Interfacial Water Structure and the Wetting of Mineral Surfaces

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Abstract

Advanced tools, including atomic force microscopy (AFM), sum frequency vibrational spectroscopy (SFVS), and molecular dynamics simulations (MDS), are being used to describe interfacial water structure and to contrast the structure of water at a hydrophilic mineral surface with that at a hydrophobic mineral surface. Specifically, this contrast is revealed from interfacial water features based on the extent of H-bonding, dipole orientation, exclusion zone thickness, and residence time. Progress in our understanding of interfacial water structure and wetting phenomena is reported for different mineral classes including sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, including both semi-soluble and soluble salts.

Keywords: AFM; SFVS; MDS; Interfacial water structure; Wetting; Contact angle

1. Introduction

Flotation separation processes are of great significance to the mining industry with millions of tons of mineral resources being processed each day for the separation and recovery of valuable mineral commodities. It is most appropriate to recognize Professor Heinrich Schubert on the occasion of his 90th year since he has made significant contributions to the development of flotation technology, including the flotation chemistry of non- sulfide minerals, particularly the flotation chemistry of potash.

Interfacial water structure and the wetting of mineral surfaces is of fundamental importance in the area of flotation chemistry, as well as having importance in other areas of technology. Now, with advanced tools, the features of interfacial water structure and wetting phenomena at mineral surfaces can be considered in greater detail. These tools include atomic force microscopy (AFM), sum frequency vibrational spectroscopy (SFVS), and molecular dynamics simulations (MDS).

Specifically, atomic force microscopy can be used not only to describe charging of mineral surfaces, but also to describe the wetting characteristics of the surface using selected cantilevers with hydrophobic tips such as a diamond-like-carbon tip (Yin and Miller, 2012; Yin et al., 2012). In this way, a hydrophobic mineral surface can be described by the magnitude of the attractive force at the PZC in the absence of electrostatic forces. Also, with AFM surface force measurements, we have the opportunity to interrogate the surfaces of small particles, such as nanometer clay particles, and from the polarity of such surfaces, describe their wetting characteristics.

In the case of sum frequency vibrational spectroscopy the surface spectra reveal information regarding the structure and the degree of coordination of water molecules at the mineral surface (Shen and Ostroverkhov, 2006). In this way, the extent to which interfacial water molecules are hydrogen bonded to each other and at the surface can be described based on the frequencies observed for OH vibrations. The SFVS spectra for the hydrophilic surface state, a surface well wetted by water, reveal characteristic absorption peaks for water with complete tetrahedral coordination (ice-like water at $\sim 3200\text{ cm}^{-1}$) and with incomplete tetrahedral coordination (liquid-like water at 3400 cm^{-1}), but no peak for the free OH stretch (vapor-like water at $3600\text{--}3700\text{ cm}^{-1}$). In contrast, the SFVS spectra for

the hydrophobic surface state reveal a strong and distinct absorption at 3600–3700 cm⁻¹ corresponding to the free OH stretching vibration which supports the notion of a water exclusion zone (~ 3 Å in thickness) at hydrophobic surfaces.

Finally, molecular dynamics simulations are being used in flotation chemistry (Du et al., 2012) not only to describe interfacial water features (extent of H-bonding, dipole orientation, exclusion zone thickness, residence time), but also to describe wetting phenomena both from sessile drop simulations and from bubble attachment simulations (Jin et al., 2014; Jin and Miller, 2016). In this way, wetting characteristics are examined and hydrophobic surfaces are distinguished from hydrophilic surfaces. Results from MDS contact angle simulations show that hydrophobic surfaces are characterized by the presence of a water exclusion zone, interfacial water dipoles parallel to the surface, a short residence time for interfacial water molecules (usually less than 10 ps), and incomplete wetting.

Progress in our understanding of interfacial water structure and wetting phenomena is reported for different mineral classes including sulfides, oxides/hydroxides, layered silicates (phyllosilicates), and salt-type minerals, both semi-soluble and soluble salts.

2. Sulfide Minerals

The low degree of surface polarity and more hydrophobic character distinguish the sulfide mineral class from other mineral classes. This feature accounts for the fact that the hydrophobic surface state can be created at low concentrations of short chained collector molecules. The sulfide minerals are also distinguished by the fact that generally their surfaces are thermodynamically unstable with respect to oxidation and hydrolysis which increases the surface polarity and hydration. This instability of the sulfide mineral surfaces makes analysis and generalization regarding their wetting characteristics more difficult.

