

# Review of Asphaltenes in an Electric Field

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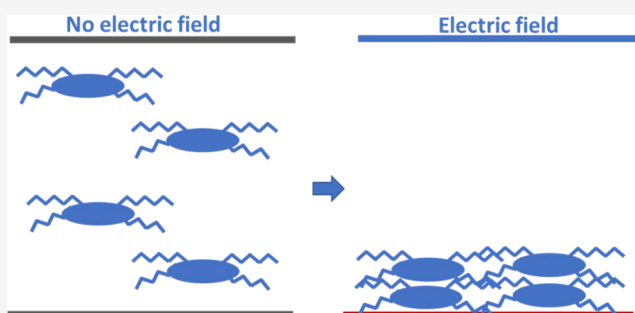
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**ABSTRACT:** Asphaltenes are regarded as troublesome components of crude oils as their precipitation and deposition inside production wells and downstream infrastructure often result in a reduction of production capacity and, in critical cases, production shut-in. It has been shown that asphaltene deposition on conductive surfaces can be controlled by the application of an electric field. The electric field has been used to either inhibit or accelerate asphaltene deposition. This paper reviews asphaltene behavior in an electric field. It describes the structure and electric properties of asphaltenes as well as their electrokinetic behavior. State-of-the-art asphaltene electrodeposition and separation from both model and crude oils using electric fields are also discussed.

The influence of parameters such as asphaltene chemistry, crude oil composition, pH, electric field strength, and flow conditions on the asphaltene electrodeposition process is addressed, and the effect of asphaltene interactions with themselves and other crude oil components is evaluated. A comprehensive literature survey reported the electrodeposition on both positive and negative electrodes, which suggests the complexity of the process. It has been shown that asphaltene charges can be tailored by changing the process parameters. Because of the high energy efficiency and relatively simple process, asphaltene electrodeposition is currently a key solution for removal of asphaltenes from crude oils. This review also highlights the main challenges and knowledge gaps associated with the asphaltene electrodeposition process.



## 1. INTRODUCTION

Asphaltene deposition in producing wells, pipelines, and surface facilities leads to detrimental production and operational problems with great economic impact. Asphaltene precipitation and deposition in downstream and upstream processing facilities may lead to plugging of pipeline and wellbores, deposition of solids in storage tanks, corrosion and fouling of safety valves,<sup>1</sup> and formation of coke in refineries.<sup>2,3</sup> Asphaltene deposition costs the oil industry billions of dollars every year, including reduction of production capacity, wells shut-in, and implications of the management techniques.<sup>4,5</sup> For instance, it was reported from an oil field in the Gulf of Mexico that the cost of a well shut-in for a cleanup operation due to asphaltene deposition was approximately \$70 million/well.<sup>6</sup> Moreover, the asphaltene management cost, which includes inhibition, treatment, and cleanup aggravates the financial burden of asphaltene deposition. The cost of chemical additives preventing the deposition of asphaltenes can be between \$330,000 and \$390,000/well per year in the Middle East.<sup>7</sup>

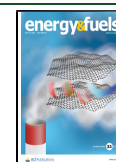
To deal with asphaltene deposition problems, two main categories of techniques have been applied: inhibition and treatment. The use of chemical inhibitors and manipulation of oil production conditions incorporate inhibition techniques, while the treatment methods comprise mechanical, thermal,

chemical, biological, and electrical approaches.<sup>8–11</sup> Most of these techniques are extremely costly. One example of a possible inhibition technique is the addition of dispersants in order to change the net charge of the asphaltene aggregates, making them more dispersible in the oil mixture.<sup>12,13</sup> However, in the case of heavy oil with a high asphaltene content, this method is inefficient and costly.<sup>14</sup> To address this disadvantage, there is an increasing interest in removal of asphaltenes from crude oil by using electrodeposition. In an asphaltene electrodeposition process, an electric field is applied to an electrode material placed in the crude oil. The electric field affects the molecular interactions within crude oil components and destabilizes the hydrocarbon system. This promotes the release of asphaltenes, which in the next step get oriented and deposited on the electrode surface.<sup>15–18</sup> The electric properties of asphaltenes are affected by many parameters such as origin/composition of crude oil, electrical properties of different crude oil components, oil dilution with solvents, pH, electric field

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Asphaltene structure and physicochemical properties	Asphaltene electrical properties	Asphaltene Electrodeposition		Effect of electric field on separation of emulsions stabilized by asphaltenes
		Electrodeposition from crude oil	Electrodeposition from model oils	
Atomic composition	Polarity	Asphaltene structure	Asphaltene-asphaltene interaction	Water droplets coalescence
Functional groups	Dipole moment and dielectric constant	Crude oil properties	Asphaltene-resins interaction	Interactions between molecules
Metal content	Electrical conductivity	Oil dilution & pH	Electric field effect	Steric effects
Solubility	Polarizability	Aggregation state	Static & dynamic deposition	
Stability	Surface charge and zeta potential	Electric field strength & current type	Flow conditions	
Aggregation	Electrokinetic mobility	Flow conditions	Effect of molecular composition & polarity	
Asphaltene-resin interaction		Streaming potential		
		Energy consumption		

Figure 1. General sketch of the review article.

strength, flow conditions, etc. This makes it difficult to predict whether the electrodeposition will take place on the cathode or the anode, and also which process parameters should be chosen to obtain controlled deposition. This review describes how electric properties of asphaltenes and their behavior in an electric field are related to the above-mentioned process parameters. The general sketch of this review article is summarized in Figure 1.

## 2. ASPHALTENE STRUCTURE

Asphaltenes are known as the heaviest, largest, densest, and most polar surface-active component of crude oils.<sup>19</sup> Asphaltenes are soluble in aromatic solvents such as toluene, benzene, and pyridine but insoluble in light paraffinic solvents including *n*-pentane (C5), *n*-hexane (C6), and *n*-heptane (C7).<sup>20–23</sup>

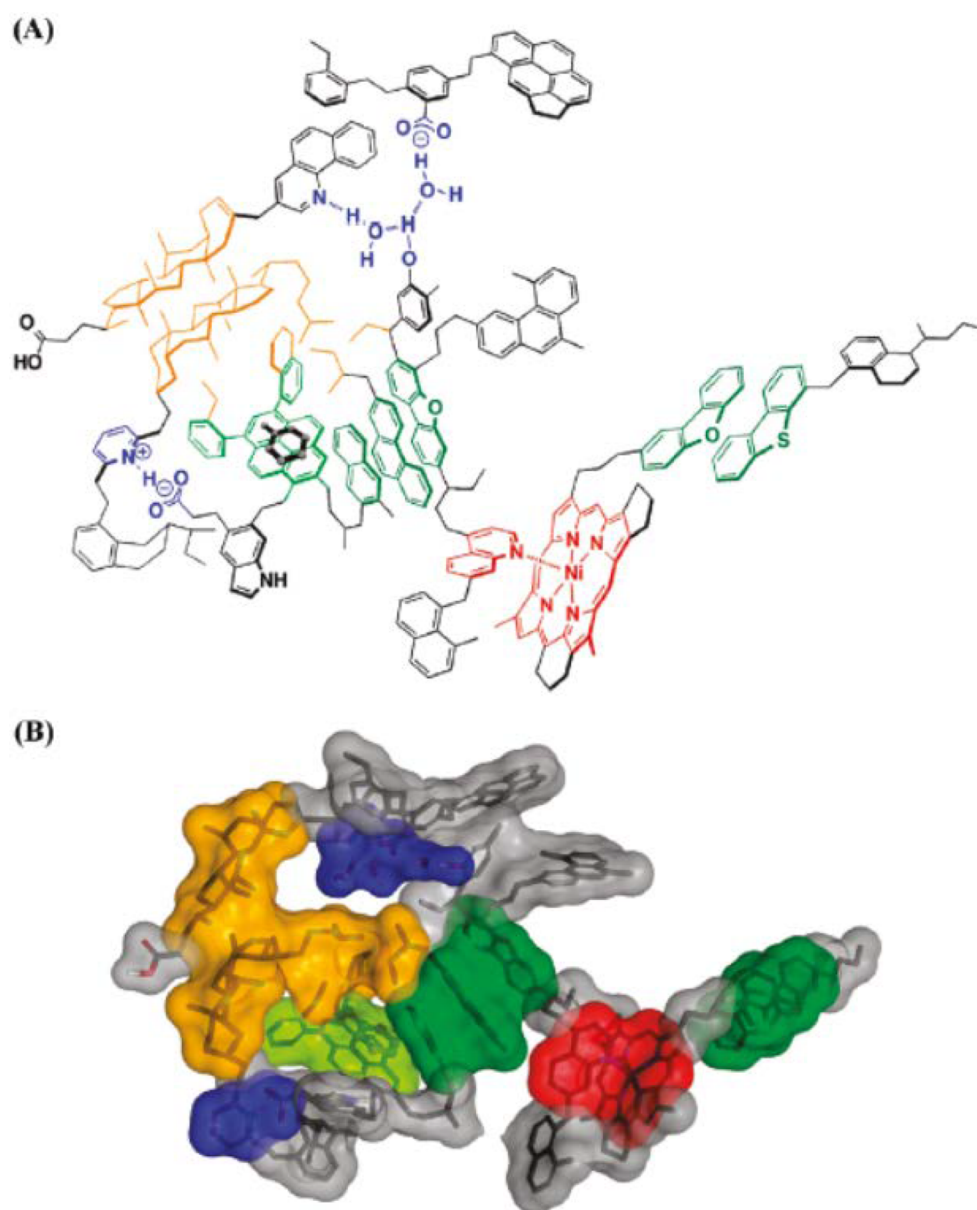
The composition and properties of asphaltenes depend on their origin and the method of their extraction from crude oil.<sup>24–26</sup> The mean asphaltene molecular weight measured using mass spectrometry<sup>27–29</sup> and molecular diffusion<sup>30,31</sup> methods is approximately 750 g/mol. The asphaltene fraction consists of molecules containing paraffinic and naphthenic chains as well as condensed aromatic hydrocarbons. Predominantly, there are 6–8 fused rings which are found in polycyclic aromatic hydrocarbons (PAHs) of petroleum asphaltene.<sup>32–34</sup>

