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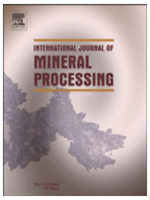

AFM surface force measurements conducted between gold surfaces treated in xanthate solutions

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ABSTRACT

Surface forces have been measured *in situ* between gold surfaces hydrophobized by self-assembly of xanthates from aqueous solutions using an atomic force microscope (AFM). The measurements conducted in potassium amyl xanthate (KAX) and potassium ethyl xanthate (KEX) solutions showed long-range hydrophobic forces, with the force curves showing no evidence for nanobubbles on the surfaces. The strongest hydrophobic force was observed at contact angle above 90° and in pure water, with a decay length of 29.5 nm. Both the contact angle and hydrophobic force increased with increasing xanthate concentration. At an excessively high concentration, the hydrophobic force diminished substantially. When the xanthate solution was replaced with pure water, however, a strong hydrophobic force reappeared, suggesting that the presence of residual xanthate ions in solution is detrimental to obtaining a strong and long-range hydrophobic force. This finding is consistent with the observation that hydrophobic force becomes weaker in the presence of NaCl in solution.

1. Introduction

The first direct measurement of hydrophobic force was reported by Israelachvili and Pashley (1982). Many investigators reported similar results (Herder, 1990; Pashley et al., 1985; Rutland et al., 1992; Yoon and Ravishankar, 1994), while others showed that it was due to coalescence of pre-existing nanobubbles (Attard, 2003; Ederth, 2000; Ishida et al., 2000; Parker et al., 1994; Sakamoto et al., 2002). The strongest evidence for the latter was the discontinuities (or steps) observed in the force *vs.* distance curves, and some investigators actually showed the presence of nano-scale, flat bubbles on very hydrophobic surfaces (Tyrrell and Attard, 2001; Yang et al., 2003). It was shown also that the long-range attractions disappeared when the force measurements were conducted in degassed solutions (Sakamoto et al., 2002). Follow-up experiments showed, however, that strong hydrophobic forces can still be measured between silica surfaces immersed in degassed octadecyltrimethylammonium chloride (C_{18}TACl) solutions (Zhang et al., 2005). The force curves obtained between hexadecanethiol (C_{16}-SH)-coated gold surfaces also showed steps and showed no significant hydrophobic force (Ederth, 2000). More recent studies conducted on the same system showed, however, step-free, smooth force curves exhibiting long-range hydrophobic forces (Wang and Yoon, 2008a). It was suggested that thiol-coatings made under excessively long contact times may create surface roughness, trapping nanobubbles and hindering detection of hydrophobic forces. Ederth (2000) used 16 h contact time while long-chain thiols have extremely fast adsorption kinetics on gold (Karpovich and Blanchard, 1994).

Air bubbles placed in water have interfacial tension (72.6 mN/m at 25 °C) that is substantially larger than those of hydrocarbons and fluorocarbons in water (~50 mN/m), suggesting that air bubbles are hydrophobic. The Sum Frequency Generation (SGS) spectra of the air/water interface showed a high-energy peak at ~3700 cm^{-1}, which is characteristic of the non-H-bonded (or free) OH groups that are commonly found on hydrophobic surfaces (Du et al., 1994; Scatena et al., 2001). It would not be unreasonable, therefore, to anticipate that hydrophobic force is present in the foam films produced at low surfactant concentrations. Supporting evidences include the equilibrium film thicknesses that were considerably larger than predicted by the DLVO theory (Wang and Yoon, 2004; Yoon and Aksoy, 1999) and the kinetics of film thinning that were much faster than predicted from the Reynolds lubrication theory (Wang and Yoon, 2005). It has been shown that hydrophobic force is the major destabilizing force for bubbles and foams at low surfactant concentrations (Wang and Yoon, 2008b; Wang and Yoon, 2005). Therefore, the thinning of wetting films and hence the bubble–particle interactions occurring in flotation may also be considered a hydrophobic interaction. In fact, the presence of hydrophobic force was first recognized while studying the rupture mechanisms of wetting films (Blake and Kitchener, 1972). More recently, the presence of both long- and short-range hydrophobic forces in the wetting films of water formed on gold surfaces hydrophobized by xanthate has been shown (Pan et al., 2011; Pan and Yoon, 2010). Further, the direct force measurements conducted between an air bubble and a hydrophobic surface

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actually showed that bubble–particle attachment occurs due to the presence of a long-range hydrophobic force in the wetting film (Ishida, 2007).

