Asphaltene migration and separation in presence of aggregation in electroosmotic–electrophoretic microchannel transport

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HIGHLIGHTS

- A model is discussed for microchannel electrokinetic asphaltene transport.
- Band velocity and separation resolution characterizes asphaltene transport.
- Electrokinetics massively affects asphaltene transport with aggregation effects.

GRAPHICAL ABSTRACT
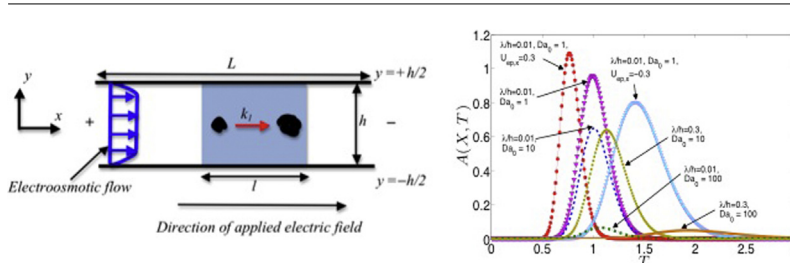
ABSTRACT

In this paper, we provide a model to study the microchannel asphaltene transport and separation in presence of combined electroosmotic–electrophoretic transport and finite asphaltene aggregation effects. We invoke a perturbation-based analysis to develop analytical expressions for asphaltene band velocity (characterizing asphaltene electromigration) and separation resolution (characterizing separation of asphaltene species varying in aggregation or electrophoretic behaviors). We observe that the extent of the aggregation effects in affecting the asphaltene transport is strongly dictated by the nature of the electroosmotic–electrophoretic transport, and the net separation, too, is dictated by a non-trivial interplay of these two effects. Such coupled aggregation–advection–electrophoreting dynamics of asphaltene, in context of microfluidic transport, holds the key for understanding essential characteristics of asphaltene, relevant for its treatment during heavy oil upgrading.

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1. Introduction

Understanding the characteristics of asphaltene, the heaviest and the most viscous and polar component of heavy oil, holds the key for upgrading of heavy oil, which is a crucial alternative in the context of continuous depletion of conventional energy resources [1–12]. It has been known for several decades that asphaltene molecules are charged, and depending on the solvent in which they are dissolved/dispersed, or their structural configuration (e.g., whether they are in micellar form or monomeric form) they may exhibit the entire plethora of charge characteristics, ranging from very strong positively charged to very strong negatively charged [13–32]. Charge on asphaltene molecules, in addition to serving a very important purpose of providing asphaltene stability against possible aggregation and flocculation effects [13,27–29,33], has been used by researchers to transport and manipulate asphaltene molecules electrophoretically by the application of strong electric fields, leading to applications such as determination of asphaltene charge, mobility and zeta potential, separation of asphaltene [16,26,24,34,28,13].

Analysis of electric field-induced asphaltene separation has remained incomplete, since it does not account for the possible

role of the electric-field induced flow field (or electroosmosis). Such combined electrophoretic-electroosmotic transport of asphaltene can become specially relevant in microfluidic platforms [4], recently employed in determining different issues of asphaltene dynamics [35–38]. In this study, we pinpoint the role of combined electroosmotic–electrophoretic transport in the migration and separation of charged asphaltene molecules in a microfluidic channel. In our model, we also account for the aggregation reactions of the asphaltene moieties – therefore, our study provides the first model that describes the microfluidic transport and separation of asphaltene molecules in presence of interacting electrokinetic and aggregation effects.

The mathematical framework of the present study is based on the same perturbation model used in our previous study [4]. Such a perturbation-based model has been used in several previous studies to unravel different theoretical aspects of micro-nanofluidic transport [39–48]. This perturbation model takes advantage of the disparate axial and transverse length scales associated with a microchannel to develop the analysis, and provides distinctly simplified and usable analysis as compared to other continuum and non-continuum-based models used for tracking asphaltene dynamics [35,36,38,49–51]. The model is built on certain key assumptions, as described in detail in our previous paper [4]. In addition to these assumptions, the present model requires a few more assumptions. First and foremost, we assume that the asphaltene molecules are transported in a system that allows the formation of electric double layer (EDL) at both the asphaltene and the microchannel surface – this will occur provided we are principally studying the asphaltene transport in an aqueous medium with added electrolyte, and such systems are commonly encountered involving different applications involving asphaltene transport and separation [24,31,52–57]. Second, we assume that the asphaltene ionization (and hence its electrophoretic mobility) is strictly dictated by the bulk values of pH and ion concentrations and do not depend on the spatial variation (within the EDL) of the pH and the ion concentration. Third, we assume that the asphaltene aggregation effects [dictated by the corresponding Damköhler number (Da_0) [4]] is independent of the asphaltene charge. Finally, we assume that the aggregation model that we employ does not account for the intrinsic polydispersity issues associated with the solvent-mediated asphaltene aggregation effects [58]. The central results of the paper are the asphaltene electromigration (characterized by the corresponding band velocities [4,39–41]) and separation (characterized by the separation resolution [4,39–41]) obtained as an interplay of the aggregation and combined electroosmotic–electrophoretic effects. First, we observe that the extent to which the aggregation effects lower the electromigration speed is strongly dictated by the electroosmotic flow profile – for flow profile with larger spatial extent of wall-bound velocity gradients (characterized by larger relative EDL thickness values) lowering of the asphaltene electromigration velocities, on account of aggregation effects, is much more prominent. The second issue, which follows from the first result, is that we find on account of such variation of speeds, asphaltene molecules can be separated based on their aggregation and electrophoretic dynamics, with the electroosmosis dictating the efficiency of the separation process for given aggregation dynamics.

