Available online at www.sciencedirect.com
ScienceDirect
Colloids and Surfaces A: Physicochem. Eng. Aspects 317 (2008) 1–9
COLLOIDS AND SURFACES A
www.elsevier.com/locate/colsurfa

Study of asphaltenes adsorption onto different minerals and clays
Part 1. Experimental adsorption with UV depletion detection

Dorota Dudášová*, Sébastien Simon, Pål V. Hemmingsen[1], Johan Sjöblom

Ugelstad Laboratory, Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

Received 16 April 2007; received in revised form 24 August 2007; accepted 13 September 2007
Available online 18 September 2007

Abstract

The adsorption of asphaltenes of five different origins from Gulf of Mexico, West Africa, North Sea and Brazil onto inorganic particles (kaolin, $CaCO_3$, $BaSO_4$, FeS, Fe_3O_4, TiO_2 and SiO_2 (hydrophilic and hydrophobic)) has been studied by means of the depletion method by assaying asphaltene concentration by UV–vis spectrophotometry (batch partioning method). The aim of this work is to investigate how adsorbed asphaltenes alter the particle properties. The saturation adsorbed amounts of the asphaltenes on minerals (0.26–3.78 mg/m^2) were in the same order of magnitude as the adsorption of asphaltenes on metals. Langmuir (type I) isotherms were observed. We found that adsorption depends more on particle type than on the origin of the asphaltenes. The adsorption was discussed from the point of quantity (maximum adsorbed amount, Γ_{max}) as well as of quality (affinity constant K). The potential interactions formed upon adsorption were analyzed. In our systems with excluded water we found polar interaction and surface precipitation as well as H-bond formation. We analyzed a correlation between adsorbed amount and elemental composition. We found a correlation between amount of nitrogen in asphaltene sample and its adsorbed amount on the particle. We did not find any correlation with particle wettability nor specific surface area.

Keywords: Asphaltenes; Adsorption; Minerals; Surface; Wettability; Hydrophobization

1. Introduction

In gas and crude oil production water is known as produced water. In general, produced water is a mixture of dispersed oil in water (o/w), dissolved organic compounds (included hydrocarbons), residual concentration of chemical additives from the production line, heavy metals, dissolved minerals and suspended solids [1]. The reservoir itself may release inorganic particles, like sand, fines (defined as particles having a diameter smaller than 2.5 μm, also referred to as PM2.5) and clay. If sea water is injected for enhanced recovery, or if one get natural break through of sea water into the reservoir, formation of insoluble, inorganic scale may occur. The formation water that exists naturally within the reservoir pores usually contains significant amounts of divalent cations like calcium, magnesium, barium and strontium. These cations can react with anions, like sulfate and carbonate, from sea water to produce precipitated scale particles. In addition, organic particles like asphaltenes and waxes may precipitate due to changes in pressure and temperature from the reservoir to the production facility [2]. The solids separation problem arises from the fact that small particles are/cannot be removed by hydrocyclones or membrane separation—micro filtration membranes have pore size ∼0.1 μm, hence undesirable in produced water. During the line production, the particles undergo several changes. One of the most important changes is wettability alteration, where particles in contact with crude oil surface-active components (e.g. asphaltenes) will change from hydrophilic to hydrophobic (or less hydrophilic) [3–5].

Asphaltenes comprise a major portion of surface-active crude oil components [6] and are defined as the crude oil fraction insoluble in alkanes such as pentane or heptane and soluble in toluene. Asphaltenes are polyaromatic compounds of large molecular weight, ranging from less than 500 to 2000 g/mol [7,8]. The molecules are composed of condensed (fused) aromatic rings linked with aliphatic chains and naphthenic rings. They include a large variety of chemical species, containing sulphur, nitrogen, heavy metals and functional groups such as acids

---

* Corresponding author. Tel.: +47 7355 0924; fax: +47 7359 4080.
E-mail address: dudasova@chemeng.ntnu.no (D. Dudášová).

[1] Currently at Statoil, R&D Center, Trondheim, Norway.

0927-7757/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.colsurfa.2007.09.023

and bases [9–11]. They are surface active and able to spontaneously form water-in-oil emulsions [12,13]. Recent papers by Stanford et al. [14,15] indicate that there is different affinity of certain components at least for water–oil interface. They found that o/w interface adsorption is heteroatomic class-depended. Fossen et al. found that different asphaltene fractions have different interfacial and solvent properties [16,17]. Asphaltenes can also adsorb onto different surfaces, from pipelines (causing undesirable plugging) to particles being responsible for particle wettability alteration [18]. They also have high affinity towards clay mineral surfaces [19]. They have a strong tendency to self-associate and form aggregates [20,21].