Flotation is the most important solid–solid separation process used in the mining industry. In this process, air bubbles selectively collect hydrophobic particles on the surface and rise out of a suspension, leaving hydrophilic particles behind. It has been shown that the kinetics of flotation increases with particle hydrophobicity (Yoon and Mao, 1996). Therefore, the control of particle hydrophobicity is of critical importance in flotation practice. For the flotation of sulfide minerals and precious metals, short-chain alkyl xanthates are widely used as hydrophobizing agents. The adsorption mechanisms are electrochemical in nature, in which xanthate ions are oxidized to chemisorb on the surface forming metal xanthates, while molecular oxygen (O_2) dissolved in water is reduced to water or hydroxyl ions (Woods, 1971). Only conducting minerals such as sulfide minerals and precious metals can host such reactions, making xanthate to be a highly selective hydrophobizing agent against non-conducting minerals such as silica and clay.

In the present work, surface force measurements were conducted between gold surfaces hydrophobized by spontaneous adsorption of short-chain xanthates from aqueous solutions using an AFM. The measurements were conducted *in situ* without ever exposing the hydrophobized surfaces to air so that the possibility of forming bubbles on the surfaces is minimized. The results were compared with contact angle measurements conducted at different concentrations and immersion times. In addition, the adsorption of xanthate ions onto gold was studied using the Reflection Absorption Infrared Spectroscopy (RAIRS) and Quartz Crystal Microbalance (QCM). It is hoped that the results will be useful for better understanding the mechanisms of xanthate adsorption and finding the origin of hydrophobic force.

2. Experimental

2.1. Materials

Potassium amyl xanthate (KAX, $C_5H_{11}OCSSK$, >90.0%) and potassium ethyl xanthate (KEX, C_2H_5OCSSK, >90.0%) were obtained from TCI America. They were dissolved in acetone (HPLC grade, Fisher Scientific, Inc.), filtered, and recrystallized with diethyl ether (≥99.9%, Sigma-Aldrich, Inc.) (Rao, 1971). Alkyl xanthates are unstable under ambient conditions and can be readily oxidized; therefore, they were recrystallized at least twice before use. High-purity sodium chloride (NaCl, 99.999%) from Sigma-Aldrich was used as electrolyte. Gold (III) chloride solution (~30 wt.% in dilute HCl, 99.99%, Aldrich) was used to make gold xanthate precipitates. Spectroscopic grade KBr powder (Graseby Specac, Ltd.) was used for IR transmission spectroscopy. A Nanopure water treatment unit (Barnstead Nano-pure II) was used to obtain deionized water with a resistivity of 18.2 MΩ cm^{-1} at 25 °C. The feed to the deionization unit was double-distilled water. All of the aqueous solutions used in the present study were prepared using the Nanopure water.

