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# Wettability estimation of low-permeability, siliceous shale using surface forces

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ABSTRACT

This work evaluates shale/oil wettability and wettability alteration by solutions whose pH ranges from 3 to 12. The reservoir rocks are siliceous shale that are fractured and low permeability oil-bearing rocks. Wettability alteration is evaluated in terms of estimated thin-film stability, contact angle, and fines migration. Previously, we presented core-scale spontaneous countercurrent imbibition and forced displacement results for the crude oil/brine/rock system. The new surface forces results for stability of wetting films and contact angle compare favorably to the previously measured Amott index to water. The pH = 3 and pH = 12 solutions result in greater water wettability in comparison to neutral pH brine. The possibility of fines migration, that is one of the scenarios of wettability alteration, is explored. Results show that a balance of the surface forces as a function of brine chemistry explains wettability alteration of these siliceous shale samples. The trend of small contact angles for the aqueous phase for basic and alkaline solutions is consistent with the oil recovery characteristics, and fines migration does not trigger wettability alteration for this particular crude oil/brine/rock system.

## 1. Introduction

In the San Joaquin Valley (CA), the uppermost productive formations are heavy-oil sands that are underlain by the so-called diatomite. As depth increases, the rock undergoes diagenesis and transitions from amorphous to semi-crystalline opal. Various siliceous shale rocks such as the Brown and Antelope Shales lie beneath the diatomite. Generally, the metamorphism due to burial of diatomaceous oozes has led first to opaline cristobalitic chert and porcelanite and with greater depth and time to quartzitic chert and porcelanite (Bramlette, 1946; Murata and Nakata, 1974). Burial diagenesis results in loss of porosity and permeability; however, the oil resources in siliceous shale rocks are of great interest because of significant oil accumulations. Additionally, siliceous shale rocks are fractured systems. Takahashi and Kovscek (2010) reported that these reservoir rocks are either mixed-wet or moderately oil-wet, based on oil recovery by spontaneous countercurrent imbibition and by forced displacement. These characteristics result in complicated and difficult to produce oil resources.

The wettability of reservoir rock is a critical factor in controlling the displacement efficiency and ultimate oil recovery. In an oil reservoir, the reservoir rocks are categorized as water-wet, oil-wet, and intermediate-wet in terms of contact angles (Craig, 1971). In water-wet rocks the wetting phase has affinity toward the rock, while in oil-wet rocks the non-wetting phase has affinity toward the rocks. Intermediate-wet rocks have neither a strong affinity for water nor oil (Craig, 1971). Mixed-wet rocks have the properties of both water- and oil-wetness, and refer to distinct and separate water-wet and oil-wet surfaces that coexist within porous media (Salathiel, 1973). Kovscek et al. (1993) used thin-film forces and asphaltene adhesion to pore surfaces to explain the origin of mixed wettability. The fluid wetting the rocks occupies the small pore space and pore corners thereby resisting or influencing the flow paths and oil remains continuous through lenses or rivulets that bridge pore walls adjacent to pore corners.

In short, understanding of wettability is critical to determine recovery characteristics in multiphase flow. Buckley et al. (1989) presented conditions for adhesion of several crude oils to a particular solid surface. The conditions were varied by pH and ionic strength, and predicted using a balance of surface forces in combination with the ionizable surface group model. Predicted results reproduced the conditions under which oil adheres to the surface satisfactorily. The stable wetting films resulted from the surface forces between the crude oil and the pore wall. Stable water films on rock grains prohibit adhesion of the crude oil to the pore wall.

Another critical factor to determine the wettability is fines migration. Schembre et al. (2006) presented a relationship between temperature and wettability, based on fines detachment from pore walls. The surface underlying where fines are attached is water-wet, because oil never contacted the surface. If the fines are released by environmental variability such as temperature, pH, and salinity changes, water-wet surfaces are exposed. This scenario explained the experimental results of wettability changes of diatomite core samples (amorphous silica) as temperature increased.

This manuscript explores wettability of siliceous shale rocks based on surface forces, and explains wettability alteration in terms of thin-

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film stability on the pore surface. Fines migration is not found to play a significant role. The thin-film perspective is useful because direct observation of the wettability of pore surfaces within rock is practically impossible. This work complements our previous core-level experimental study of water-based oil recovery from siliceous shale (Takahashi and Kovscek, 2010).

## 2. Background

DLVO theory was developed simultaneously by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). This theory describes the surface forces in the vicinity of a charged colloidal surface in an electrolyte solution. It is useful to explain the stability of colloids in lyophobic solutions and the wettability of solids.

### 2.1. Disjoining pressure and contact angle

The augmented Laplace–Young equation is

$$P_c = \Pi + 2C_m\sigma \tag{1}$$

where $P_c$ is the capillary pressure defined as the pressure of the bulk fluid phase minus the pressure of the film phase, $\Pi$ is the disjoining pressure (Derjaguin et al., 1987), $C_m$ is the mean curvature of the interface, and $\sigma$ is the interfacial tension. When the surface is flat, $C_m$ is 0, and the disjoining pressure is equal to the capillary pressure. The disjoining pressure is, thus, a key factor in determining the stability of the thin film on the surface.

