



## Effects of electrolytes on the stability of wetting films: Implications on seawater flotation

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### ABSTRACT

Surface force measurements were conducted using the force apparatus for deformable surfaces (FADS) to better understand the stability of the wetting films formed on hydrophobic surfaces in the presence of KCl and MgCl<sub>2</sub>. The measurements were conducted using thiol-coated gold surfaces as robust model hydrophobic surfaces. The results obtained in pure water show that the wetting films of water on weakly hydrophobic surfaces are metastable due to the presence of a repulsive double-layer force in the films. At high concentrations of KCl, the wetting films become unstable due to double-layer compression, causing them to rupture. In the presence of MgCl<sub>2</sub>, both contact angles and hydrophobic forces decrease due to the adsorption of the hydrolysis products such as MgOH<sup>+</sup> ions and Mg(OH)<sub>2</sub> precipitates on the surface. The FADS data obtained in the present work were analyzed using the Frumkin-Derjaguin isotherm to determine the roles of the short- and long-range hydrophobic forces in determining the stability of the wetting films formed on hydrophobic surfaces. The results of the present study are discussed in view of the roles of electrolytes in seawater flotation.

### 1. Introduction

Blake and Kitchener (1972) showed that the wetting film of water formed on a methylated silica surface was metastable due to the repulsive double-layer force present in the film. In the presence of  $0.86 \times 10^{-2}$  mol/L KCl, however, the film became unstable and ruptured catastrophically at a critical film thickness ( $h_c$ ) of 64 nm, which was attributed to double-layer compression. The authors thought that this observation had a bearing on the kinetics of bubble-particle contact and the salt flotation of weakly hydrophobic minerals such as coal. It had been known that naturally hydrophobic minerals such as talc, sulfur, graphite, and coal were floatable in solutions of high electrolyte concentrations (1–2%) (Klassen and Mokrousov, 1963). Blake and Kitchener attributed the film rupture to the appearance of a *hydrophobic force* when the double-layer force was suppressed. The authors thought obviously that the former was a shorter range force than the latter. The 1972 publication of Blake and Kitchener was the first on record to use the term hydrophobic force.

Shortages of fresh water in high Andes Mountains forced the local copper industry to use seawater to produce copper and molybdenite concentrates by flotation. The seawater near the City of Antofagasta, Chile, contains 0.48 mol/L Na<sup>+</sup> ions and 0.065 mol/L Mg<sup>2+</sup> ions and

0.0043 mol/L Ca<sup>2+</sup> ions (Ordóñez et al., 2013). In view of the salt flotation mechanisms discussed above, flotation in seawater should be easier than in freshwater. Indeed, the induction time of collector-coated chalcopyrite decreased and its contact angle increased in artificial seawater (Drelich and Miller, 2012). It has also been shown that flotation rate and recovery increased sharply as KCl concentration was increased from  $10^{-3}$  to 1 M (Laskowski et al., 1992). In plant operations, however, copper recoveries are slightly lower than in fresh water, while molybdenite flotation is suppressed substantially at a pH where pyrite flotation is efficiently suppressed. The problem associated with the seawater flotation is attributed to the adsorption of MgOH<sup>+</sup> ions and Mg(OH)<sub>2</sub> and Ca(OH)<sub>2</sub> precipitates on molybdenite (Rebolledo et al., 2017). For the case of the latter, depression mechanism is considered similar to slime coating. Indeed, the use of sodium hexametaphosphate improved molybdenite recovery. It has also been shown that the recovery of both the copper and molybdenite flotation improves by pretreating a seawater to remove Mg<sup>2+</sup> and Ca<sup>2+</sup> ions (Jeldres et al., 2017).

It appears that difficulty in seawater flotation of porphyry and andesite copper ores containing molybdenite lies in the depressing action of the hydrolysable cations, i.e., Mg<sup>2+</sup> and Ca<sup>2+</sup> ions, on molybdenite flotation, rather than the Na<sup>+</sup> ions which are more abundant. It is,

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therefore, the objective of the present work to study the effects of both the mono- and divalent cations on the stability of the wetting films formed on hydrophobic surfaces. The approach taken in the present work is to measure the surface forces between air bubble and model hydrophobic surfaces in the presence of KCl and MgCl<sub>2</sub> at different pHs using the force apparatus for deformable surfaces (FADS) (Pan and Yoon, 2016). The results may be useful for better understanding the effects of the different electrolytes on seawater flotation.

## 2. Experimental

### 2.1. Materials

A Direct-Q water purification system (Millipore) was used to obtain ultrapure water with a resistivity of 18.2 MΩ/cm. All the glass beakers were cleaned by immersing them in base baths (potassium hydroxide saturated with isopropanol solution) overnight, rinsed thoroughly with the ultrapure water, and dried under an air-clean bench. Sulfuric acid (98%) from Spectrum Chemical MFG and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35%) from Fisher Scientific were used to clean substrates and cantilevers. 1-butanethiol (C<sub>4</sub>SH, 99%) from TCI America dissolved in ethanol (200 proof, Decon) was used to hydrophobize the gold substrates. Both potassium chloride (KCl, 99.95% purity) and magnesium chloride (MgCl<sub>2</sub>, 99.99% purity) were from Alfa Aesar and used as received.

### 2.2. Sample preparation

The cantilevers used for FADS measurements were fabricated in-house from a double-side polished silicon wafer with dimensions of 15 × 3 × 0.05 mm. Both sides of the cantilevers were vapor deposited with 70 nm thick layers of gold (99.999% purity) by means of an electron beam physical vapor deposition system (PVD 250, Kurt J. Lesker). Prior to the gold coating, a 5-nm thick layer of chromium (99.99% purity) was deposited first to improve adhesion between gold and silicon.