Asphaltenes are mainly composed of carbon, hydrogen, nitrogen, oxygen, and sulfur, as well as small amounts of iron, vanadium, and nickel (in ppm levels).<sup>35</sup> The hydrogen and carbon content in asphaltenes extracted from different crude oils varies within a small range and is  $8.1 \pm 0.7\%$  and  $82 \pm 3\%$  respectively. The hydrogen/carbon (H/C) ratio in asphaltenes extracted from different sources was found to be almost constant ( $1.15 \pm 0.05\%$ ). In comparison, the content of heteroatoms, such as oxygen and sulfur, vary from 0.3–4.9% (oxygen) and 0.3–10.3% (sulfur). The nitrogen content varies

between 0.6% and 3.3%.<sup>21</sup> Exposure of asphaltenes to an oxygen atmosphere can substantially alter the oxygen content.<sup>36</sup> In general, the heteroatom functional groups of asphaltenes are S: thiophene, sulfide, sulfoxide; N: pyrrolic, pyridine, quinoline, and O: hydroxyl, carbonyl, carboxyl.<sup>22,37</sup> Vanadium and nickel are mainly present in crude oils in the form of porphyrin complexes.<sup>38,39</sup>

Heavy oils have a considerable amount of asphaltene-resinous components, heteroatoms (S, N, and O), and metals (vanadium and nickel).<sup>40</sup> The asphaltenes in heavy oils contain iron, vanadium, and nickel (up to 1%), of which the proportion of vanadium is more than 80%.<sup>41,42</sup> Vanadylporphyrins, one of the most common forms of crude oil metalloporphyrins, play an important role in asphaltene aggregation, fouling, and deposition.<sup>43–45</sup>

Polar and aromatic functional groups present within the internal molecular structure of asphaltene, including carboxylic acids, carbonyls, phenols, pyrrolic, and pyridinic nitrogen, have the capability of forming hydrogen bonds. These groups can donate or accept protons inter- and intramolecularly.<sup>46,47</sup> It has been found that sulfur and oxygen heteroatoms strongly contribute to the aggregation of asphaltenes particularly in *n*-heptane solution,<sup>48</sup> and the oxygen-containing compounds possibly drive asphaltene aggregation through hydrogen bonding.<sup>49</sup> The most likely mechanisms of asphaltene aggregation involve  $\pi$ - $\pi$  interactions between aromatic sheets (electrostatic and/or van der Waals forces),<sup>50</sup> hydrogen bonding between functional groups (significant in the presence of water), coordination interactions,<sup>51</sup> and acid-base interactions (Figure 2).<sup>46,50</sup> Because of the presence of polyaromatic hydrocarbon structures,  $\pi$ - $\pi$  stacking is considered as the major interaction mechanism.<sup>49,52</sup> However, the steric hindrance caused by the aliphatic side chain can limit the aggregation process.<sup>53,54</sup> It is suggested that all of the above-mentioned forces play a significant role in asphaltene-



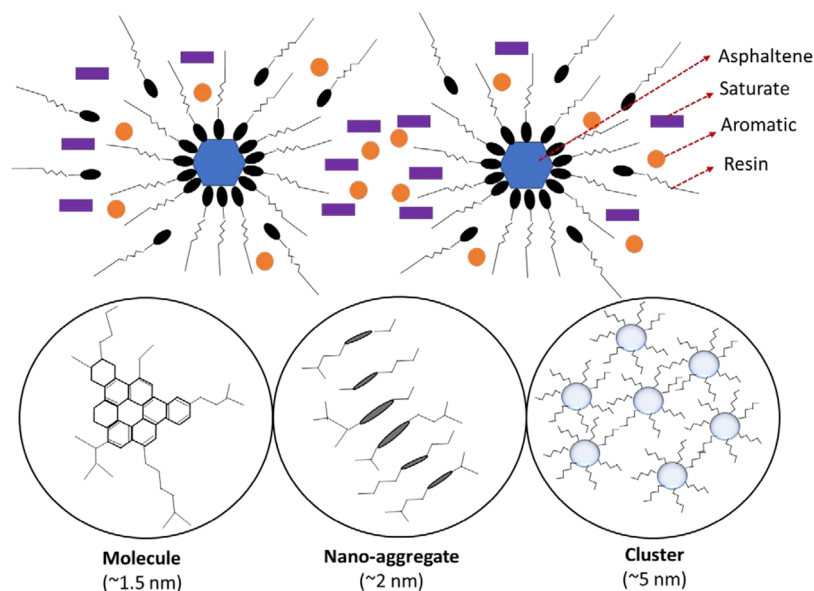
**Figure 2.** Schematic representation of a supramolecular assembly composed of host and guest species in a representative asphaltene aggregate. Associations between molecules are color-coded in (A) the molecular depiction and (B) the space-filling version: acid–base interactions and hydrogen bonding (blue), metal coordination complex (red), a hydrophobic pocket (orange),  $\pi$ – $\pi$  stacking (face-to-face dark green; within a clathrate containing toluene, light green).<sup>50</sup> Reproduced with permission from ref 50. Copyright 2011 American Chemical Society.

asphaltene and asphaltene–surface interactions, and thus contribute to the asphaltene adsorption and deposition processes.<sup>55</sup>

It is believed that resins have the greatest impact on the stability of asphaltene molecules in crude oil as they contribute to smaller aggregate formation<sup>56</sup> and thereby prevent separation of the asphaltene molecules.<sup>36,57,58</sup> Resins are also polar components of crude oil and are soluble in pentane and heptane but insoluble in propane. Structurally, resins are akin to asphaltenes, but they have a higher H/C ratio (1.2–1.7), lower aromaticity, and lower molecular weight compared to asphaltenes.<sup>23,59,60</sup> Relatively longer aliphatic side chains and smaller chromophores contribute to higher solubility of resins in aliphatic solvents.<sup>61</sup> Because of their interactions with asphaltenes, resins can deter the asphaltenes aggregation process.<sup>48</sup> Resins can function as a bridging material that

connects the polar asphaltenes to the nonpolar saturates in crude oils through various mechanisms, e.g., micelle-type formation,<sup>37</sup> peptization of the asphaltene core,<sup>62</sup> or supramolecular growth.<sup>50</sup> It is believed that due to the opposite surface charges of resins and asphaltenes fractions, the resins–asphaltenes molecular interactions are preferred over asphaltene–asphaltene interactions.<sup>21,36,63</sup> Any change in surface charge interactions between asphaltenes and resins can alter the attractive forces leading to asphaltene destabilization.<sup>64</sup> The extent by which resins affect asphaltenes stability depends on their dielectric properties.<sup>59</sup> Electrical conductivity studies showed that resins can neutralize part of the asphaltene charges by adsorbing on their surface.<sup>65</sup>

The stability of asphaltenes in petroleum fluids can also be disrupted by several other stimuli, including pressure, temperature, concentration, and composition of the injected solvents,



**Figure 3.** Top, asphaltene stability in micelles. Bottom, aggregation process with size analysis.<sup>68</sup> Reproduced with permission from ref 68. Copyright 2012 American Chemical Society.

e.g., steam, CO<sub>2</sub>, nitrogen, methane, etc. However, the process of asphaltene aggregation and precipitation is more sensitive to pressure than other thermodynamic and process parameters.<sup>21,66,67</sup> Asphaltenes exhibit hierarchical nanocolloidal aggregation in both reservoir crude oils and solvents.<sup>68,69</sup> The aggregation starts by the formation of nanoaggregates of asphaltene molecules. Next, because of further changes in the thermodynamic conditions, the nanoaggregates may develop into clusters. The clusters of nanoaggregates can further agglomerate to form macroaggregates.<sup>68,70</sup> Figure 3 describes the aggregation process of asphaltene molecules and shows the average size of different asphaltene species.

### 3. ELECTRICAL PROPERTIES OF ASPHALTENES

**3.1. Polarity.** The polarity of asphaltenes influences destabilization, aggregation, precipitation, and consequently deposition of asphaltenes during production, transportation, and refining of crude oils.<sup>21,36,71</sup> The polarity of asphaltenes has often been related to the high content of heteroatoms as well as the metal content in the molecular structure which is also a primary reason for the high dipole moment of petroleum fluids. Moreover, because of unique electronic structure and reactivities (such as an asymmetric molecular orbital arrangement, uneven charge distribution, and unique electronic absorptions), the large dipole moments of nonalternant PAHs (five-membered carbocycle) present in the asphaltene structure could also impart significant polarity to petroleum hydrocarbons.<sup>72</sup> Once the stability of a system is disturbed, the polar sides of the asphaltene molecules interact with each other leading to the agglomeration and precipitation of asphaltenes. The asymmetrical charge distribution and bonding structure within asphaltene molecules due to the presence of elements having different electronegativities can generate dipoles with partial negative ( $\delta^-$ ) and partial positive ( $\delta^+$ ) charges.

**3.2. Dipole Moment and Dielectric Constant.** The product of charge density and distance between the centers of positive and negative charges within the molecule is defined as the *dipole moment*. The dipole moment is a measure of the polarity of a molecule generated by the distribution of the

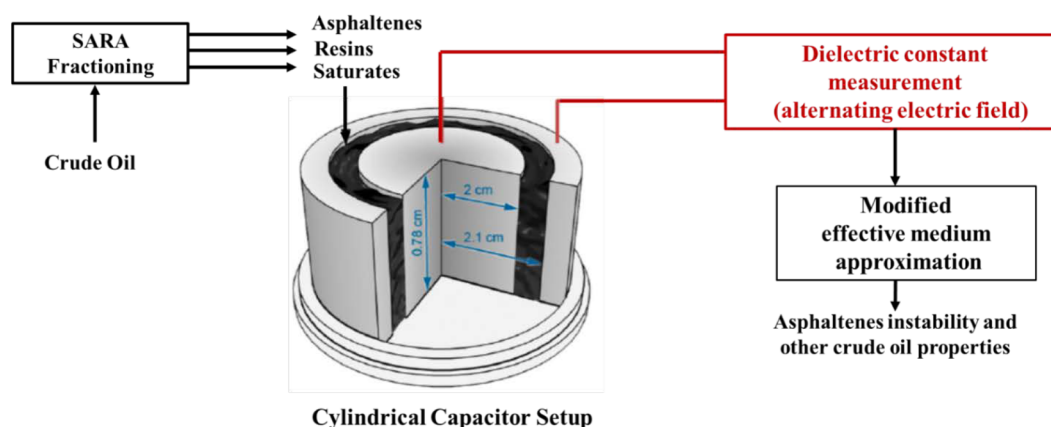
functional groups and metallic elements, and it is dependent on the structure and size of the molecule. Another electrical property used to describe materials is the *dielectric constant*, which is also called *relative permittivity*. Relative permittivity is the factor describing how many times the electric field between the charges is decreased in a given medium (material) relative to a vacuum. Both dipole moment and relative permittivity of asphaltenes and its comparison with different crude oil components are discussed below and are summarized in Table 1.