The total disjoining pressure is the sum of the electrical double layer, $\Pi_{DLR}$, the London–van der Waals, $\Pi_{LVA}$, and the structural forces, $\Pi_s$ (e.g., Buckley et al., 1989; Hirasaki, 1991b).

$$\Pi_t = \Pi_{DLR} + \Pi_{LVA} + \Pi_s \tag{2}$$

#### 2.1.1. Electrical double layer

The electrical double layer force is estimated using zeta potentials, $\zeta_1$ and $\zeta_2$, for the surface potentials of the interfaces, and is approximated by (Gregory, 1975)

$$\Pi_{DLR}(h) = n_b k_B T\left(\frac{2\psi_{r1}\psi_{r2}\,cosh(\kappa h) - \psi_{r1}^2 - \psi_{r2}^2}{(\,sinh(\kappa h))^2}\right) \tag{3}$$

where $\psi_{ri}$ is the reduced potential, ($\psi_{ri} = e\zeta_i/k_BT$), $\kappa$ is the reciprocal Debye–Huckel double layer length, $n_b$ is the ion density in the bulk solution, and $k_B$ is the Boltzmann constant.

The zeta potential, $\zeta$, is calculated with the Gouy–Chapman relation expressed as (Buckley et al., 1989)

$$\psi(x) = \frac{2k_BT}{e}\, ln\frac{[1 + \gamma\, exp(-\kappa x)]}{[1 - \gamma\, exp(-\kappa x)]} \tag{4}$$

where

$$\gamma = \frac{exp\left(\frac{\psi_{r0}}{2}\right) - 1}{exp\left(\frac{\psi_{r0}}{2}\right) + 1} \tag{5}$$

where $\psi_{r0}$ is the reduced potential given by

$$\psi_{r0} = \frac{e\psi_0}{k_BT} \tag{6}$$

and $\psi_0$ is the surface potential. The surface potential is given by the Nernst equation.

$$\psi_0 = -2.3\left(\frac{k_BT}{e}\right)(pH - pH_0) \tag{7}$$

where $pH_0$ is the isoelectric point of the surface.

If it is assumed that the shear plane is located at a distance of $x$ from the surface, the zeta potential, $\zeta$, is

$$\zeta = \psi(x) \tag{8}$$

In this work, an $x$ equal to 0.6 nm was used (Takamura and Chow, 1983; Chow and Takamura, 1988).

#### 2.1.2. London–van der Waals force

The London–van der Waals (dispersion) force between the two similar materials is usually attractive; therefore, this force is recognized as the strength of the attachment between the two bodies. In a two-parallel plate system, the retarded London–van der Waals attractive force is expressed as (Gregory, 1981)

$$\Pi_{LVA}(h) = -\frac{A\left(15.96\frac{h}{\lambda_{lw}} + 2\right)}{12\pi h^3\left(1 + 5.32\frac{h}{\lambda_{lw}}\right)^2} \tag{9}$$

where $A$ is the Hamaker constant in an oil/water/solid system, $\lambda_{lw}$ is the London wavelength, and $h$ is the distance between the two plates.

The Hamaker constant for oil/silica in water is approximately $1\times10^{-20}$ J (Takamura and Chow, 1983; Hirasaki, 1991b). Melrose (1982) used the Hamaker constant ranging from 0.3 to $0.9\times10^{-20}$ J. In this study, $1\times10^{-20}$ J was used as the Hamaker constant, and the London wavelength is assumed to be 100 nm (Gregory, 1981).

#### 2.1.3. Structural force

The structural forces are short-range interactions at a distance of less than 5 nm, whereas the London–van der Waals and electrical double layer forces are long-range interactions compared to the structural forces (Hunter, 2001). The structural interaction is calculated from (Hirasaki, 1991a)

$$\Pi_s(h) = A_s e^{-\frac{h}{h_s}} \tag{10}$$

where $A_s$ is the coefficient and $h_s$ is the characteristic decay length for the exponential model. In this study, it is assumed that the coefficient is $1.5\times10^{10}$ Pa and the decay length is 0.05 nm as suggested by Hirasaki (1991a).

#### 2.1.4. Contact angle

The contact angle, $\theta$, is measured through the aqueous phase. It is the angle formed by extrapolating the meniscus shape through the thin-film region to the solid surface. At the meniscus position the disjoining pressure is essentially zero. The curvature of the meniscus is assumed to be constant. The contact angle obtained from integrating the augmented Young–Laplace equation is Hirasaki (1991a)

$$1 - cos\theta = \frac{1}{\sigma}\left(P_c h_0 + \int_{h_0}^{\infty}\Pi dh\right) \tag{11}$$

The behavior of a disjoining pressure isotherm is categorized as one of three states: unconditionally stable, metastable, and unstable. The unconditionally stable state, that always represents positive disjoining pressure, indicates complete wetting whereas the unstable