The gold-coated cantilevers were cleaned in a freshly prepared piranha solution (7:3 by volume of H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>) at 90 °C for 1 min, thoroughly washed with ultrapure water, and then dried in a particle-free N<sub>2</sub> gas stream. The cleaned gold surfaces were hydrophilic, with advancing (θ<sub>a</sub>), equilibrium (θ<sub>e</sub>) and receding (θ<sub>r</sub>) water contact angles of 53, 30, 0°, respectively. The contact angle measurements were conducted using the sessile drop technique immediately after the gold-coated cantilevers were cleaned. It should be noted that the contact angles of gold increase over time when the surfaces are exposed to the ambient (Smith, 1980). Gold has a large Hamaker constant (20–50 × 10<sup>-20</sup> J) and hence can readily adsorb organic impurities from the atmosphere and acquire a degree of hydrophobicity. Therefore, the surface hydrophobization procedure described below was carried out immediately after the cleaning step.

After the gold coating, a cantilever was hydrophobized by immersing it in a 10<sup>-5</sup> M C<sub>4</sub>SH-in-ethanol solution for a period of time to achieve a desired hydrophobicity as measured by contact angle. The longer the immersion time, the higher the contact angle. The hydrophobization step was carried out immediately after a gold-coated cantilever had been cleaned and rinsed thoroughly with water and subsequently with ethanol.

### 2.3. Force measurement

Fig. 1 is a schematic representation of the force apparatus for deformable surfaces (FADS) developed by the authors to monitor the changes in the surface forces (disjoining pressures) in the thin liquid films (TLF) of water formed between a bubble and a flat surface. A more detailed description of the instrument has already been described (Pan and Yoon, 2016). The measurement is initiated by slowly moving an air

bubble up toward the cantilever spring above by means of a piezo stage, while recording the optical interference patterns (Newton rings) generated during film thinning due to the changes in bubble curvature. The surface, underside of a cantilever spring, is rendered hydrophobic by C<sub>4</sub>SH adsorption, and the measurement is conducted in a solution of known pH and electrolyte concentration. The TLF of water formed on a hydrophobic surface is usually unstable and hence thins fast before rupture; therefore, the fast-evolving optical fringes are recorded by means of a high-speed camera. The recorded images are then analyzed *off-line* to determine the film thicknesses using the microinterference method (Sheludko, 1962) as a function of time and the data are used to reconstruct the spatiotemporal film profiles. Analysis of the profiles in the manner described in the theory section below allows one to calculate the curvature changes associated with film thinning, which in turn are used to calculate the surface and hydrodynamic forces involved in film thinning.

The forces calculated from the curvature changes are compared with those measured simultaneously using the cantilever spring. The direct force measurement is based on monitoring the spring deflections using a fiber optic sensor based on the Fabry-Pérot interferometry. From the deflections and the spring constant, one can obtain a force vs. time and force vs. film thickness curves at any point in a TLF. Detailed procedures for determining the spring constants will be described elsewhere.

Thus, the FADS is designed to study bubble-surface interactions using an air bubble effectively as a force sensor. According to Exerowa and Kruglyakov (1998), the microinterferometry method of measuring film thicknesses has a sensitivity limit of 0.2 nm. Between this and the usual surface tension of water (~70 mN/m), one may estimate the sensitivity limit for the FADS apparatus to be ~1.4 × 10<sup>-11</sup> N.

## 3. Theory

When an air bubble is pressed against a flat surface in water, the intervening liquid drains in accordance to the Reynolds lubrication equation,

$$\frac{\partial h}{\partial t} = \frac{1}{12\mu r} \frac{\partial}{\partial r} \left( rh^3 \frac{\partial p}{\partial r} \right) \quad (1)$$

where  $p$  is the hydrodynamic (or excess) pressure in the wetting film,  $h$  is film thickness,  $t$  is time,  $r$  is the radial distance from film center, and  $\mu$  is viscosity. Integrating Eq. (1) twice yields,

$$p = 12\mu \int_{r=\infty}^r \frac{1}{rh^3} \left[ \int_{r=0}^r r \frac{\partial h}{\partial t} dr \right] dr \quad (2)$$

under the boundary conditions that  $p = 0$  at  $r = \infty$  and  $\partial p/\partial r = 0$  at  $r = 0$ . Eq. (2) can be reduced to an approximate form,

$$\frac{dh}{dt} = -\frac{2h^3 p}{3\mu R^2} \quad (3)$$

under conditions of flat films and no slip boundary condition. A normal pressure balance along a horizontal film gives,

$$p = p_c - \Pi \quad (4)$$

where  $p_c$  is the capillary pressure and  $\Pi$  is the disjoining pressure. The former can be determined using the Young-Laplace equation,

$$p_c = \frac{2\gamma}{R} - \frac{\gamma}{r} \frac{\partial}{\partial r} \left( r \frac{\partial h}{\partial r} \right) \quad (5)$$

where  $R$  is the bubble radius and  $\gamma$  is the surface tension at the air/water interface.

The second term of Eq. (4) comes into play at  $h < \sim 250$  nm. Thus, film thinning is driven initially by  $p_c$  but is controlled by surface forces during later stages. Contributions from surface forces can be determined using the extended DLVO theory (Xu and Yoon, 1989, Yotsumoto and Yoon, 1993, Yoon and Mao, 1996),

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