Electrokinetic behavior of asphaltene particles

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A B S T R A C T

The effect of electrostatic field on the aggregation rate and aggregate size of asphaltene particles precipitated from three different crude oil samples suspended in a mixture of toluene and n-heptane (a model oil) was investigated. An electrode-embedded glass micro-model utilizing a high-voltage direct current power supply was utilized in this study. The asphaltene particle size and the rate of aggregation under the electric field were monitored using a high-resolution optical microscope and the average aggregate size for asphaltene particles was estimated using image processing software. To investigate the effects of structural parameters on asphaltene aggregation rate, aggregate size and electro-deposition, the elemental analyses for the three asphaltene samples were carried out and the mass ratios for C, H, N, S and O elements present in the asphaltene samples were determined. Also, the functional groups of asphaltene molecules were analyzed using the FTIR technique. Asphaltene molecules with larger chromophore and higher complexity exhibited faster aggregation behavior under the electrical field. The asphaltene aggregation rate was found to be directly proportional to the number of hetero-atoms on asphaltene molecules. The effects of parameters such as the electric field intensity, exposure time, asphaltene concentration, the amount of precipitant, and the asphaltene molecular structure on the asphaltene aggregation rate and aggregate size under the electrostatic field were also investigated. The electrostatic field strongly affected the aggregation rate of asphaltene particle; under an electrostatic field, asphaltene particles tended to aggregate faster and this may have resulted in faster and a larger quantity of asphaltene particles that precipitated out of the quiescent mixture of toluene and n-heptane. It should be also stated that for higher voltage applied to the mixture, a higher aggregation rate and larger aggregate size of asphaltene particles were observed.

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1. Introduction

Asphaltene is a heavy fraction of crude oil with a complex poly-aromatic structure that is soluble in aromatic solvents such as toluene but insoluble in light normal alkanes such as n-pentane and n-heptane [1–4]. Interest in the characteristics and properties of asphaltene originates from the severe operational problems caused at the different stages of petroleum production due to asphaltene phase separation, asphaltene flocculation and deposition [5]. Identifying the conditions leading to asphaltene precipitation from crude oils has been a major challenge for researchers over the past decades, and many attempts

have been made to understand the effects of several parameters such as pressure, temperature and crude composition on asphaltene phase behavior [1,6–10]. It has been recently shown that, due to the molecular complexity and high polarity of the asphaltene molecules, their electro-kinetic behavior such as natural streaming potential can have an important role in their instability and, hence, in their precipitation and deposition tendencies [11–17]. The electro-kinetic properties such as electrical conductivity, electrophoresis and electro-deposition of asphaltene particles under an electrostatic field have been extensively studied [11,12,16,18,19]. In these publications, it has been shown that asphaltene molecules can be polarized and gain electric charge while they are exposed to the electrostatic field. It should be emphasized that neither the mechanism of asphaltene charging nor the conditions leading to electro-deposition have been well

understood to date. In most studies, it has been concluded that asphaltene molecules possess a predominantly positive charge in a number of non-aqueous solvents such as nitromethane [20], heptane [21], ethanol [21], and mixtures of heptane and toluene [22]. On the other hand, negatively-charged asphaltene deposits were observed in experiments conducted in crude oil samples [14,19,23,24]. An electrostatic field can be utilized for various applications in the petroleum production and processing such as the electric de-emulsification [25] in which direct current electric voltage is applied to break water–oil emulsions [14]. It should be mentioned that the precipitation of asphaltene molecules has been previously described based on the electrical charge interactions between asphaltene and resin molecules in crude oil. It is controversially believed that the resin content has the greatest impact on the stability of asphaltene molecules in crude oil and that the resin-asphaltene molecular interaction is highly dominated by the opposing surface charges of resins and asphaltene moieties [13]. Any disruptions in such electrostatic and surface charge interactions between asphaltene and resins can change the attraction forces and result in the destabilization of colloidal asphaltene particles [26,27]. Recent studies on the electrical conductivity of asphaltene particles have broadened the understanding of their molecular association [28,29], however, studies on solid asphaltene electrical conductivity showed that solid asphaltene particles mimic semiconductor behavior. It has been observed that due to the structural phase transition, the conductivity increases at higher temperatures [30]. More detailed investigations of asphaltene electro-kinetics such as electrophoresis, and adsorption properties using different crude oils strongly confirmed the charge-bearing characteristics and streaming potential of asphaltene molecules [22,31–33]. It was concluded that protonation and dissociation reactions of asphaltene functional groups results in asphaltene surface charging and its electrophoretic mobility [34]. However, solvent-induced polarity causes reversed electrophoretic mobility of destabilized asphaltene particles. Asphaltene particles dispersed in a polar solvent (water) present a negative electrophoretic mobility, whereas when dispersed in a non-polar solvent (toluene), the particles present positive electrophoretic mobility [33]. In this way it has been shown that the net negative surface charge of colloidal asphaltene is the main cause of deposition on metal pipes due to potential differences across them [7]. Such charge neutralization might be used to manage and control the asphaltene precipitation and deposition [35]. A recent study by Hashmi and Firoozabadi [36] tried to elucidate the existing vagueness of asphaltene surface charge; they suggested that asphaltene particles possess heterogeneous surface charges where some moieties may exhibit a small net positive charge and others a negative surface charge. Other parameters such as metallic components and acid–base functional groups contribute to the surface charge, which may vary with the source of the crude oil, and other characteristics of the crude oils such the molecular weights and densities [36].