The adsorption of asphaltenes onto minerals has been extensively studied [22–27] because, as already mentioned, asphaltene adsorption on the formation rock alters the wettability of rocks [18] and reduces oil production from the reservoir. Particles identified as bitumen-associated solids have been found in real system [28,29]: the surfaces of these inorganic–organic assemblies are rendered asphaltene-like by adsorption of polar, aromatic, toluene-insoluble, organic matter. According to Buckley and Liu [30], there are two interaction mechanisms which contribute to wetting alteration by asphaltenes in the reservoir rock: interactions between polar groups in the crude oil and the surfaces and colloidal interactions which are responsible for particle surface alteration by adsorption of asphaltene aggregates. Colloidal interactions are most significant near the onset point of asphaltene precipitation [18]. We will discuss these interactions later in results and discussion part.

Adsorption of asphaltenes is generally studied by extracting asphaltenes from the crude oil and resolubilizing them in the model solvent (e.g. toluene). From these studies, two different types of adsorption behavior of asphaltenes have been reported. For some systems asphaltene adsorption on minerals follows the Langmuir (type I) behavior [24,31,32], indicating that there is a monolayer formation of adsorbed asphaltenes onto the surface. For other systems, formation of multilayers has been reported [22,25]. Observed “steps” on the adsorption isotherms are believed to indicate changes in the state of asphaltene molecules in the solution and at the mineral surface [23]. This is related to the asphaltene association and further formation of hemimicelles on the mineral surface. Multilayer formation is closely related to aggregate formation and precipitation of asphaltenes in the bulk [33]. There is still no satisfying explanation for this behavior.

The adsorption is affected by several factors:

- The origin and chemistry of the crude oil; Asphaltenes from different sources have different properties.
- The adsorbed amount depends on the asphaltene molar weight: it has been shown [34] that in the case of polydisperse systems (e.g. asphaltenes in heptane/toluene 50:50, vol% in our case) the high molecular weight species will preferentially be adsorbed onto surfaces.
- The amount of resins present in the asphaltene sample [35,36] due to different isolation methods, contact time or precipitation agent used.
- The polarity of solvent used for redissolvation [22,37].
- Pre-wetting of the particles (water wetted hydrophilic particle adsorb less asphaltenes than “dry” one) [38,39].
- The surface chemistry of the particles and the nature of exchangeable cations [40] in the clay structure.
- Contact time [26,41,42] and temperature.

Reversibility of asphaltene adsorption onto solid surfaces was examined by several authors. Acevedo et al. [27] reported asphaltene adsorption to be either an irreversible process or the desorption step is very slow, less than 3% after 1 week. Hannisdal et al. [4] and other authors [43–45] found in adsorption studies by using a Quartz Crystal Microbalance technique, some desorption of weekly bound (or deposited) asphaltenes. Those asphaltenes were washed off by rinsing with solvent within a few seconds after solvent injection and desorbed amounts were about 10%.

This paper is the second in a series of articles aiming at determining how particle properties are altered by adsorption of various crude oil components in order to find the best way of removing suspended particles from produced water in petroleum industry. This paper deals with the adsorption properties of the most active components of crude oils (asphaltenes) at the solid/liquid interface by focusing on the influence of particle surface chemistry and asphaltene solubility properties. This work will give an insight into the mechanisms of adsorption of crude oil components on particles. We used particles with different surface properties (surface area, surface chemistry and surface charge). The adsorption is measured by the depletion adsorption method, using UV spectrophotometry to assay the asphaltene concentration.

2. Experimental

2.1. Materials

2.1.1. Asphaltene precipitation

Asphaltene samples from five different crude oils were extracted by adding an excess of *n*-pentane (VWR, >98%) in ratio 1:40 (according to the ASTM D2007-80 procedure). The mixture of crude oil and *n*-pentane was stirred for 24 h at room temperature. The precipitated crude oil fraction (asphaltenes) was filtrated through a 0.45 μm Millipore filter and washed with additional *n*-pentane. After filtration, the asphaltenes were dried under nitrogen atmosphere for the next 24–48 h and their dryness was controlled by weighting. The crude oils have been analyzed with respect to SARA components (saturates, aromatics, resins and asphaltenes); density, viscosity, acidity and water content (Table 1). Characteristics of the asphaltenes (bulk elemental analysis, C/H molar ratio, flocculation point) are shown in Table 2.

2.1.2. Particles—adsorbents

The particles used in our study are typical clays and scales: kaolin (fine powder) (Aldrich, USA/Germany); $CaCO_3$ (98.2%) (Specialty Minerals Inc., USA); FeS (99.7%) (DLFTZ, Chang Hing, China); $BaSO_4$ (99%) and Fe_3O_4 (98+ %) (Nanoamor,