The dipole moment and dielectric constant are directly related to the asphaltene structure. Thus, the measured values of dipole moment and dielectric constant are dependent on crude oil type from which asphaltenes are extracted, type of *n*-alkanes used to extract asphaltenes, metal content in the asphaltene structure, and temperature. Many authors determined the dipole moment by measuring the dielectric constant of various crude oil components in toluene solution.<sup>61,73–75</sup> It was found that the dielectric constant of asphaltenes, resins, and crude oils was in the range of 5–18.4, 3.8–5.1, and 2.1–2.6, respectively, whereas the dipole moment of asphaltenes and resins was in the range of 3–7 D and 2–3 D respectively.<sup>61,73,74</sup> Larger dipole moment values (17–32.9 D) were reported for asphaltenes extracted from heavy crude oils. Asphaltenes extracted from heavy oil by *n*-heptane had larger dipole moment values (28.4–32.9 D) than the corresponding *n*-pentane asphaltenes (17–23.3 D).<sup>75</sup> The higher values observed for asphaltenes extracted with *n*-heptane were ascribed to a smaller interlayer spacing between stacking layers, larger aromatic ring structure, and mean number of stacking layers.

The dielectric constant of bitumen has been shown to be influenced by each fraction of the bitumen, and the magnitude of the contribution to the overall dielectric constant was shown to be in the following order: asphaltenes > resins > aromatics > saturates.<sup>76</sup> Similar conclusions were drawn by Punase and Hascakir, who measured the dielectric constant of different crude oil components from nine different crude oil samples using a cylindrical capacitor system presented in Figure 4.

Table 1. Summary of Dipole Moment and Dielectric Constant of Asphaltene and Other Components of Crude Oil Measured by Different Authors

Samples	Methods	Dipole moment (Debye, D)	Dielectric constant	Important findings	Ref
Asphaltenes in toluene	Dielectric spectroscopy	5.3	5–7	By raising the temperature, the dielectric constant increases due to dissociation of aggregates.	73
Asphaltenes in toluene	Dielectric spectroscopy	3–7	5.5–18.4	Dipole moment of asphaltenes increased with carbon number of precipitating <i>n</i> -alkanes.	61
Resins in toluene		2–3	3.8–5.1		
Crude oils in toluene		44.3–59.5	2.1–2.6		
Asphaltenes extracted from crude oil in toluene	Dielectric cell connected to an impedance analyzer	53.8–63.5		Asphaltenes extracted from solid deposits were more polar than the asphaltenes extracted from crude oils.	78
Asphaltenes extracted from solid deposit in toluene					
Solid asphaltenes	Dielectric spectrometer		4.3–5.4	Hopping transport of electrons between asphaltene molecules may facilitate self-association of asphaltenes in crude oils.	86
C7-Asphaltenes in toluene	Calculated from the mean molecular weight and variation rate of dielectric permittivity of samples in toluene	28.4–32.9		Asphaltenes extracted from heavy oil by <i>n</i> -C7 had larger dipole moment values than the corresponding <i>n</i> -C5 asphaltenes.	75
C5-Asphaltenes in toluene (asphaltenes extracted from heavy crude oils)		17.0–23.3			
C7 asphaltenes in Toluene at –60 °C	High resolution dielectric, conductivity impedance, and gain phase modular system	17–20		Dipole moments of the aggregated population are five times greater than of nonaggregating particles.	79
C7 asphaltenes in toluene at –40 °C		21–27			
C7 asphaltenes in toluene at –20 °C		20–31			
C7 asphaltenes in toluene at 0 °C		20–39			
C7 asphaltenes in toluene at 20 °C		20–59.9			
Asphaltenes	Cylindrical capacitor		3.3–5.0	Asphaltenes represent the most polar fractions of crude oil.	77
Resins			1.8–2.61	The dielectric constant of resins was correlated with the physical properties of crude oil samples.	
Saturates			1.58–1.91		
Deasphalted oils			2.0–3.77		
Crude oils			1.72–2.34		



**Figure 4.** Description of the cylindrical capacitor to measure the dielectric constant of bulk crude oil as well as their individual saturates, aromatics, resins, and asphaltenes (SARA) fractions.<sup>77</sup> Reproduced with permission from ref 77. Copyright 2017 American Chemical Society.

Their results showed that asphaltene exhibited the highest dielectric constant and inorganic minerals (calcium carbonate, magnesium carbonate, sodium chloride, sodium sulfate, etc.) which are present in asphaltenes at the ppm level greatly influenced the dielectric constant of the asphaltene fraction. It was also concluded that the dielectric constant of resins was more correlated with the physical properties of crude oils.<sup>77</sup>

Asphaltene samples collected from the solid deposit of an oil field exhibited a strong tendency to form aggregates in the toluene solution at a very low concentration compared to the asphaltene samples collected from the crude oil of the same oil field.<sup>78</sup> The lower solubility of asphaltenes from deposits was ascribed to their higher polarity (dipole moment) compared to asphaltenes from crude oils.

The dipole moment of asphaltenes was found to increase with increasing temperature.<sup>79</sup> It has been shown by Zhang et al. (2015) that a temperature increase above  $-5\text{ }^{\circ}\text{C}$  resulted in an increase in dipole moment values. The increase was ascribed to the temperature driven aggregation of asphaltene molecules. Furthermore, the dipole moments of more polar asphaltene aggregates were five times greater than those before aggregation.<sup>79</sup>

**3.3. Electrical Conductivity.** Electrical conductivity (EC) represents the ability of material to conduct an electric current. EC measurements have been utilized to understand behavior of asphaltenes alone and their interactions with other crude oil components in different solvents.<sup>78,80–86</sup> It has been shown that the crude oils rich with asphaltenes had a higher conductivity than other oils.<sup>80</sup> The conductivity of crude oil solution was suggested to be governed not only by the amount of asphaltenes in the crude oil but also by their aggregation state and mobility. The crude oil diluted with heptane showed a lower conductivity than those same oils diluted with the same amount of toluene. The observation was ascribed to more pronounced aggregation of asphaltenes in heptane compared to toluene and the formation of larger aggregates.<sup>82,85</sup> Later, by comparing the DC conductivities at various concentrations of asphaltenes, it was concluded that the most aromatic components of crude oils are captured by toluene, in which they contribute to high conductivity, while the fractions of crude oils that form nanoaggregates are captured by *n*-heptane and are characterized by low conductivity.<sup>87</sup> It has been also suggested that electrical conductivity may originate from a rapid charge exchange between asphaltene colloidal particles and that the self-association of asphaltenes in crude oil can be

facilitated by the electron transfer between asphaltene molecules.<sup>86</sup>

Temperature has a large effect on the electrical conductivity of asphaltenes, as it strongly affects asphaltene–asphaltene interactions and aggregation. At low temperatures, the interactions between polar side chains dominate, while at high temperatures,  $\pi$ – $\pi$  interactions involving flat polyaromatic structures of asphaltenes molecules become dominant.<sup>86</sup> Increased oil viscosity contributes to lower conductivity at low temperatures. In general, the relationship between crude oil electrical conductivity and temperature was exponential.<sup>80</sup> Similar results were reported by Rocha et al. (2019), who employed an impedance spectroscopy method to measure the electrical conductivity of heavy and medium crude oils, and water in oil (W/O) emulsions at  $30\text{ }^{\circ}\text{C}$  and  $50\text{ }^{\circ}\text{C}$ .<sup>81</sup> The results revealed that an increase in temperature results in an increase in electrical conductivity. On the other hand, the dielectric constant was decreased for all samples upon a temperature increase. A decrease in electrical conductivity and increase in dielectric constant were observed when water was added to the crude oils.<sup>81</sup>

In some earlier studies,<sup>84,88</sup> AC conductivities of asphaltenes were measured as a function of concentration in solvents of varying relative permittivities (dielectric constants), and results indicated that in solvents of low dielectric constant the asphaltene fraction was ionized. It was further revealed that asphaltenes consisting mainly of free ions at low concentrations and ion pairing lead to a decrease of conductivity. However, strong dipole–ion interaction was also observed at high concentrations of asphaltenes in some solvents, which led to an increase in conductivity.<sup>84</sup> Precipitation of asphaltenes was manifested in the rapid change of electrical conductivity.<sup>88</sup> Later, the rheological behavior of suspensions composed of silicon oil and asphaltene particles was investigated under DC electric fields.<sup>89</sup> It was found that the asphaltene suspensions showed a weak electrorheological (ER) response, which was dependent on the electric field intensity and asphaltene concentration. The asphaltene suspension showed a Bingham plastic behavior, and yield stress was dependent on the strength of the electric field. This indicated that the ER behavior is related to the formation of weak aggregated structures. The interfacial polarization generated by the differences in conductivity between silicon oil and asphaltene particles was suggested to be the mechanism driving the electrorheological behavior. At high electric field intensity,

Table 2. Summary of the Electrokinetic Phenomenon of Asphaltenes in Different Solutions

