the weight of asphaltene generated throughout the process. This value was used as our adsorption blank. The aforementioned process was repeated considering different configurations. The first one was the inclusion of an electric potential of 30 V on the electrodes. This generates an electric field of 100 V/m (Voltage (V)/ length (m)). The remaining two configurations also added a magnetic field. In the second scenario, a transformer located within the connecting tube of the H-type cell and fed with 120 V was used. This generates a static magnetic field

with a magnetic flux density of 0.10 mT. The third scenario was a similar one, but instead of the transformer, it incorporated a triple phase stator. Energized with, an alternating current of four amperes was used, leading to a dynamic magnetic field with the same magnetic flux density (0.10 mT). Finally, both solutions were loaded with 1% w/w magnetite nanoparticles. Hence, was repeated the four previously described scenarios (blank, electric field, and magnetic fields). In all cases, obtained asphaltenes were characterized as mentioned below.

2.4. Characterization of deposited asphaltenes

Aiming at verifying that the obtained deposits belong to asphaltenes, was characterized the products in the same way as the original asphaltenes. The infrared, UV-Vis, was used, with the already mentioned equipment.

2.5. Characterization of magnetic nanoparticles

The nanoparticles were characterized by diffraction pattern was achieved using a diffractometer Bruker D8 Advance with DaVinci geometry and compared against the theoretical pattern of magnetite from the crystallographic database PDF-4. Finally, a morphologic characterization was carried out using a scanning electron microscopy (SEM) Quanta FEG 650.

3. Results and discussion

3.1. Characterization of extra heavy crude oil and asphaltenes

Table 1 shows the SARA composition of EHCO oil and supports the idea of it being an extra heavy oil. This category can be assigned because the oil contains 16.8% w/w of asphaltenes. Based on the classification provided by Santos, *et al.* in 2014, the extra heavy oil category begins at 14.1% w/w. Nonetheless, another indicator of the oil category is its API gravity, ranked at 8.5 °C at 25 °C. Santos, *et al.* also report that extra heavy oils exhibit an API gravity below 10 [8].

Table 1. SARA composition of an EHCO oil sample.

SARA	An EHCO Oil (%)
Saturates	16.6
Aromatics	29.3
Resins	37.3
Asphaltenes	16.8

As mentioned in the methodology section, asphaltene was extracted from oil using ASTM D6560 [5]. Moreover, Figure 1(a) shows the infrared spectra for the asphaltenes from EHCO oil. Even though the composition and structure of asphaltene fractions depend on the origin of the oil, some common functional groups can be identified [9]. They are similar to those reported by Hosseini, *et al.* during 2016. Here, was observed signals corresponding to the functional groups CH₂ and CH₃ in the region between 2800 cm⁻¹ and 3000 cm⁻¹. This represents the aliphatic fraction of asphaltene, which can be verified with the signals between 1400 cm⁻¹ and 1600 cm⁻¹ [10].

The most characteristic fraction of an asphaltene is its polyaromatic nucleus since it provides most of the properties. Signals corresponding to such condensed aromatic rings can be identified by analyzing the region between 500 cm⁻¹ and 900 cm⁻¹ of the spectra (Figure 1(b)). This confirms the observations done by Wilt, *et al.* in 1998, who also used spectroscopy to characterize asphaltenic fractions [11]. Figure, similarly, shows the corresponding UV-Vis spectra. Here, it is possible to identify characteristic bands between 300 nm and 400 nm that belong to the chromophore groups resulting from the polycyclic aromatic fraction [10,11].

3.2. Results of characterization of magnetic nanoparticles

As it was already mentioned in the methodology, nanoparticles were characterized using SEM that showed an approximate size of 18 nm (Figure 2(a)). Moreover, the X-ray diffraction pattern (Figure

2(b)) corroborates the crystalline structure of magnetite, which belongs to card 00-065-0731 from the PDF-4 crystallography database [12]. The red pattern represents the information from the database, while the blue one belongs to the spectra from magnetite nanoparticles. Since both patterns match for values of 2θ , was conclude that the sample belongs to magnetite nanoparticles with an approximate size of 18 nm.