In this work, asphaltene particles were precipitated from three different crude oil samples and added to a mixture of toluene and n-heptane in order to understand their electro-kinetic behavior. A glass micro model was equipped with two electrodes, an optical microscope, and a high-voltage, direct current (HVDC) power supply. To understand the effects of structural parameters on asphaltene aggregation rate and aggregate size, elemental analyses of the three asphaltene samples were conducted and the mass ratios of C, H, N, S and O elements were determined. Also, the effects of parameters such as electric field intensity, exposure time, asphaltene concentration, and precipitant strength on the asphaltene aggregation and electro-deposition were investigated.

2. Materials and methods

Asphaltene particles were precipitated from three crude oil samples having three different API gravity using the standard ASTM-D6560-12 method [37]. The results of SARA (saturates, aromatics, resin, and asphaltene) analyses for these three crude oil samples are presented in Table 1. As shown in Table 1, the heaviest crude oil with API = 12.8 is labeled as "Type A", the crude oil with medium API gravity (23.8) is labeled as "Type B" and the lightest crude oil (API = 31) is labeled as "Type C". This nomenclature will be used throughout this manuscript for the crude oils and their corresponding asphaltene samples. The standard procedure of Clay-Gel Absorption Chromatographic method (ASTM D2007-93) was used for the SARA fractionation analysis.

To synthesize the model oil, normal heptane with a purity of 99.9% was purchased from Merck Company and used to precipitate the asphaltene particles from the above three crude oil samples. Toluene with the purity of 99% (Merck Co.) was used to dissolve the asphaltene particles. In order to prepare homogenous mixtures, the asphaltene particles were initially dissolved in toluene and stirred for one hour using a magnetic stirrer. Then, n-heptane was gradually added to the mixture and stirred for an additional 30 min. All samples were prepared at a heptane to toluene ratio of 30:70 except preliminary experiments aimed at studying the effect of precipitant (n-heptane) concentration. Prior to each experiment, the model oil was sonicated at a frequency of 40 kHz for two minutes to disperse all asphaltene particles uniformly and break any pre-formed aggregates or particles' cross-links. Moreover, to ensure that no asphaltene precipitation occurred during the preparation procedure, the concentration of asphaltene in the mixture or model oil was monitored using spectrophotometry [38]. It should be noted that the synthesis of this asphaltene suspension was performed at ambient temperature and at only two asphaltene concentrations, 1 g/l and 3 g/l. All of the electrokinetic tests were conducted under static conditions. For the sake of considering the precipitant effect on asphaltene aggregation, a set of preliminary experiments was conducted to observe whether the particles precipitated due to precipitant addition or the applied electrostatic field. These preliminary control experiments were performed at varying heptane concentrations in order to determine the visual on-set point of the asphaltene particles without applying the electrostatic field. It is a well-accepted in the literature that, in visual studies, the asphaltene on-set point is the point at which the average asphaltene particle size grows larger than 0.5 μm in diameter [39]. For most of the test solutions, it took at least 18 h for asphaltene particles to appear (to grow larger than 0.5 μm), whereas the duration for the electrostatic tests was less than two hours. We also note that, when applying an electrostatic force, the asphaltene particle grow about two orders of magnitude (greater than 10 μm) during the first minutes of the experiments alone.

3. Analysis of asphaltene chemical structure

Detailed analysis of three asphaltene samples in order to determine their chemical structures was done by Amin et al. [40] at the

Table 1
SARA analysis and the API gravity of crude oil used in this work.

	Crude Type A	Crude Type B	Crude Type C
Saturates (wt.%)	21.83	42.0	51.75
Aromatics (wt.%)	53.59	43.0	34.45
Resins (wt.%)	9.58	8.0	8.5
C7-Asphaltenes (wt.%)	14.7	7.0	5.3
API gravity (°)	12.8	23.8	31.0