Samples	Charges on asphaltenes	Measuring method	Important findings	Ref
Asphaltene in aqueous suspension	–	Microelectrophoresis apparatus	Electrokinetic behavior of asphaltenes was dependent on pH, ionic strength, composition, and degree of hardness of the electrolyte solution.	99
Asphaltene in nitromethane	+		Asphaltene particles were negatively charged at neutral pH, while a charge reversal was observed at higher pH values in multivalent cation solutions.	
Asphaltene in aqueous suspension	–	Zetasizer	Asphaltenes interact with resins that take part in binding or coprecipitation rather than adsorption.	100
Asphaltene in toluene solution	+		Asphaltene interaction with resins did not significantly change the electrophoretic mobility.	
Asphaltenes in electrolyte solution (Na <sup>+</sup> and Ca <sup>2+</sup> )	–	Zetasizer	Surface charge at the asphaltene is a result of the protonation and dissociation reaction of surface functional groups.	101
Asphaltene-silica in aqueous solution		Zetaphoremeter	pH-dependent ionizable groups are present on the asphaltene surface.	102
Asphaltenes in toluene/heptane	Both + and –	Zeta phase analysis light scattering (PALS) apparatus	Charges on asphaltenes originate from the metal ion dissociation in addition to the dissociation of acidic groups (–OH and –SH) or basic groups (pyridinic groups) on the asphaltene surface.	107
Asphaltenes in nitromethane	+	Electrophoresis	Charges on asphaltenes is sufficient to produce particle mobility by electrophoresis techniques.	109
Asphaltenes in heptane and ethanol	+	Electrophoresis	Forces responsible for the flocculation of asphaltene particles are mainly van der Waals' attractive interactions.	110
Asphaltenes in toluene/heptane	Bimodal (+, –)	Zeta phase analysis light scattering (PALS) apparatus	Asphaltene colloids display both positive and negative surface charges.	113, 114
			Positive charge may arise from the presence of metals	
			Metallic components and acid–base functional groups contribute to the net surface charge	
Asphaltenes (downhole deposits) in toluene	+	Nonaqueous capillary electrophoresis	Asphaltene molecules possess neutral and positively charged fractions. Charge on asphaltenes play an important role in precipitation/aggregation and deposition.	111
Asphaltenes in heptane/heptol	+	Microelectrophoresis technique	Asphaltene molecule was strongly affected by the electric field and reorganized under the field.	15
			Larger asphaltene aggregates reduce the charge density of asphaltene particles.	
			By increasing the flow rate of injected fluid into the micromodel, the electrophoretic mobility increases.	

disruption of the aggregated structures was observed, which was found to be caused by the particle motion.<sup>89</sup>

Conductivity measurements have been often applied to define the asphaltene concentration at which the aggregation starts, i.e., critical nanoaggregate concentration (CNAC). CNAC is typically at the concentration order of mg/L for many asphaltenes, but it is dependent on the type of asphaltene and solvent.<sup>90,91</sup> In addition to the primary asphaltene aggregation of nanoaggregates, there is a secondary aggregation process of cluster formation called the critical clustering concentration (CCC). CCC is typically at the concentration on the order of g/L.<sup>92</sup> Both aggregation processes can be followed by changes in electrical conductivity.<sup>93,94</sup>

There are few studies where authors compared the DC conductivities at concentrations below and above CNAC, and they indicated that the asphaltene nanoaggregates started to form at very low concentrations in toluene solution, and their aggregation number was less than 10.<sup>59,87</sup> It was also established that resins were less conductive than asphaltenes and did not have a significant impact on CNAC or CCC of asphaltenes in toluene.<sup>87,95</sup> However, in nitrotoluene, resins were shown to decrease the DC conductivities of asphaltene clusters.<sup>65</sup> In a heptane/toluene mixture, resins have a propensity to aggregate with asphaltene, decrease the conductivity, and enhance their stability in the mixture.<sup>59</sup>

**3.4. Polarizability.** The high polarity of asphaltene structures is related to the high molecular *polarizability* of asphaltenes. Polarizability is a tendency of a molecule to acquire an electric dipole moment when subjected to an electric field. Molecular polarizability is expressed as  $\alpha = p/E$ ,

where  $p$  is a dipole moment induced in response to the electric field  $E$ . The molecular polarizability is related to the refractive index (RI) by the Lorentz–Lorenz equation:<sup>92,96</sup>

$$RI = \left( \frac{n^2 - 1}{n^2 + 2} \right) = \frac{N_a \alpha \rho_m}{3M}$$

where  $N_a$  is the universal Avogadro's number,  $\rho_m$  is the density of the material,  $\alpha$  is the polarizability,  $n$  is the refractive index, and  $M$  is the molecular weight of the molecule. Asphaltenes and resins have the highest polarizability and RI values, whereas the paraffinic components have the smallest RI values in the crude oil mixture.<sup>97</sup>

**3.5. Surface Charge and Zeta Potential.** Electrokinetic experiments can be used to gain information about electrical properties (e.g., charge and potential) of colloidal particles through measurements of electrophoretic mobility. The electrokinetic methods including electrophoresis and zeta potential measurements can be used to evaluate the relation between asphaltene surface charges and their aggregation, precipitation, adhesion, and deposition.<sup>98</sup> Table 2 summarizes the data present in the literature on the surface charge/zeta potential of asphaltenes in different polar and nonpolar media, measured using electrokinetic-based methods.

**3.5.1. Electrokinetic Properties of Asphaltenes in Aqueous Solutions.** The electrokinetic properties of asphaltenes in aqueous solution have been the subject of many research studies.<sup>99–106</sup> It was found that the electrokinetic properties of asphaltenes were dependent on pH, ionic strength, composition, and degree of hardness of the electrolyte solutions.<sup>99–101</sup>

In electrolyte solutions (containing  $\text{Na}^+$  and  $\text{Ca}^{2+}$  ions), asphaltene particles showed a negative zeta ( $\zeta$ ) potential at neutral pH conditions,<sup>99–101</sup> while in multivalent cation solutions, a charge reversal was observed at higher pH values.<sup>99</sup> It was suggested that the surface charge at the asphaltene particles was a result of protonation and dissociation reactions of surface functional groups.<sup>101</sup> Similar results were found in another study where the interactions between asphaltenes and silica particles were determined by electrokinetic studies.<sup>102</sup> It was found that asphaltene–silica interactions in aqueous solution exhibited a time-dependent characteristic, and electrostatic repulsive forces developed with increasing incubation time, suggesting molecular rearrangements at the asphaltene–water interface. Furthermore, an increase in pH caused an increase in the range and magnitude of repulsive asphaltene–silica interactions, implying the presence of pH-dependent ionizable/polarizable groups on the asphaltene surface. Surface charge density of the asphaltene particle also increased with increasing pH. The addition of salt caused a decrease in the range and magnitude of the forces, suggesting that the forces were electrostatic in nature.<sup>102</sup> It was also observed that asphaltenes interact with resins without significantly changing the electrophoretic mobility of the asphaltene particles.<sup>100</sup>

In another research study, an analytical model was used to calculate the  $\zeta$  potential of asphaltene in aqueous medium.<sup>103</sup> It was observed that with added salt, the  $\zeta$  potential decreased monotonically with pH, whereas for the case without added salt, the  $\zeta$  potential showed nonmonotonic variation with pH with two extrema at very low and very high pH, i.e., for low pH, the asphaltene was positively charged, while for high pH, asphaltene was negatively charged.<sup>103</sup> Later, Vega et al. (2009) found that in aqueous  $\text{NaNO}_3$  solution, the  $\zeta$  potential of asphaltene was negative between pH 3.5 and 10.5,<sup>104</sup> whereas when 50:50 water + ethylene glycol was added to the solution, then the  $\zeta$  potential was found to be more negative between pH 4.3 and 10.5, and the isoelectric point shifted to pH 4.2. The authors deduced from this electrokinetic behavior that the ethylene glycol molecules adsorb in the Stern layer and affect the electric characteristics of the interface.<sup>104</sup> Moreover, when asphaltenes were treated with aqueous copper sulfate solution, the  $\zeta$  potential values were positive for all pH values analyzed due to the interaction of  $\text{Cu}^{2+}$  with metal contents of asphaltenes.<sup>105</sup>

It was demonstrated that the volume of *n*-heptane used to extract asphaltenes from crude oil was an important parameter that determines the electrical surface properties of asphaltenes in aqueous solution. Parra-Barraza et al. (2003) measured the  $\zeta$  potential of asphaltenes in aqueous solution where asphaltenes were extracted from crude oil with different volumes of *n*-heptane.<sup>106</sup> According to the crude oil/*n*-heptane proportions used, asphaltenes were identified as 1:5, 1:15, and 1:40. It was found that at acidic pH (below the isoelectric point), asphaltene becomes positively charged because of the protonation of nitrogen-containing basic surface groups. However, asphaltene 1:5 exhibited an isoelectric point (IEP) at pH 4.5, whereas asphaltenes 1:15 and 1:40 showed an IEP at about pH 3. At neutral and higher pH, deprotonation of acidic functional groups occurred, resulting in a negative surface charge on asphaltenes.<sup>106</sup>

**3.5.2. Electrokinetic Properties of Asphaltenes in Non-aqueous Solutions.** Several authors explored the electrokinetic properties of asphaltenes and other crude oil components in

solvents less polar than water.<sup>99,100,107,108</sup> Experiments conducted in nitromethane<sup>99</sup> and toluene<sup>100</sup> solutions indicated that asphaltene particles were positively charged. Several studies were conducted to explore the effect of molecular characteristics of asphaltenes on the  $\zeta$  potential and electrophoretic mobility in toluene and heptane solutions. Wang et al. (2009) extracted asphaltenes from two different crude oils. Karamay asphaltenes were rich in carboxyl groups and calcium, while Lungu asphaltenes were rich in nickel, vanadium, and pyrrolic structures.<sup>107</sup> Karamay asphaltenes were found to be negatively charged, while Lungu asphaltenes were found to be positively charged in toluene/heptane solutions. The authors suggested that the charges could have been developed by metal ion dissociation in addition to the dissociation of acidic ( $-\text{OH}$  and  $-\text{SH}$ ) or basic groups (pyridinic groups) on the asphaltene surface.<sup>107</sup> In another study, Hosseini et al. (2016) investigated how the electrostatic fields influenced both aggregation rate and size of asphaltene particles extracted from three different crude oils in a toluene and *n*-heptane mixture.<sup>108</sup> They suggested that the asphaltene electrokinetic behavior is significantly controlled by its structural characteristics such as number of heteroatoms on asphaltene molecules, structural complexity, and molecular characteristics.<sup>108</sup>

