



Kinetics and isotherms of asphaltene adsorption in narrow pores



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ABSTRACT

New data relating to the kinetics and adsorption isotherms of asphaltene in consolidated sandstone core samples are reported. The data were obtained from the measurements of electrokinetics of consolidated sandstone core samples in asphaltene/toluene solutions and petroleum oils. The numerical reduction in the (negative) zeta potential of the sandstone samples were attributed to the adsorption of positively charged molecules of asphaltenes. The hydrodynamics thickness δ of adsorption of asphaltene were followed by monitoring the pressure increase that occurred as the adsorbed layer restricted the rock pores and applying Poiseuille's equation. The flow rates indicated a plateau of asphaltene adsorption at a pore blocking thickness of about $\delta/r = 0.3$, which was also the point at which the streaming current reached a plateau. After increasing to about 30% of the pore radius, the adsorbed layer thickness δ stopped growing either with time or with concentration of asphaltene in the flowing liquid. Alternative hypotheses involving asphaltene adsorption isotherms have been investigated. A theoretical treatment advanced describing particle adsorption in the same terms as molecular adsorption and the Langmuir isotherm, with the free energy of asphaltene adsorption on the rock surface (modeled on silica) calculated on the basis of van der Waals attraction. Acceptable agreement was obtained with the electrokinetic measurements.

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1. Introduction

Asphaltenic oils flowing through reservoir formations often result in severe permeability damage near the well bore, causing a decrease in well productivity [1,2,3,4]. Besides permeability damage, the adsorbed asphaltene layers may also induce wettability alteration of the oil-bearing formation [5]. The asphaltenic flow depends significantly on the dispersive properties of the microstructure formation, its stability, and the characteristic of flow [6,7].

The adsorption of asphaltene is controlled by a number of factors, such as stability of colloidal asphaltene in the oil phase, the thickness and stability of water film adsorbed on rock pore surfaces, and the nature of the rock mineral surfaces [8,9]. The magnitude of the interaction forces between the three previous factors control the degree to which such adsorption is irreversible with respect to the remediation treatment.

Asphaltenes are defined operationally as the polar fraction of crude oil that can be precipitated by the addition of low molecular weight alkanes but that are soluble in aromatic solvents (i.e., toluene, diesel) [10–12]. Asphaltene structures were found to be comprising several condensed aromatic discs, each of them representing asphaltene molecule core, with approximately parallel planes stacked one over another. The chains of aliphatic and/or naphthene-cyclic systems are attached

with asphaltene aromatic discs with known structure of asphaltene molecules [13–15]. The molecular weight of asphaltene ranges from one thousand to several hundred thousand with a microparticles density of approximately 1.2 g/cc and a spheroidal shape 30 to 65 Å in diameter [16].

To investigate the extent of formation damage by asphaltenes in crude oil, this work has used electrokinetic technique to study the adsorption of asphaltenes in rock pores. Alternative hypotheses involving uniform adsorption have been investigated with a theoretical treatment describing asphaltene adsorption isotherm calculated on the basis of van der Waals attraction. Acceptable agreement was obtained.

2. Theoretical background

The kinetics of adsorption of molecules can be contributed by transport toward the surface by diffusion, attachment and reformation to the interface. The shape and flexibility of the molecules may play a role on the kinetics process at a timescale [6,7]. To assess the contributions of each of the three processes, it is essential to measure the kinetics of adsorption under hydrodynamic conditions.

Most researchers investigate the kinetics of adsorption by monitoring changes in the concentration of asphaltene or polymer in a dispersion of adsorbent particles or capillaries [9,17]. This method is less suitable to describe the kinetics process since the hydrodynamic conditions are nonuniform and difficult to specify. Others investigated the

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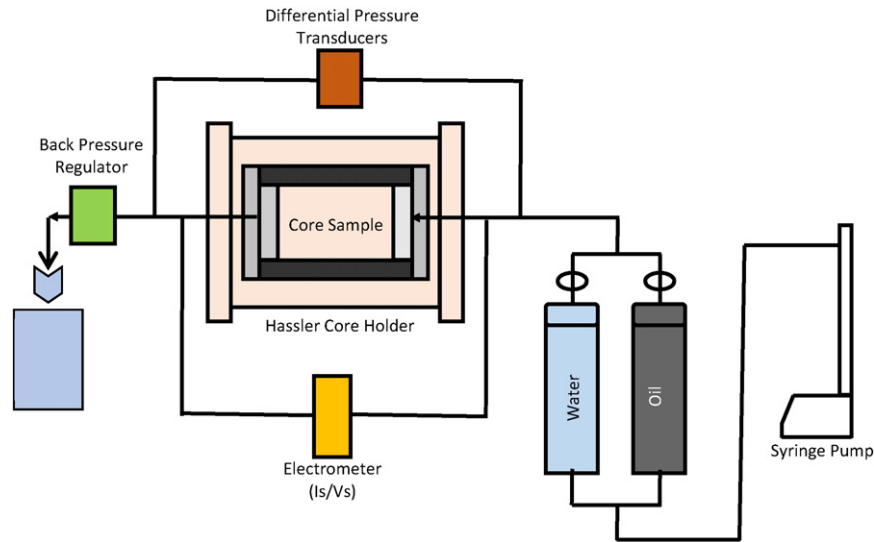