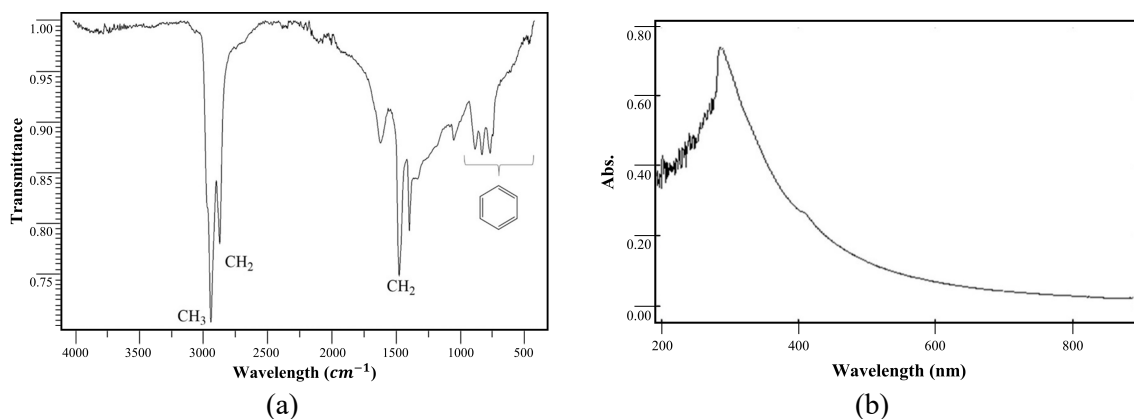


Figure 1. Characterization of asphaltenes extracted from an EHCO sample by (a) IR spectroscopy and (b) UV-Vis spectroscopy.

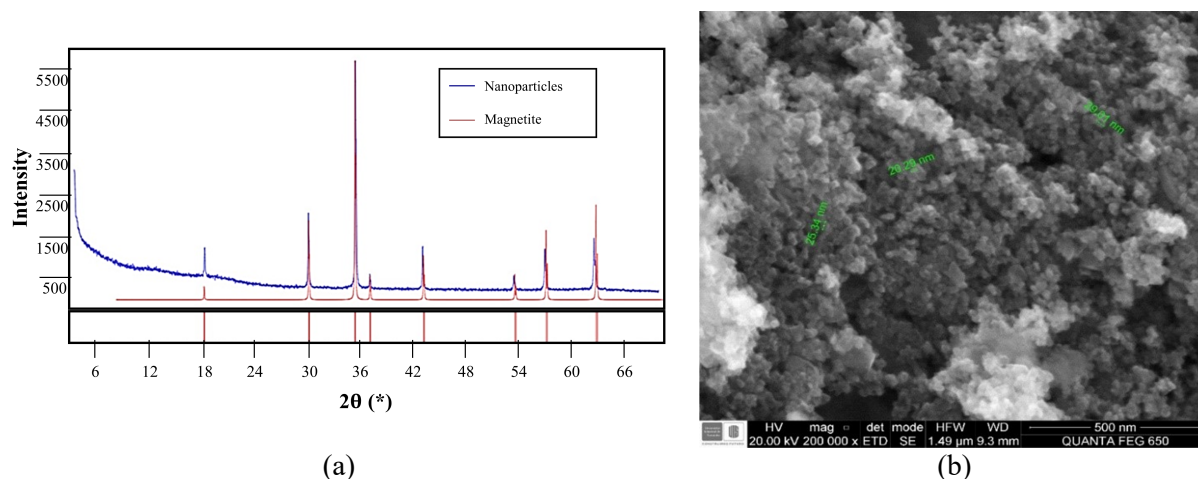


Figure 2. Characterization of magnetic nanoparticles (a) XRD pattern of nanoparticles and (b) SEM micrograph.

3.3. Results of electrodeposition processes

Two solvents were used for the electrodeposition: toluene and chloroform. Table 2 provides the deposits achieved (in milligrams) for the first case and considering scenarios with no magnetite addition. The most critical case is when no fields are used, where only four milligrams were deposited in the anode and in the cathode. By adding the electric field, those values increased to six and five milligrams, respectively. But, when also using the static magnetic field, no change was observed. However, when the magnetic field becomes dynamic, a substantial increase is achieved, yielding deposits of 15.0 mg and 19.0 mg (anode and cathode, respectively). Even if Lesin, *et al.* reported in 2010 and 2011 that oil can have magnetic nanomaterials [12], in this case, we only have the asphaltene fraction in toluene. Hence, magnetism can be disregarded as the cause for the increase. Even so, it is worth remembering that the dynamic magnetic field induces an electric field, which also interacts with asphaltenes. Because of this, more asphaltene molecules are affected, increasing their mobility and allowing contact with the

electrodes. Just like in the works of Taylor (1998) and Khvostichenko (2009), obtained similar values for the deposits in the anode and in the cathode [13].