**3.6. Electrophoretic Mobility.** Both characteristics of the asphaltenes (e.g., elemental composition, functional groups, surface charge, aggregate size) and process parameters such as current type (DC/AC), potential applied, diluent type, dilution ratio, and residence time can influence the electrophoresis of asphaltenes, i.e., their movement in the electric field.<sup>16,82</sup> For the first time, Wright and Minesinger (1963) employed an electrophoresis method to study asphaltenes. They established that asphaltenes carry a positive charge, and this charge is sufficient to induce particle mobility in ordinary electrophoresis.<sup>109</sup> The electrophoretic mobility of asphaltenes in nitromethane was determined and found to be between 3.26 and 5.36  $\mu\text{m}\cdot\text{cm}/\text{V}\cdot\text{s}$  for different asphaltenes. Later, it was found that the electrophoretic mobility of the asphaltenes was substantially lower in *n*-heptane compared to ethanol or nitromethane.<sup>110</sup>

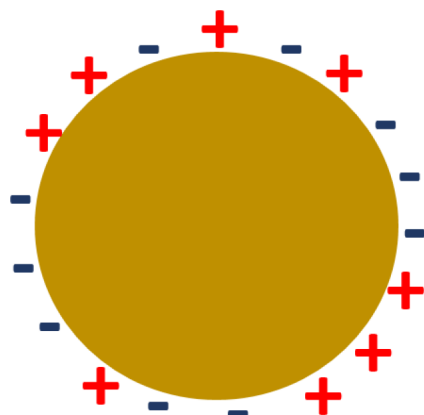
To separate and characterize asphaltene samples obtained from different downhole deposits, Kok et al. (2011) used a nonaqueous capillary electrophoresis method.<sup>111</sup> It was found that the asphaltene field deposit was present in the form of nanoaggregate clusters and consisted of two major fractions in different dilute solutions: a smaller neutral fraction and a larger positively charged fraction. The results also revealed dissimilar charge distribution and charged fraction of aggregates in the asphaltene sample obtained from the stable crude oil deposits (+2 charge) compared to the samples obtained from an unstable one (+1 charge). The relative distribution and abundance of charged fractions could explain the variation in asphaltene stability of the different investigated crude oils as well as their affinity to form wellbore deposits.<sup>111</sup>

In contrast to Kok et al. (2011), Azari et al. (2018) estimated the average net charge of an asphaltene molecule to be  $5.62 \times 10^{-28}$  C/molecule, which corresponds to  $3.51 \times 10^{-9}$   $e^-$ /molecule.<sup>15</sup> As this value is less than  $1e^-$ , it has been concluded that asphaltene molecules do not possess an intrinsic electric charge, and the apparent charge is generated by rearrangement of the asphaltene molecular structure in the solvent. The authors also found that the charge density of asphaltene particles is reduced by “aggregation”.<sup>15</sup> Moreover,



Gaikwad et al. (2015) estimated surface charge density of the asphaltene nanoaggregates to be  $43.7 \text{ nC/cm}^2$  in air.<sup>112</sup>

The relationship between the colloidal asphaltene electrophoretic mobility and dispersant concentration was investigated by Hashmi and Firoozabadi (2011, 2012).<sup>113,114</sup> The authors suggested that when no dispersants are present, a bimodal surface charge is displayed by colloidal asphaltenes in nonpolar suspension, with the same fractions of positive and negative surface charges, as depicted in Figure 5. The results



**Figure 5.** Schematic illustration of charge distribution over the asphaltene particle surface. In the absence of dispersants ( $C = 0$ ), the asphaltene colloids display both positive and negative surface charges.<sup>113</sup> Reproduced with permission from ref 113. Copyright 2011 Royal Society of Chemistry.

revealed that the net surface charge of the asphaltene is dependent on the chemical composition of asphaltenes such as content of metallic components and acid–base functional groups, which can vary depending on source of extraction, molecular weights and oil densities, maturation, and migration history within the reservoir. However, electrophoretic mobility was increased with the increase of dispersant concentration.<sup>113,114</sup> In another study, Hashmi and Firoozabadi (2012) showed that asphaltene colloid aggregation can be avoided by electrostatic repulsion which stabilizes the colloids.<sup>115</sup> It was suggested that the aggregation and separation upon asphaltene transport via microchannels is mainly controlled by the magnitude of the electroosmotic and the electrophoretic effects.<sup>116</sup>

## 4. ELECTRODEPOSITION OF ASPHALTENES

Electrodeposition is one of the promising approaches to control asphaltene removal by using an electrical potential. It exploits the net surface charge of asphaltene molecules and aggregates to remove them from the crude oil. The electrodeposition can be done before transportation of oil to prevent later flow-assurance problems. During the electrodeposition process, the electric field destabilizes the hydrocarbon equilibrium, and asphaltene is first precipitated out of the liquid phase. Afterward, the asphaltenes are attracted via an electric field and deposited onto one or both electrodes.<sup>63</sup> This mechanism has been schematically presented in Figure 6.

### 4.1. Electrodeposition of Asphaltenes from Crude Oils

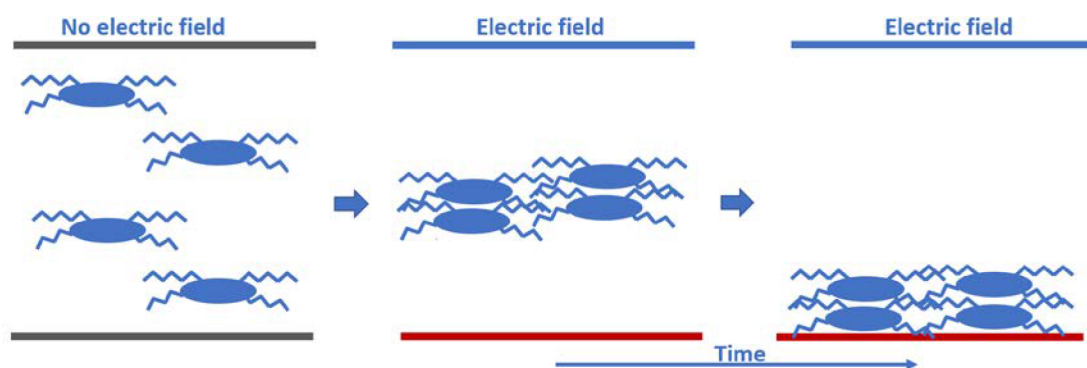
Electrodeposition of asphaltenes was for the first time conducted by Precksho et al. (1943). The authors destabilized crude oil by the application of an electric field and found that asphaltenes can be deposited on a positive electrode as they possess negative charges.<sup>117</sup> The electrodeposition on the positive electrode and the negative charge of asphaltenes is in line with the findings reported later by many authors.<sup>16,117–127</sup> Many other authors reported, however, deposition on the negative electrode and a positive charge of asphaltenes.<sup>16,63,123–125,128–130</sup> A comprehensive overview of scientific work reporting the negative and positive charge is given in

Table 3 along with the information about the conditions (medium/solution and electric field type) at which electrodeposition was achieved. There are several factors that govern the asphaltene electrodeposition process and determine on which electrode the deposition will take place. These factors are highlighted in Figure 7 and are discussed below in detail.

#### 4.1.1. Asphaltene Structure and Crude Oil Composition

Perhaps by far the most important parameter that affects the electrodeposition process is the differences in the structure of asphaltenes originating from different crude oils (i.e., the presence of different functional groups as well as heteroatoms as described in detail in Section 2: Asphaltene Structure as well as relative proportions between different crude oil components. According to Taylor (1998), the mass of asphaltene deposited on the electrode is typically governed by<sup>63</sup> (1) the amount of asphaltenes present in the crude oil; (2) the fraction of resins; (3) the amount of asphaltenes already precipitated, (4) alkane type and its relative dilution. Taylor's findings suggest that the proportions between different crude oil components are decisive in the electrodeposition process.

4.1.2. Aggregation State and Interactions with Other Crude Oil Components. Taylor (1998) emphasizes the



**Figure 6.** Schematic representation of asphaltene destabilization and electrodeposition in an electric field.

Table 3. Summary of Electrodeposition Studies of Asphaltenes Conducted by Different Authors

Oil sample	Charge on asphaltenes	Electric field	Important findings	Ref
Crude oil	–	Streaming potential	Crude oil can be destabilized by the application of an electric field, and asphaltenes were deposited on a positive electrode.	117
Crude oils	–	Streaming potential	Streaming potentials can lead to the precipitation of asphaltenes, and deposition occurred on positive electrodes.	126
Crude oil	–	Streaming potential	Destabilization of asphaltene in oil production systems may occur if the surface charge and attraction forces between resins and asphaltenes are disturbed.	121
Crude oil dilution with mineral oil	+	Streaming potential	Oxidation of the asphaltenes increased the viscosity of the crude oil and enhanced the coalescence and precipitation of the asphaltene particles.	128
Crude oil	–	DC current	Asphaltene particles were deposited on the anode. All the asphaltenes can be extracted from the crude oil.	127
Light and heavy crude oil	–	DC elect. field	Higher voltages (500 V) were required for destabilization of the heavier crude oils. Most of the asphaltenes deposited during 1 h of the experiment. Application of a DC current to crude oil for an optimized time may extract all asphaltene particles dissolved in crude oil.	120
Crude oil	–	DC current densities 10, 20, 30 A/m <sup>2</sup>	The amount of deposit increased with the experiment time and current density. Eighteen percent of original asphaltic material in crude oil was arrested on the anode.	119
Crude oil + heptane	–	DC elect. field	Electrodeposition has the potential to induce asphaltene deposition from crude oils in the presence of brine. Application of DC resulted in rapid deposition on the anodic surface.	118
Crude oil + dilution with pentane, hexane, and heptane	–	DC elect. field, Bench scale vessel	High dilution with heptane increased the electrodeposition rate. One kilogram of asphaltene is removed by 10 kJ energy.	18
Crude oil in the presence of formation water	–	DC current densities 10, 20, 30 A/m <sup>2</sup>	Deposition on the cathode occurred at a high dilution and a lower electric field. Deposition on the anode occurred at a lower dilution and a higher electric field. Deposition occurred on both anode and cathode. However, deposition on the cathode was observed at a higher current density. The presence of formation water with crude oil stimulated the electrodeposition of asphaltenes.	122
Crude oil hexane	+	DC field with 4 kV/cm strength	Crude oil dilution with hexane favored deposition.	129
Asphaltenes in nitrobenzene in the absence of resins	+ and –	DC voltage	Water addition resulted in enhanced asphaltene precipitation. Threshold electric field is required for asphaltene deposition.	123
Crude oil dilution with alkane	+	DC electric field strength, 2.8 kV/cm	At low voltage, asphaltene was positively charged, and at high voltages, asphaltene was negatively charged.	63
Asphaltenes, maltenes, and bitumen in toluene	+ and –	QCM, DC voltage, 250 V/cm	At lower dilution with <i>n</i> -alkanes, deposited material possessed a negative charge. Higher dilution resulted in positively charged deposits. Positively charged asphaltenes are surrounded by negatively charged resins in oil. Max. asphaltene deposition is attained at a 30:1 dilution of crude oil with heptane. Mass deposit decreased with increasing alkane chain length. In toluene-diluted bitumen, electrodeposition of both positive and negative species is observed, and the specific mass (i.e., mass over charge) is found to be higher for the positive species. Solids deposited from bitumen are mainly negatively charged in toluene. Deposits on the anode contained more oxygen, chlorine, fluorine, and sulfur but less nitrogen-based functional groups than those deposited on the cathode.	125
Crude oil	–	DC electric field strength, 4 kV/cm	Flocculated solid material rather than a nanosized asphaltene aggregate undergoes electrodeposition.	16
Asphaltene + heptane	+	DC electric field strength, 2 kV/cm	The net charge of asphaltic particles depends on the balance between dissolved and flocculated asphaltene fractions.	124
Crude oil + heptane	–	DC electric field strength, 2 kV/cm	The net charge of asphaltenes is not their inherent property and is affected by external parameters, such as the concentration of additives and the method of preparation.	124
Asphaltene + heptane	+		Resins neutralized the asphaltene particle charge.	

