Colloids and Surfaces A: Physicochem. Eng. Aspects 482 (2015) 241–247

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Studies on bitumen–silica interaction in surfactants and divalent cations solutions by atomic force microscopy

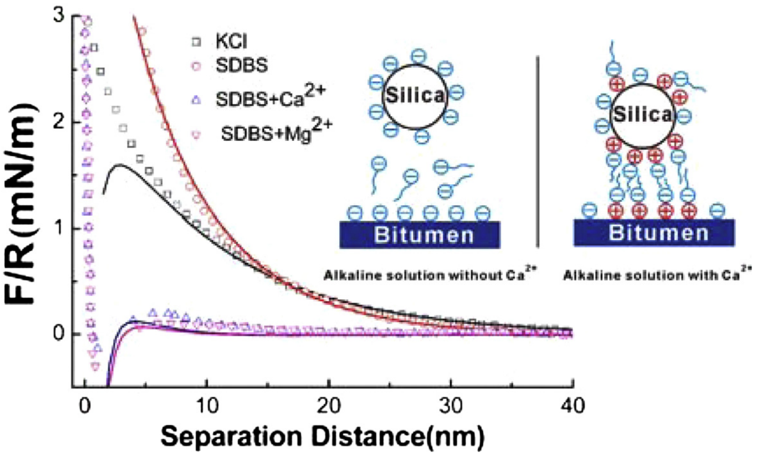
Yan Zhang[a,b,c], Mingshan Ding[a,b], Juan Liu[a,b], Weihong Jia[a], Sili Ren[a,*]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physic, Chinese Academy of Sciences, Lanzhou 730000, PR China
[b] Graduate School, University of Chinese Academy of Sciences, Beijing 100049, PR China
[c] School of Traffic and Transportation, Lanzhou Jiaotong University, Lanzhou 730070, PR China

HIGHLIGHTS

- Surfactant and metallic ions play synergistic effect on bitumen–silica interactions.
- Ca^{2+} and Mg^{2+} act as either barrier or bridge affecting the surfactants adsorption.
- The interaction forces could be well interpreted by the extended DLVO theory.
- The findings have a guideline of controlling the oil sands processing condition.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 January 2015
Received in revised form 7 May 2015
Accepted 19 May 2015
Available online 23 May 2015

Keywords:
Oil sands
Atomic force microscope
Surfactants
Divalent metal ions
DLVO theory
Surface wettability

ABSTRACT

Synergistic effects of surfactants and divalent metal ions on bitumen–silica interaction were investigated in various pH solutions by using atomic force microscope (AFM). Zeta potential measurements were carried out and the extended DLVO theory was employed to interpret the bitumen–silica interaction behaviors. The AFM force measurements showed that the presence of cationic surfactant of dodecyltrimethylammonium chloride (DTAC) caused a strong long-range attractive force and high adhesive force, which were considerably reduced as divalent metal ions of Ca^{2+} or Mg^{2+} added in the acid solutions. However, the long-range repulsive force changed to attractive force compounded with a relative high adhesion when both the anionic surfactant of sodium dodecylbenzene sulfonate (SDBS) and divalent metal ions of Ca^{2+} or Mg^{2+} presented in the alkaline solution. Mechanism on bitumen–silica interaction behaviors at various conditions was discussed. It was suggested that changes of surface wettability arising from the adsorption of surfactants on silica and bitumen surfaces were responsible for the variation of the bitumen–silica interactions. The preferential adsorption of the divalent metal ions of Ca^{2+} or Mg^{2+} on silica and bitumen surfaces acted as either a barrier to prevent the cationic surfactants from

---

* Corresponding author at: NO.18, Tianshui Middle Road, Lanzhou City, Gansu Provience, 730000, PR China. Tel.: +86 931 496 8051; fax: +86 931 827 7088.
E-mail address: slren@licp.cas.cn (S. Ren).

http://dx.doi.org/10.1016/j.colsurfa.2015.05.012

adsorbing or a bridge to anchor the anionic surfactants. The generation of the hydrophobic attraction between bitumen and silica was supported by the extended DLVO theory. It is believed that the findings in this work have a guideline of controlling the oilsands processing condition to obtain a high bitumen recovery and good froth quality.

1. Introduction

Oil sands are unconsolidated sand deposits impregnated with high-molar-mass viscous petroleum, which is an important unconventional oil resource and normally termed bitumen [1]. With the depletion of conventional crude oils and the continuously increasing demand on petroleum, recovering bitumen from oil sands becomes increasingly important to world's energy supply. The largest oil sand deposits in the world are located in the northern areas of Alberta, Canada. In 2005, the production in Canada was close to 1.3 million barrels per day [2].