Adding nanoparticles led to the deposits in most cases data worsened. But, combining nanoparticles with the dynamic magnetic field led to a noteworthy improvement. In fact, 104 mg were deposited in the anode and 26 mg in the cathode. Moreover, was observed a kinetic effect within the solution, which was generated by the movement of nanoparticles under the effect of the magnetic field. This movement favors contact of asphaltenes with the electrodes, hence improving the deposition. This effect was not detected with the static field.

Solutions with chloroform. By using no field at all, only four milligrams were deposited in the anode and three milligrams in the cathode. Even if the conductivity of the solvent is higher, the adsorption is similar to that of toluene. However, the effect of the fields is more evident. This way, using the electric field led to a deposit of 17 mg in both, anode and cathode. This effect follows the results reported by Fotland, who mention that solvent polarity provides a higher conductivity to the asphaltenic solution and, hence, improves deposition. Moreover, there was an effect after adding the static magnetic field, slightly rising deposition values. Even so, the most outstanding result was for the dynamic magnetic field, since 52 mg and 50 mg were deposited in the anode and the cathode, respectively.

Once again, was added nanoparticles and repeated the tests, arriving to the data shown in Table 2. In a similar fashion to the case of toluene, most scenarios remained stable or slightly improved. However, the last scenario (dynamic magnetic field) more than doubled the deposits, yielding 129 mg in the anode and 173 mg in the cathode. This is also due to the kinetic effect derived from the interaction between nanoparticles and dynamic magnetic field. However, the effect is more noticeable here because of the increased conductivity of the solution.

Table 2. Amount electrodeposited in anode and cathode in the electrodeposition process.

Electrodeposition process	Asphaltene deposits in anode (mg)	Asphaltene deposits in cathode (mg)
Toluene 4% Asphaltene blank	4	4
Toluene 4% Asphaltene - Electric field	6	5
Toluene 4% Asphaltene - Transformer magnetic field	6	5
Toluene 4% Asphaltene - Stator magnetic field	15	19
Toluene 4% Asphaltene blank + 1% MNP	2	2
Toluene 4% Asphaltene - Electric field + 1% MNP	6	4
Toluene 4% Asphaltene - Transformer magnetic field + 1% MNP	6	4
Toluene 4% Asphaltene - Stator magnetic field + 1% MNP	104	26
Chloroform 4% Asphaltene blank	4	3
Chloroform 4% Asphaltene - Electric field	17	17
Chloroform 4% Asphaltene - Transformer magnetic field	22	20
Chloroform 4% Asphaltene - Stator magnetic field	52	50
Chloroform 4% Asphaltene blank + 1% MNP	6	4
Chloroform 4% Asphaltene - Electric field + 1% MNP	18	16
Chloroform 4% Asphaltene - Transformer magnetic field + 1% MNP	28	19
Chloroform 4% Asphaltene - Stator magnetic field + 1% MNP	129	173

In most electrodeposition processes, amounts deposited in anode and cathode are similar. However, this behavior changes when dynamic magnetic fields and nanoparticles are included. In such a scenario, electrodeposition exhibits a preference. For the experiments with toluene, was observed a higher deposit in the cathode (173 mg). One reason for this tendency can be that more asphaltene particles are affected because of the dynamic magnetic field. This, in turn, may lead to better understanding the nature of asphaltene charge. This charge is the result from the possible interactions between solvent and nanoparticles, since asphaltenes can modify their charge based on the chemical environment, as mentioned by Kokal [2]. Nonetheless, a complete identification of such interaction requires a deep elemental analysis, which goes beyond the scope of this work.