Table 3. continued

Oil sample	Charge on asphaltenes	Electric field	Important findings	Ref
Asphaltenes + heptane	+	Static and dynamic exp., electrical fields of 0.5, 1, 1.5, and 2 kV/m	In asphaltene/heptane/toluene systems, the charge of the deposit varies from positive to neutral to negative, depending on the method of preparation of the mixture and the toluene content. Current is transported by the dissolved asphaltene fraction rather than the solid asphaltene particles Deposition on the negative electrode increases by increasing the intensity of the electric field. 0.5 kV/m has a very small effect on asphaltene deposition.	130

importance of interactions between asphaltenes and other crude oil components especially resins as an important factor determining where and when the electrodeposition process occurs.<sup>63</sup> It is proposed that the asphaltene–resin complexes are stabilized by short-range electrical forces in crude oils. When the solvent properties are modified, the balance in the system is disrupted, and the new interfaces between the asphaltenes and resins are created. Consequently, van der Waals' attractive forces begin to dominate and lead to aggregation and precipitation.<sup>63</sup>

**4.1.3. Crude Oil Dilution.** Initially, Lichaa and Herrera (1975) found that by diluting the crude oil with a mineral oil during the electrodeposition experiments, asphaltenes were removed from the crude oil by deposition on the negative electrode; i.e., the asphaltenes were positively charged.<sup>128</sup> Later, it was suggested by Taylor (1998) that the stable asphaltenes in crude oils possessed very small net charges and were not affected by the direct current electric field. Upon destabilization with *n*-alkanes, however, electrodeposition took place. At lower dilutions, where partial destabilization took place, the deposited material possessed a small net negative charge, whereas higher dilutions resulted in positive charges of deposits. Taylor proposed that the asphaltene nucleus that is positively charged is surrounded by negatively charged resins, which results in screening of the asphaltene charges. He also suggested that there exists an optimum dilution of crude oil with heptane (30:1) at which the asphaltene attained maximum deposition.<sup>63</sup>

Later, Hashmi and Ghosh (2015) used crude oil and heptane-diluted crude oil in their experiments and investigated the possibility of controlling asphaltene deposition in metal pipes by applying a direct current.<sup>118</sup> The observations suggested that asphaltenes had a negative surface charge. The application of DC current resulted in quick and excessive asphaltene deposition on the anode. Little or no deposition was observed at the cathode. It was revealed that the surface charge of asphaltene–resin colloids was determined by the amount of *n*-heptane diluting the crude oil. Higher dilution was found to increase the effect of DC potential in terms of the deposition rate and quantity of the deposited material. On the basis of the experimental results, it was proposed that the asphaltene deposition in a flow system can be controlled by the optimal cathodic polarization.<sup>118</sup>

In another investigation, Asaadian et al. (2017) studied the stability of a crude oil in a direct current electric field and upon dilution of oil with *n*-hexane and water.<sup>129</sup> It was suggested that asphaltenes possessed positive charge in the pure crude oil; however, the precipitation on both electrodes in crude oil indicated that the positively charged asphaltene particles are surrounded by negatively charged resins and a dipole charge system exists between the asphaltenes and resins. The results have also shown that to start the asphaltene deposition, a threshold electrical field is required, which is dependent on the oil composition, size distribution of asphaltene particles, and their stability. A higher deposition rate was observed with higher *n*-hexane dilution of the crude oil. Adding water to asphaltene–toluene solutions caused more pronounced asphaltene precipitation. By reversing the current, a large amount of precipitate was redissolved in oil.<sup>129</sup> It is reported that polar heteroatoms present within the asphaltene structure are involved in the formation of hydrogen bonds with water. The hydrogen bonding enhances the aggregation of asphaltene monomers.<sup>131</sup> The more pronounced deposition in the

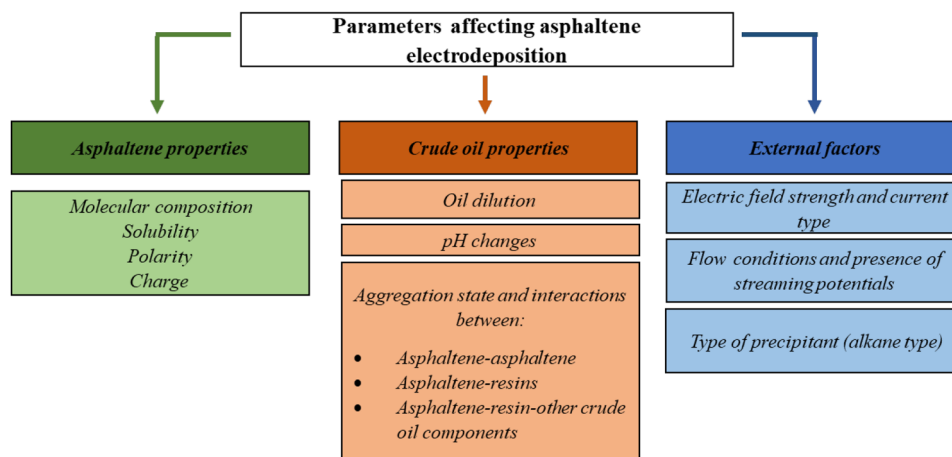


Figure 7. Parameters affecting the asphaltene electrodeposition process.

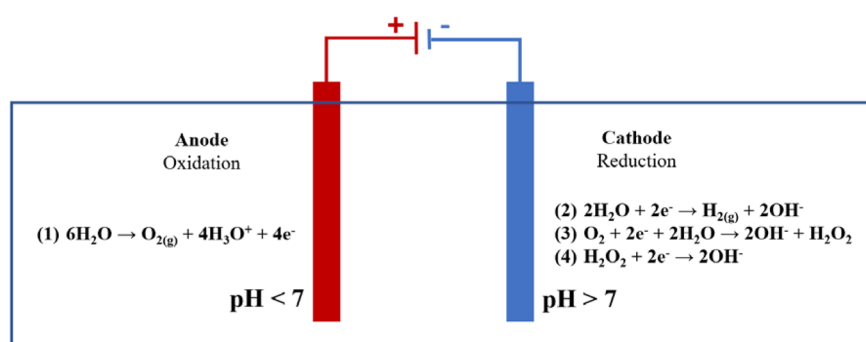


Figure 8. Electrochemical processes expected at the cathode and anode contributing to local pH changes close to electrodes.

presence of aqueous solution is in line with the findings reported by Khalifeh and Belhaj (2016). The authors have shown that the presence of formation water in crude oil enhances the destabilization of asphaltenes under the DC electric field.<sup>122</sup> Recently, Xia et al. (2019) conducted electrodeposition experiments in which they varied the dilution ratio of heavy oil using pentane, hexane, and heptane.<sup>18</sup> They found that the increase in the dilution ratio allowed for more efficient asphaltene precipitation. The electric field strength required for the electrodeposition was also lower after dilution. Moreover, the net charge of the asphaltene was affected by the electrodeposition process because of which the deposition was observed on both the anode and the cathode. Higher dilution ratios along with lower electric field strengths favored deposition onto the cathode, while lower dilution ratios and higher electric field strengths resulted in deposition on the anode. The observations were explained by the higher content of resins at a low dilution ratio at which adsorption of resins–asphaltene aggregates is possible. The interactions led to shielding of the electric field effect.<sup>18</sup>

**4.1.4. Electric Field Strength and Current Type.** Belhaj et al. (2013) reported that electrodeposition from light crude oil resulted in significant amounts of asphaltene deposits however destabilization of heavy crude oil required higher voltages.<sup>120</sup> In a study, Abu Khalifeh et al. (2014) observed that the mass of the material electrodeposited from crude oil increased with the current density. The authors reported also a faster deposition rate at a higher current density.<sup>119</sup> Later, Khalifeh and Belhaj (2016) observed a gradual increase in the deposition of asphaltenes on anodes as the current density

increased. However, cathode deposition was also observed at a higher current density. They observed that 18% of the asphaltenes from the crude oil was arrested on the anodes for a current density of 30 A/m<sup>2</sup> and duration of 24 h.<sup>122</sup>

**4.1.5. Effect of Electric Pulse Method.** It was found by Tao and Xu (2006) that by the application of an electric pulse method, the viscosity of asphaltene-rich crude oil can effectively be reduced. The pulsing led to temporary aggregation of the asphaltene particles in the crude oil which contributed to the crude oil viscosity reduction.<sup>132</sup>