2. Theory

2.1. Model for the species transport

The theoretical framework starts by considering the transport of a plug of asphaltene molecules in a microchannel, as shown in Fig. 1. The transport is caused by combined
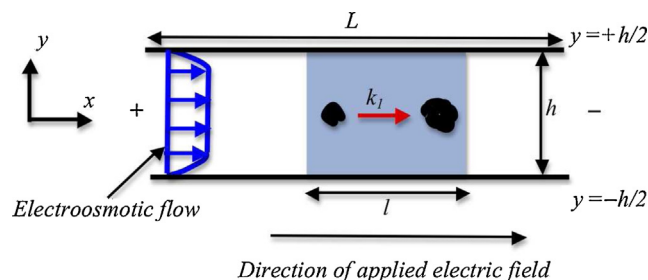

Fig. 1. Schematic showing the microchannel (of height h and length L) transport of the asphaltene plug of length ℓ in presence of an applied electric field triggering a combined electroosmotic–electrophoretic transport (schematic is not to scale and we have $h \ll \ell$). We also demonstrate the possible asphaltene aggregation occurring inside the plug, with the aggregation being considered to be a kinetically driven first-order process with rate constant k_1 [4]. Here, we have magnified the size of the asphaltene aggregate sizes: in reality it is several orders smaller than the microchannel height.

electroosmotic–electrophoretic effects (induced by application of an external axial electric field, see Fig. 1). Further, the transported asphaltene molecules can be in either of two forms: non-aggregated and aggregated, and these two states are interconnected by reaction kinetics [4]. Also, similar to our previous study [4], we consider that the aggregation behavior being much more pronounced than the de-aggregation, we are able to express the concentration entirely as the concentration of non-aggregated species [4]. The model assumes that the asphaltene is necessarily in contact with a polar solvent (like water), which allows it to express its surface charges and develop an EDL neutralizing these charges. Also we make no specific assumption about the sizes of the asphaltene moieties – in fact, in addition to considering that the asphaltene may only exist into two forms, we make an implicit assumption that the asphaltene sizes are always much smaller than the microchannel dimension (in case this condition was not valid we would have required to adjust the model in a manner similar to our previous studies [39–41]). Here we shall characterize the transport of asphaltene plug (introduced in the microchannel at $t = 0$) by a band velocity u_b (which is an average velocity of the plug [4,46,39–41]), and a dispersion coefficient [4,46,39–41]. The species conservation equation for non-aggregated asphaltene molecules considered in a reference frame moving with this band velocity u_b, therefore, can be expressed as:

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}[(u_p - u_b)c] + \frac{\partial}{\partial y}(v_p c) = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} - k_1 c, \qquad (1)$$

where c is the concentration of the non-aggregated asphaltene, D_x and D_y are the axial and the transverse diffusivities, u_p and v_p are the asphaltene axial and the transverse migration velocities and k_1 is the rate constant governing asphaltene aggregation. Also

$$u_p = u + u_{rel,x} = u + u_{ep,x}, \quad v_p = v + v_{rel,y} = v, \qquad (2)$$

where u and v are advection velocities arising from the fluid flow, and $u_{rel,x}$ and $v_{rel,y}$ are the velocities of the non-aggregated asphaltene molecules relative to the flow, assuming the asphaltene molecules to be non-neutrally buoyant species. These relative velocities can be expressed as $u_{rel,x} = u_{ep,x}$ (where $u_{ep,x}$ is the velocity of axial electrophoretic transport [39–41]) and $v_{rel,y} = 0$. Also the background flow is considered to be steady, fully-developed electroosmotic transport in a parallel plate microchannel, so that $u = u(y)$, but $v \equiv 0$.

Therefore, Eq. (1) reduces to:

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x}[(u + u_{ep,x} - u_b)c] = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} - k_1 c. \qquad (3)$$