3.4. Characterization of deposits

Figure 3(a) show the infrared spectra for the deposits in the anodes when using toluene. Figure 4(a) on the other hand, show cathodes when using chloroform. In all cases, signals corresponding to CH_2 and CH_3 can be observed between 2800 cm^{-1} and 3000 cm^{-1} , and between 1400 cm^{-1} and 1600 cm^{-1} , which also belong to CH_2 . Aromatic signals are also observed, and they are in the region between 500 cm^{-1} and 900 cm^{-1} . No signals for iron are observed in the spectra [14].

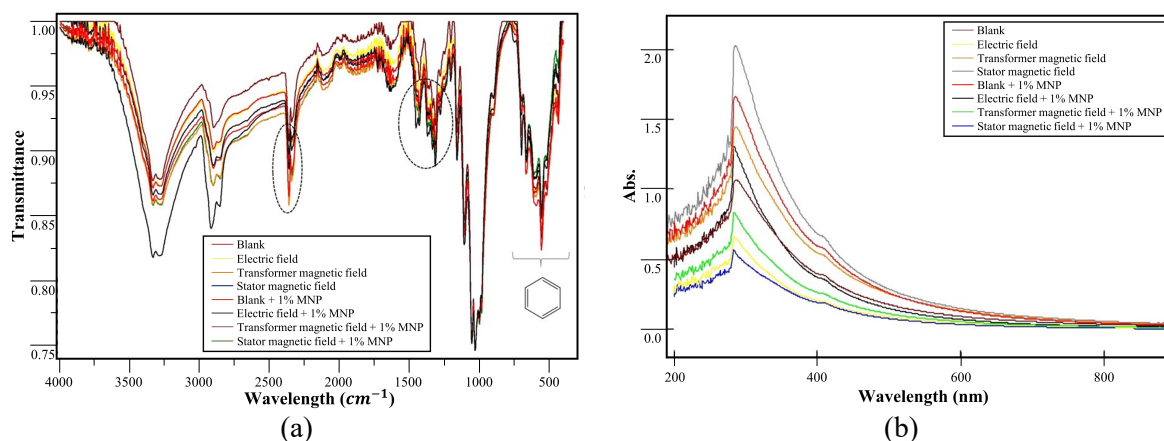


Figure 3. Spectra of asphaltenes deposited in anodes using toluene as the electrodeposition medium. (a) IR spectrum and (b) UV-Vis spectrum.

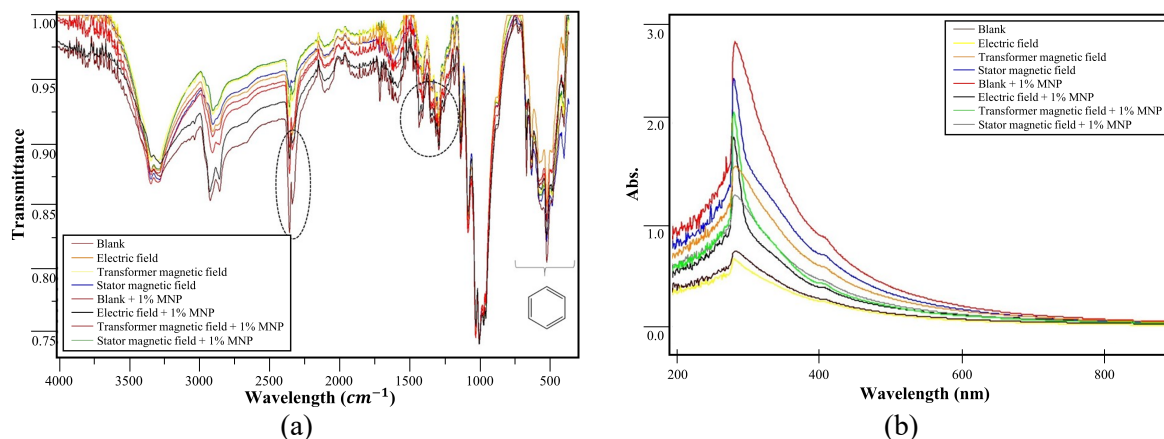


Figure 4. Asphaltenes deposited in cathodes using chloroform as the electrodeposition medium. (a) IR spectrum and (b) UV-Vis spectrum.