**4.1.6. Streaming Potentials.** Streaming potentials are potentials that occur when an electrolyte is forced to move by pressure gradient through a channel (e.g., within porous medium) with charged walls. One of the first who suggested that streaming potentials could lead to the precipitation of asphaltenes from oil in the reservoir porous rock was Katz and Beu (1945).<sup>126</sup> Later, Leontaritis and Mansoori (1987) suggested that the potential differences across metal pipes is the primary cause of negatively charged asphaltene deposition on their surfaces.<sup>121</sup> In 1997, Mansoori introduced a mathematical model used for the preventive measures of asphaltenes deposition in pipelines.<sup>133</sup> He considered the effect of “streaming potential”, i.e., a potential difference created due to crude oil flow along the flow conduit, on asphaltene deposition. Mansoori suggested that asphaltene deposition is partly due to a solubility effect and partly due to a colloidal phenomenon. Asphaltene particles are electrokinetically active by causing electrostatic charge generation and are also affected by stronger electrostatic charges.<sup>133</sup>

4.1.7. *pH*. Moore et al. (1965) reported negative charge on the asphaltenes; however, charge reversal occurred when the crude oil was treated with 15% HCl for 24 h.<sup>134</sup>

In most of the studies considering asphaltene in the electric field, almost exclusively physical (electrostatic) interactions of asphaltenes with electrodes and other crude oil components are discussed. However, electrochemical processes going on at the electrodes surfaces in the presence of water seem to be neglected. If the potential applied to two electrodes present in aqueous solution is higher than the water electrolysis potential (1.23 V), water is split according to the following reactions at the anode, eq (1), and the cathode, eq (2) given in Figure 8. At potentials below the water electrolysis potential, reduction of oxygen present in water may take place at the cathode as described in eqs (3) and (4).<sup>135</sup> These processes change the pH in the vicinity of electrodes.<sup>136</sup> The pH close to the anode becomes acidic due to an increased concentration of hydrogen ions, while close to the cathode the pH becomes alkaline due to an increased concentration of hydroxyl ions.<sup>137,138</sup> For example, it has been shown that during electrolysis of water with an initial pH of 4.5, using direct current (20 V) the pH at the anode was reduced to a value of 3 within a minute only. At the same time, the pH close to the cathode increased to more than 10.<sup>138</sup> The pH variations close to electrodes may affect asphaltene electrodeposition processes as asphaltenes are highly sensitive to pH.<sup>57,104,139–141</sup> At high or low pH, asphaltenes functional groups become charged. It is thus expected that asphaltene molecules and aggregates may be affected differently by pH depending on their location between the cathode and the anode and depending on what the actual local pH in this location is. For better understanding of the nature of asphaltenes as well as their electrodeposition processes, efforts should be made to separate the effect of pH variations from the electrostatic and electrophoretic effects. To this end, the experiments at lower potentials than the water splitting potential in an oxygen-free environment are suggested.

4.1.8. *Energy Consumption during Electrodeposition*. The total energy input required to perform asphaltene electrodeposition is the sum of the energy input for building up the electric field strength  $E_b$  (see eq 5) and energy consumption during the electrodeposition  $E_d$  (eq 6).<sup>18</sup>

$$E_b = 0.5 CV^2 \text{ where } C \approx \epsilon A/d \text{ when } A \gg d^2 \quad (5)$$

where  $C$  is the capacitance,  $V$  is the electric field strength,  $\epsilon$  is the dielectric permittivity of oil,  $A$  is the electrode surface area, and  $d$  is the distance between the electrodes.

$$E_d = Vit \quad (6)$$

where  $I$  is the current during the electrodeposition and  $t$  is the electrodeposition time.

With low current and capacitance, the energy input is extremely low. It has been estimated by Xia et al. (2019) that to recover 1 kg of asphaltene, 10 kJ energy input is required,<sup>18</sup> which is an equivalent of 25 s of work of a 40 W bulb.<sup>18</sup> The high energy efficiency and simple operation make the asphaltene electrodeposition a promising method to remove asphaltenes from crude oils.

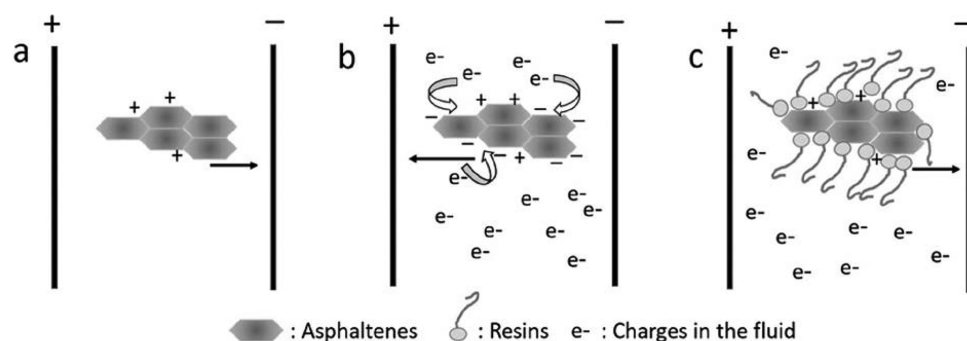
**4.2. Electrodeposition of Asphaltenes from Model Oils.** The complexity of crude oil composition and the multitude of interaction possibilities between different crude oil components pose a challenge for scientists trying to describe asphaltene electrodeposition mechanisms. To get a

better understanding of the effect of asphaltenes' molecular composition and polarity, flow conditions, as well as the influence of electric field strength on the asphaltene electrodeposition process, a simplified and well-defined model oil system was studied by several authors.

4.2.1. *Charge Reversal Due to Asphaltene–Asphaltene Interactions*. Eldib (1962) reported a charge reversal of asphaltenes in nitrobenzene solution in the absence of resins when the applied (DC) voltage was increased. At low voltages, the asphaltenes were shown to be positively charged, and at high voltages they were negatively charged.<sup>123</sup> He suggested that it is not exclusively the interactions between asphaltenes and resins that are responsible for charge reversal, but the interactions between asphaltene molecules and aggregates may contribute to it as well. Similar conclusions were drawn by Khvostichenko and Andersen (2009) who studied the electrodeposition of asphaltic solids from crude oil, crude oil mixtures with heptane, as well as isolated asphaltenes on metal electrodes under direct current electric fields.<sup>16</sup> They found that the asphaltic material deposited from the crude oil had a net negative charge, while the isolated asphaltene suspended in heptane possessed a net positive charge. When the electrodes with precipitate were transferred from the oil to heptane, the negative charge of the oil deposit reversed to positive. It was manifested by the movement of the deposited material from the anode to the cathode. When crude oil was mixed with an increasing amount of heptane prior to the application of an electric field, a gradual decrease of the amount of anodic deposit coinciding with an increase of the amount of cathodic deposit was reported. The charge reversal did not take place when small amounts of crude oil were added to heptane under a DC electric field.<sup>16</sup> This led to the conclusion that flocculated solid material rather than a nanosized asphaltene aggregate took part in the electrodeposition.<sup>16</sup> Later, the same authors concluded that the net charge of asphaltene particles is dependent on the method of asphaltene sample preparation.<sup>124</sup> The asphaltene charge was negative in crude oil–heptane mixtures and positive in asphaltene–heptane mixtures. In mixtures containing asphaltene, heptane, and toluene, the charge of the asphaltene deposit varied from negative to neutral to positive, depending on the mixture preparation method and the content of toluene. Addition of resins to asphaltene and heptane mixtures resulted in neutralization of the asphaltene charge.<sup>124</sup> In another study, Khvostichenko and Andersen (2010) observed a sharp increase in conductivity upon transition from systems with asphaltene deposition to systems without deposition. On the basis of this observation, the authors concluded that the electrical current is transported by the fraction of dissolved asphaltenes rather than the solid asphaltene particles.<sup>124</sup>

4.2.2. *Electric Field Effect on Asphaltene Charge Reversal*. Electrodeposition of asphaltene on copper electrodes from a synthetic oil using varying electric field strength and solvent type were studied by Xia et al. (2019).<sup>17</sup> The authors observed that the native positive charge on the asphaltenes can be switched to negative using a high current density. The electric field strength along with crude oil viscosity controlled the electrophoretic mobility of asphaltenes. The electrophoretic mobility of asphaltenes was only slightly reduced in the presence of resins; however, resins significantly inhibited asphaltene charge alteration.<sup>17</sup>

4.2.3. *Mechanism of Charge Reversal in the Absence of Resins*. Xia and Kostarelo (2020) have proposed the



**Figure 9.** The electrophoretic movement of asphaltenes: (a) under low electric field strength; (b) under high electric field strength; (c) under high electric field strength with the effect of resins.<sup>142</sup> Reproduced with permission from ref 142. Copyright 2020 Elsevier.

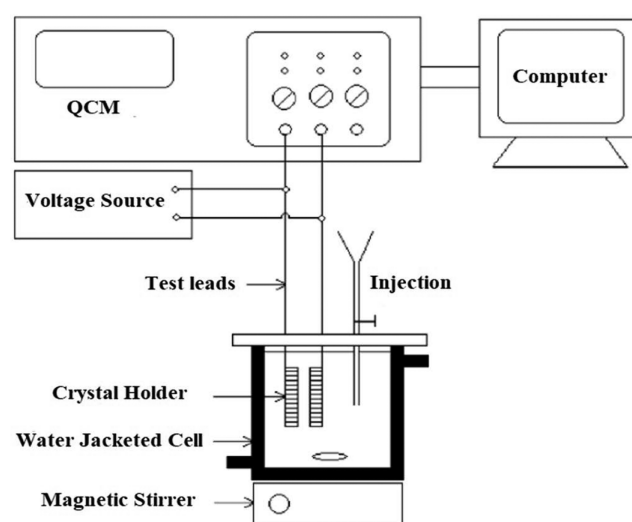
mechanism driving asphaltene charge reversal at high electric field strengths.<sup>142</sup> It was suggested to be as follows: Under low electric field strength, because of the electrostatic forces (electrophoretic effect), the positively charged asphaltenes move toward the negative electrode. Under such circumstances, interactions between asphaltenes are limited as only few dissociated molecules exist in the fluid. This contributes to a low current flow (low conductivity). However, when the electric field strength is increased above a threshold value, the dissociation rate of molecules close to the electrodes exceeds the recombination rate, which leads to the local ionization of the molecules. The ionization process increases the amount of charge in the fluid, and the active sites of asphaltenes retain a net negative charge. This results in an overall negative charge of asphaltenes and thus their deposition on the positively charged electrode. This mechanism is schematically presented in Figure 9a,b.