Fig. 1. Schematic of the experimental setup.

measurements of the adsorbed layer thickness on the solid surfaces. Several techniques have been applied to determine the thickness of the adsorbed layer, such as macroscopic flow methods, disjoining pressure measurements, surface force methods, and photon correlation spectroscopy [18,19,20,21,22].

In this work, a direct method is presented to assess the kinetics adsorption of asphaltenes in rock cores under hydrodynamic conditions using a continuous measurement of streaming current method. Along with the streaming current method, the application of Poiseuille's flow law is used to describe the hydrodynamic thickness of the adsorbed asphaltenes on the rock pore surfaces.

2.1. Electrokinetics of reservoir rocks

The electrokinetic effects in porous systems are defined as the movement of part of the electric double layer (EDL) from the charged pore surfaces when a liquid is forced through the system. The movement of a liquid through the capillaries carries a net charge (mobile part of the EDL) and it gives rise to *streaming current*, consequently a potential

difference (*streaming potential*) [23,24]. The electrokinetic method is fundamental and sensitive and a high picoammeter is required to measure the streaming current in low electrolyte concentrations such as asphaltenic oils.

The adsorption of asphaltenes on reservoir rock pore surfaces has been investigated experimentally by the electrokinetic measurements of rock cores under flow conditions. In low electrolyte concentration, such as hydrocarbon system, the surface conductivity of reservoir rocks will dominate streaming potential measurements and therefore also any derived electrokinetic potentials [25]. Surface conductivity is not involved in streaming current measurements, though the pores' A/L ratio is required, where A and L are the cross-sectional area and length, respectively, of the effective capillaries. In this work, the zeta potential of reservoir rock in petroleum fluids is calculated from the streaming current method.

$$\frac{I_s}{\Delta P} = \frac{\varepsilon \zeta A}{\eta L} \quad (1)$$

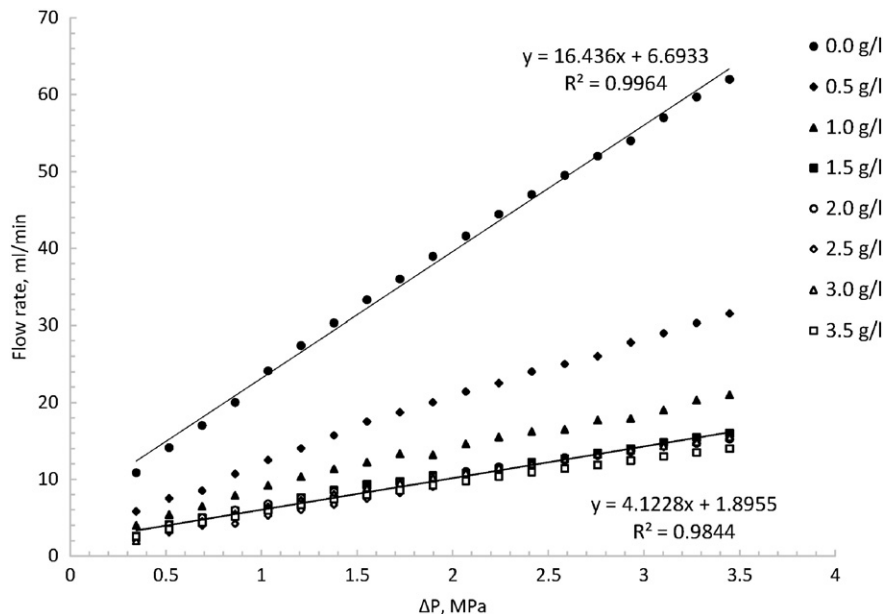


Fig. 2. Flow rate efficiencies in Berea sandstone core sample as a function of the applied pressure difference at different asphaltene concentrations in toluene.

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