Thus, it can be concluded that there is no magnetite in the deposits, nor there is a presence of the interaction between nanoparticle and asphaltene. As it was done for the asphaltenes extracted from EHCO oil, was generated the UV-Vis spectra for all electrodeposition scenarios. Figure 3(b) belong to deposits in the anode (for toluene), while Figure 4(b) belong to the deposits generated in cathode for chloroform. Just as it happened with the infrared spectra, there is no signal for iron or for magnetite. By revising the spectroscopic and visual characterization of electrodeposited asphaltenes (in both, toluene and chloroform), was can guarantee that they belong to asphaltenic molecules. When comparing them against the results of asphaltenes extracted from EHCO oil, was found no significant differences. This suggests there are no interactions, or reactions, that generates an asphaltenic derivate.

4. Conclusions

Interaction between asphaltenes and solvent is quite important in the behavior of their electrical properties. If the solvent has a low polarity (e.g. toluene), asphaltenes would exhibit a low response to an electric field. Conversely, if a polar solvent (e.g. chloroform) is used, the response increases. Our data reveal that deposits can be doubled by changing the solvent. Such a response results from the interaction between functional groups in the asphaltene surface. While the interaction is low for toluene, for chloroform it leads to more charged locations within the asphaltene. This verifies the work previously carried out by other authors. Furthermore, was included experiments using external electric and magnetic fields. Results were diverse, as explained in the results section. However, adding a magnetic material to the electrodeposition solutions does not modify the electrical nature of asphaltenes. Nonetheless, it does facilitate mobility within the solutions, depending on the configuration of the applied magnetic field. In all cases, was observed that free asphaltenes may have as much positive charge as negative. Polarity will depend, above all, on the functional groups at the surface, as well as on the way they interact with the solvent.

References

- [1] Wright J R, and Richard R M 1963 Description and calibration the glass cell used for the electrophoretic *Journal of Colloid Science* **23**(6) 223
- [2] Kokal S, Thompson T, Laurier S, and Selim S 1995 Electrokinetic and adsorption properties of asphaltenes *Colloid and Surfaces* **94** 253
- [3] Fotland P, Hilde A 1996 Electrical conductivity of asphaltenes in organic solvents *Fuel Science and Technology International* **14**(1) 37
- [4] Gonzalez G, Neves G, Saraiva S M, Lucas E F, and Dos Anjos de Sousa M 2003 Electrokinetic characterization of asphaltenes and the asphaltenes-resins interaction *Energy and Fuels* **17**(4) 879
- [5] American Society for Testing and Materials (ASTM) 2017 *Standard Test Method for Determination of Asphaltenes in Crude Petroleum and Petroleum Products*, ASTM D6560 (USA: American Society for Testing and Materials)
- [6] American Society for Testing and Materials (ASTM) 2018 *Standard Test Method for Separation of Asphalt into Four Fractions*, ASTM D4124 (USA: American Society for Testing and Materials)
- [7] American Society for Testing and Materials (ASTM) 2018 *Standard Test Method for Density, Relative Density, or API Gravity of Crude Petroleum and Liquid Petroleum Products by Hydrometer Method*, ASTM D1298 (USA: American Society for Testing and Materials)
- [8] Santos R G, Loh W, Bannwart A C, and Trevisan O V 2014 An overview of heavy oil properties and its recovery and transportation methods *Brazilian Journal of Chemical Engineering* **31**(03) 571
- [9] Alboudwarej H, Rajesh K J, Svrcek W S, and Yarranton H W 2004 Spectrophotometric measurement of asphaltene concentration *Petroleum Science and Technology* **22**(5) 647
- [10] Wilt B K, Welch W T, and Rankin J G 1998 Determination of asphaltenes in petroleum crude oils by Fourier transform infrared spectroscopy *Energy and Fuels* **6**(24) 1008
- [11] International Centre for Diffraction Data (ICDD) 2018 *PDF-4 Database* (Newtown Square: International Centre for Diffraction Data)
- [12] Lesin V I, Koksharov A, and Khomutov G 2010 Magnetic nanoparticles in petroleum *Petroleum Chemistry* **50**(2) 102
- [13] Khvostichenko D S, and Andersen S I 2009 Electrodeposition of Asphaltenes. 1 Preliminary studies on electrodeposition from oil-Heptane mixtures *Energy and Fuels* **23** 811
- [14] Ying-Sing L 2012 Infrared and Raman spectroscopic studies on iron oxide magnetic nanoparticles and their surface modifications *Materials, Magnetic, and Magnetic Materials* **324**(8) 1543