To recover bitumen from oil sands, bitumen has to be liberated or detached from sand grains. In hot-water extraction processes, surfactants play critical role in mediating interactions between bitumen and sand in the aqueous solution. During the extraction process, surface active species are often released from bitumen into the slurry and found to be carboxylates, sulfates/sulphonates and long chain amines which ionizes in aqueous solution by protonation [3,4]. Adsorption of various types of surfactants on bitumen, quartz solid or mineral clay significantly affects the surface/interface nature in three characteristics including the surface wettability, interfacial tension and surface zeta potential, that are of significance to the bitumen extraction. In early 1944, Clark [5] proved that the presence of surfactants is not always beneficial as it may induce hydrophobicity by undesired adsorption and subsequent flotation of unwanted solids. In 1967, Bowman [6] assumed that the surface charge of bitumen was determined by the natural surfactants with carboxylic groups. Brown and Neustadter [7] suggested that the presence of surfactants in crude oils in the form of protonated nitrogenous species might be responsible for the coagulation of fine silica with the oil over the acidic pH range. Schramm et al. [8] reported that the released carboxylates were essential for effective bitumen flotation. Liu et al. [3] found that the bitumen–water systems contain dodecylamine hydrochloride (DAH), sodium dodecyl sulfate (SDS) and sodium polyacrylate (NaPa) three major types of surfactants. Effect of surfactants addition on the oil detachment from solid surfaces under dynamic conditions was investigated by Rowe et al. [9] It was found that both polyethylene glycol octylphenol ether (Triton X-100) and sodium dodecyl sulphate (SDS) surfactants enhanced the oil detachment from the sand surface with increasing solution pH. While for cetyltrimethyl ammonium bromide (CTAB) solutions, the oil droplet was found to clean best at low pH. Cao et al. [10] observed that while hexadecane did not coagulate with quartz particles in the entire pH range tested (from 3 to 11), when the pH was raised to the level where first-order metal hydroxyl species and/or metal hydroxides were formed, the presence of multivalent metal ions significantly increased the mutual coagulation between the hexadecane and quartz.

With the development of colloidal force probe technique of atomic force microscope (AFM), it was possible to directly measure the interaction forces between bitumen and various solids [4,11,13]. By analyzing the bitumen–solids interaction behaviors, much information could be obtained to deepen our understanding on the water-based bitumen extraction processes. In this study, synergistic effect of surfactant, metal ions and the aqueous pH on bitumen–silica interaction behaviors was investigated by using AFM. It was found that the surfactant played very different effect on bitumen–silica interactions in the presence of divalent metal ions at various pH solutions. The objective of this work is to provide new insights into the mechanism of bitumen liberation from solids surface. The findings will be of great importance to understand how the bitumen liberation was affected by various physicochemical factors.

2. Experimental

2.1. Materials

Bitumen toluene solvent-extracted from oil sands (Zhalaiteqi, Inner Mongolia in China) was used for preparing the bitumen coating on silicon substrate. Silica microspheres ($\sim 8\,\mu m$) purchased from Duke Scientific Co. (USA) were used as the model of sand grains for colloidal force measurement. Silica powder ($\sim 3\,\mu m$) provided by Shanghai CNPC Powder Material Co. (China) was used for zeta potential measurements. HCl and NaOH used as pH modifiers were analytical purity. Surfactants of sodium dodecylbenzene sulfonate (SDBS >99.7%, Alfa), sodium dodecyl sulfonate (SDS, >99.7%, Alfa) and dodecyltrimethylammonium chloride (DTAC, >99%, Alfa) were used in the force measurements. Spectrum pure KCl was used as the supporting electrolyte, while $CaCl_2$ (99.9965%, Alfa) and $Mg(NO_3)_2{\cdot}6H_2O$ (99.99%, Shanghai Shanpu Chemical Co. China.) were used as sources of divalent cations. Ultra pure water with a resistivity of 18.2 MΩ was used throughout this study.

2.2. AFM probe and bitumen surface preparation

The silica sphere was glued with a two-component epoxy (EP2LV, 3M Co.) onto a tip of the AFM cantilever with a spring constant of 0.35 N/m for preparing the colloidal force probe. The prepared probes were kept in dustfree environment for more than 24 h. Prior to each force measurement, the probe particles were thoroughly rinsed with deionized water, toluene, and ethanol. The particles were then processed with plasma to remove the possible organic contaminants and to produce a hydrophilica surface. The exact size of the silica particles was determined with a scanning electron microscope after conducting the force measurement.

The bitumen surfaces were prepared by coating a thin layer of bitumen on silicon surface with a spin coater (SB-1B, Beijing Chuangshiweina Co., China). Single-crystal silicon wafers used as the substrate were cut into 12 mm × 12 mm pieces. Prior to coating the bitumen surface, the silicon wafers were processed with a piranha solution (a mixture of 7:3 (v/v) 98% H_2SO_4 and 30% H_2O_2) at 90 °C for 30 min, then rinsed with ultra-pure water and ethanol, and finally dried by nitrogen blow. About 10 drops of bitumen-in-toluene solution (2.5 mg/ml) were dropped within 20 s onto the substrate spinning at 4000 rpm and then kept for 30 s. The prepared bitumen surface was found to be acceptably smooth for colloidal force measurement.

2.3. Force measurement

Surface force measurement was conducted using a Nanoscope Maltimode 8.0 AFM (Bruker Co. GER) with a vendor-supplied fluid cell. Prior to the force measurements, both the probe and bitumen surfaces were immersed in a test liquid in the fluid cell and allowed