Gold spheres and gold-coated glass slides were used for AFM force measurement. The gold-coated glass slides were obtained by depositing pure gold on the surface using a vacuum evaporator. A thin layer of chromium of approximately 50 Å thickness was coated first, followed by depositing a layer (~500 Å) of gold. The chromium coating was necessary to strengthen the bonding between gold and glass substrates. AFM images of the cleaned gold surfaces showed a root mean square (rms) roughness of 0.8 nm over an area of $1 \times 1\ \mu m^2$. Gold spheres were produced by melting a gold micro-powder (1.5–3.0 μm, >99.6%, Alfa Aesar) in a high temperature furnace. The powder was placed in an alumina crucible and heated until the temperature was raised above its melting point (1064.18 °C). It was kept at 1100 °C for 15 min and then cooled down slowly. The furnace was flushed with nitrogen gas to provide an oxygen-free atmosphere. The gold spheres obtained in this manner had a wide range of sizes. Only those with radius of 3.5–7.5 μm were selected for force measurements. The gold plates were cleaned first by immersing them in a boiling piranha solution (30:70 H_2O_2/H_2SO_4) for 20 min and then washed with plenty of water to remove the residual solution. The gold spheres glued onto cantilever springs could not be cleaned with the piranha solution; therefore, the spheres were flushed with ethanol first and then exposed to a UV light source ($\lambda = 254$ nm) for 2 h before use.

2.2. Infrared spectroscopy

RAIRS has been used to study the adsorption of amyl xanthate onto gold surfaces. The infrared spectra of xanthate-coated gold surfaces were recorded using a Vertex 80v spectrometer (Bruker Optics) which was equipped with a mercury cadmium telluride (MCT) detector and a high vacuum sample chamber. The sample chamber was evacuated at 5×10^{-7} Torr to minimize the effects of background water and other contaminants. The gold plates were immersed in KAX solutions of different concentrations for different lengths of time, removed from the solution, and then blow-dried in a nitrogen gas stream. Some KAX-coated gold samples were post treated by washing in pure water or diethyl ether. The samples were then transferred to the vacuum chamber for IR measurement without delay. A cleaned bare gold substrate was used to record the background spectrum. Each sample was scanned at least 100 times in the 4000–500 cm^{-1} region and the spectral resolution was 2 cm^{-1}. Transmission IR spectra of bulk gold xanthates were recorded with a Bio-RAD FTS 3000 Excalibur S-series infrared spectrometer. The gold xanthates were precipitated by reacting gold (III) chloride solution with excess potassium xanthate solutions in accordance with the method described by Denko and Anderson (1945). KBr pellets were prepared by mixing 1 mg of gold xanthate precipitate and 250 mg of IR-grade KBr in an agate mortar, transferring the mixture to a die, and then pressing it at 15,000 lb for 2 min.

2.3. QCM experiment

The adsorption of xanthate onto gold from water was studied using a QCM (Q-sense E4, Sweden), which is mainly comprised of a 4-sensor chamber and a peristaltic pump. The change in frequency of gold-coated quartz crystal sensor (QSX 301, Q-sense sensors) was monitored in xanthate solution as a function of immersion time and recorded by computer with software (QTools). The measurements were conducted at 22 °C at the fundamental frequency (4.95 ± 0.05 MHz) of the sensor crystal and at the 3rd, 5th, 7th, 9th, 11th, and 13th overtones simultaneously. A decrease in resonance frequency reflects a mass change due to xanthate adsorption on gold-coated sensor. Immediately prior to the measurement, the QCM cell was cleaned with a running sodium dodecyl sulfate (SDS) solution driven by the peristaltic pump, while the gold sensors were cleaned in a UV-ozone cleaner and subsequently in a boiling solution of NH_4OH:H_2O_2:H_2O (1:1:3 v/v/v) for 20 min. During the measurement, a stable baseline of the QCM frequency signal was obtained first in flowing (pure) water at a rate of 0.2 mL m^{-1}. The water was subsequently replaced with a xanthate solution at the same flow rate. The decrease in frequency was recorded for the initial 84 min to monitor xanthate adsorption as a function of time. The xanthate solution was then replaced by flowing water (pure) for 74 min to record the increase in frequency due to the desorption of xanthate.

2.4. Contact angle measurement

Gold-coated glass plates were hydrophobized in xanthate solutions of various concentrations for different immersion times. Equilibrium contact angles were measured *in situ* (*i.e.*, by keeping the