**4.2.4. Role of Resins in Asphaltene Charge Reversal.** When resins adsorb onto the asphaltene surface, they occupy the active sites (dissociating functional groups). The adsorption of resins limits the asphaltenes capacity to adsorb negative charges also when the concentration of negative charges in the fluid is high. The asphaltenes retain an overall positive charge, and that is why asphaltene–resin complexes continue depositing on negative electrodes. This is depicted schematically in Figure 9c.<sup>142</sup>

**4.2.5. Static and Dynamic Deposition and Flow Type.** In a study, Kostarelos et al. (2017) ran electrodeposition experiments with model oils at high flow rates (Reynold number >106) and suggested that turbulent flow is desirable for deposition of asphaltenes onto the electrodes because it would induce greater particle movement, leading to more asphaltenes coming in close contact with the electrode, which supports deposition.<sup>143</sup> Later, Taghavi et al. (2018) determined the effect of the magnitude of the electrical field on asphaltene deposition from crude oil diluted with *n*-heptane in a static and dynamic state.<sup>130</sup> They reported that the asphaltene particles had a positive surface charge, and by applying the electric field in static experiments, some fraction of asphaltenes deposited on the negative electrode and some fraction sedimented when the negative electrode was completely covered with asphaltenes. The increase of the intensity of the electric field resulted in the increased deposition of asphaltenes on the negative electrode. During the dynamic tests, a low electric field (at the order of 0.5 kV/m) had a very little effect on asphaltene deposition.<sup>130</sup>

**4.2.6. Effects of Molecular Composition and Polarity on Electrodeposition.** In order to understand the nature of the

charge carriers in bitumen, and to determine the electrodeposited mass in toluene-based systems, Goual et al. (2006) used a quartz crystal microbalance (QCM), Figure 10.<sup>125</sup> The



**Figure 10.** Experimental setup of the QCM with a DC voltage source.<sup>125</sup> Reproduced from ref 125 with permission. Copyright 2006 American Chemical Society.

experimental setup consisted of two gold coated QCM crystals immersed in toluene solutions containing asphaltenes, maltenes, and solid free bitumen. A DC voltage was applied between the QCM crystals. By the application of a 250 V/cm field strength, cationic and anionic species were collected at the negatively and positively charged QCM crystals, respectively. The specific mass (i.e., mass over charge) was found to be higher for the positive species than it was for the negative species. Moreover, the solids separated from bitumen were mainly negatively charged, and their specific mass was relatively high. Goual et al. revealed that the species deposited on the anode contained more oxygen, chlorine, fluorine, and sulfur, but less nitrogen-based functional groups than those deposited on the cathode.<sup>125</sup> Recently, Xia and Kostarelos (2019) extracted asphaltenes from coal tar and bitumen and investigated the effect of the molecular composition and polarity on the electrodeposition process.<sup>144</sup> It was demonstrated that asphaltenes with higher heteroatom contents were more sensitive to solvent polarity regarding the electrodeposition process, as a higher electric field strength is required for the complete deposition of the more polar

asphaltenes in more polar solvents. The results also revealed that the particle size of precipitated asphaltenes governs the electrophoretic mobility, which in turn affects the performance of the electrodeposition process.<sup>144</sup>

## 5. EFFECT OF ELECTRIC FIELD ON SEPARATION OF EMULSIONS STABILIZED BY ASPHALTENES

In the electrostatic crude oil dehydration system, the main objective of the application of an electric field is to increase the collision and coalescence rate of water droplets in the emulsion.<sup>145</sup> There is a combination of dielectrophoretic and electrophoretic forces, as well as mechanical forces from gravity, inertia, and viscous effects, which act on a water droplet suspended in the continuous oil phase in an electric field.<sup>146</sup> The results of molecular dynamic simulations performed by Chen et al.<sup>147</sup> showed that the interfacial film created by asphaltenes owing to their adsorption on the W/O interface is a key factor counteracting coalescence of water droplets in the electric field. As previously described in Section 2: Asphaltene Structure, asphaltenes due to their high polarity tend to locate at the oil–water interface either in the form of single molecules or aggregated structures. As such, they tend to stabilize water in oil emulsions<sup>148,149</sup> and prevent water droplets' coalescence. Hydrogen bonding within polar functional groups was defined as a main force responsible for the formation of the elastic asphaltene film at the oil–water interface.<sup>148</sup> Both the interactions between film forming molecules and asphaltenes, and the steric effect due to the presence of large amphiphilic materials at interface are responsible for the reduced coalescence.<sup>150</sup>

It is expected that the asphaltene film present at the water–oil interface may hinder electrocoalescence in a similar way as a gravity induced coalescence,<sup>147</sup> while the interaction of asphaltenes and other crude oil components with the electric field may change the crude oil properties contributing to easier separation. Indeed, the experimental data presented by Dalmazzone et al. (2009) confirm this working hypothesis.<sup>151</sup> The application of an electric field may lead to asphaltene aggregation and/or precipitation, which may contribute to changes of the rheological properties of the crude oil and oil–water interface.<sup>132</sup>

The magnitude of the electric field and type of electrodes was also found to play an important role during the separation of asphaltene-stabilized emulsions. Mohammadian et al. (2018) developed an electrical demulsification device where the crude oil/water (O/W) emulsion was placed between the two electrodes, and a direct current was applied to the system.<sup>152</sup> It was found that the electrochemical cell had a separation efficiency of approximately 90% at an electric field voltage of 30 V, and the copper electrode (85.75%) showed higher oil removal efficiency compared to that by aluminum electrodes (62.5%).

## 6. CONCLUSIONS, CHALLENGES, KNOWLEDGE GAPS, AND FUTURE PERSPECTIVES

The review of literature presented in this paper suggests that behavior of asphaltenes in an electric field is dependent on the molecular structure and polarity of asphaltenes, crude oil composition, interactions of asphaltenes with themselves and with other crude oil components (especially resins), the pH, the strength and type of the electric field, and the flow conditions. The electric field has been utilized in destabiliza-

tion of water in oil and oil in water emulsions (electrocoalescence) stabilized by asphaltenes as well as removal of asphaltenes from crude oils via electrodeposition as well as asphaltene adsorption inhibition.

The main challenge associated with studying asphaltenes in an electric field is perhaps their varied chemical structure. The significant structural differences between asphaltene molecules extracted from different oils or even extracted from the same oil but using different extraction procedure make it very difficult to determine a uniform and well-defined electrodeposition procedure. It has been obvious from studies referred to in Section 4: Electrodeposition of Asphaltenes that asphaltene electrodeposition is strongly affected by the asphaltene origin, extraction conditions, and experimental parameters, and thus it is impossible to suggest any universal procedure that would allow for efficient asphaltene removal, but rather a removal procedure for each asphaltene system should be optimized separately. Even one asphaltene batch is expected to behave differently in different model oils/solvents in an electric field as different solvents will affect differently the electrical properties of asphaltenes such as polarity and dielectric constant and their aggregation and electrodeposition behavior. Thus, it is challenging to determine the effect of asphaltene polarity and other properties on electrodeposition behavior.

Thorough analysis of the oil composition (SARA fractionation) as well as molecular composition of asphaltenes seems to be a prerequisite for the optimization of the electrodeposition process. Asphaltene fractionation according to interfacial activities and adsorption characteristics (extended-SARA, E-SARA) can provide additional information allowing correlation of specific functional groups with certain characteristics of asphaltene aggregation, precipitation, and adsorption and may further contribute to a better understanding of electrodeposition processes.<sup>153</sup>

The major knowledge gap associated with electrodeposition and electrocoalescence from aqueous and water-containing solutions is how potential concomitant electrochemical processes such as, e.g., water electrolysis (involving local pH changes and gas bubble production) affect the electrodeposition and electrocoalescence processes. The role of local pH changes in the vicinity of electrodes on the electrodeposition of asphaltenes has not been well-defined. The contributions of electrochemical and electrophysical effects on electrodeposition and electrocoalescence have not been delineated yet.

It has been shown that large fractions of asphaltenes (up to 90 wt %) can be deposited within seconds, which suggests high efficiency of the electrodeposition as a method of removal. The energy input required to recover 1 kg of asphaltene in Xia et al. (2019) work was found to be 10 kJ<sup>18</sup> under optimized process conditions. This is an equivalent of 25 s of work of a 40 W bulb. Even if this value varies between different crude oils with different compositions and asphaltene structure, the energy consumption at the order of magnitude reported by Xia et al. should be regarded as low. The high energy efficiency and simple operation make asphaltene electrodeposition a vital method for asphaltene removal from crude oils.

Preventing asphaltene adsorption in oil wells or pipelines transporting crude oil by electrically polarizing the well tubing or pipeline seems to be an interesting approach. With conditions at which neither flow nor electric field causes asphaltene recharging, asphaltene solids can be prevented from

surface deposition by polarizing the surface so that it possesses the same charge as asphaltenes leading to electrostatic repulsion between the two. There are however certain limitations to this approach. Oil well tubings as well as pipelines are usually made of carbon steel. However, when steel is polarized anodically in the presence of water and oxygen at high enough electrochemical potentials, deteriorative corrosion reactions will occur, leading to dissolution of the steel.<sup>154,155</sup> Thus, anodic polarization of the steel-made oil well/pipeline where some portions of water are expected may not be feasible. Cathodic polarization of steel is a common way to protect the steel against corrosion,<sup>156,157</sup> but it requires the application of a sacrificial anode. Moreover, the cathodic deposition method can be applicable only to the crude oils having positively charged solids. However, it has been shown in this paper that for a given oil at given flow conditions, the asphaltene charge can be engineered by changing process parameters such as crude oil composition (dilution), pH, electric field strength, etc., which may extend applicability of cathodic polarization as a method for asphaltene deposition inhibition. Hydrogen production and possible concomitant hydrogen embrittlement of steel<sup>156</sup> need to be considered if the cathodic protection is supposed to be applied to water-containing systems.

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The authors declare no competing financial interest.

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