Several investigations have demonstrated that many sulfide minerals exhibit native floatability and can be floated without a collector. Flotation of various sulfides in the virtual absence of oxygen (i.e., in water containing less than 5 ppb oxygen) has shown the natural floatability of these minerals under such conditions (Fuerstenau and Sabacky,

1981). Under anaerobic conditions the sulfide minerals are not well wetted by water and exhibit a hydrophobic surface state, as revealed in Table 1.

MDS sessile drop contact angles for selected sulfide mineral surfaces are consistent with experimental results. See Table 1. An MDS snapshot of a water drop at a fresh pyrite (100) surface is shown in Figure 1a. According to MDS interfacial water analysis, a “water exclusion zone” of 3 Å accounts for the hydrophobic surface state of sulfide mineral surfaces under anaerobic conditions (Jin et al., 2014). These results are supported by the SFVS results for hydrophobic surfaces and X-ray reflectivity measurements. In addition, water residence times of less than 10 ps and reduced H-bonding of interfacial water molecules are further characteristics of the hydrophobic sulfide mineral surfaces. Thus, the MDS interfacial water features reveal the relatively weak interaction between interfacial water and the selected sulfide mineral surfaces, which accounts for the origin of the natural hydrophobic character of the sulfide minerals under anaerobic conditions.

Table 1. Simulated and Experimental Contact Angles for Selected Sulfide Mineral Surfaces under Anaerobic Conditions (Jin et al., 2014)

Sulfide Mineral Surface	Contact Angle, degrees	
	Experimental	MDS
Molybdenite Face	84	84
Pyrite (100) Surface	64	77
Chalcopyrite (012) Surface	74 (Random Surface)	70
Galena (100) Surface	82	66
Sphalerite (110) Surface	44	49
Molybdenite Armchair-Edge	36	55
Molybdenite Zigzag-Edge	36	26

However, due to the instability of these sulfide mineral surfaces with respect to oxidation, the surfaces become hydrophilic on exposure to air and water. For example, after oxidation of the pyrite surface with a 30% hydrogen peroxide solution for 90 seconds, the experimental sessile drop contact angle for a pyrite (100) surface dropped from 63° to 23° (Jin et al., 2015). The hydrophilic character of the oxidized pyrite surface with ferric hydroxide islands (Miller et al., 2002) is also revealed by the MDS snapshot of a water drop

wetting the pyrite surface and creating a 22° contact angle as shown in Figure 1b. In the case of the oxidized pyrite surface the interfacial water molecules form hydrogen bonds with ferric hydroxide clusters and exhibit a residence time of about 16 ps, according to the MDS interfacial water analysis. The electrostatic interaction and hydrogen bonding between the ferric hydroxide and interfacial water molecules account for the macroscopic hydrophilic character and wettability of oxidized pyrite surfaces at alkaline pH values where ferric hydroxide is stable (Jin et al., 2015).

Figure 1. Snapshot of a water drop containing 1270 water molecules spreading at (a) fresh pyrite (100) surface and (b) oxidized pyrite surface with ferric hydroxide islands. The simulation time is 1 ns. The color code for the atoms is as follows: blue, OH⁻; green, Fe; yellow, S; red, O; white, H.

In summary, under anaerobic conditions the sulfide minerals are not well wetted by water and exhibit a hydrophobic surface state. In most practical cases, sulfide surfaces will have reacted with oxygen, depending on the pH, creating polar sites and a more hydrophilic surface state.

3. Oxides/Hydroxides

Oxide minerals are generally thought to be hydrophilic and well wetted by water. However, complete wetting, as shown from recent studies, depends on hydroxylation of the mineral surface in order to provide H-bonding sites for interfacial water molecules. Certain anhydrous oxides (sapphire, rutile, hematite) have a hydrophobic character prior to hydroxylation as shown in Table 2. In some cases it seems that hydroxylation is rapid and the oxide surfaces are quickly wetted by water within minutes. In other cases the reaction with water is slow and the time for hydroxylation/wetting is extended to days.

Table 2. Experimental Contact Angles for Oxides/Hydroxides Compared to MD Simulated Contact Angles.

Oxide/Hydroxide Mineral Surface	Experimental Captive Bubble Contact Angle, pH = 5.5, With Heating, Without Plasma Cleaning	Experimental Captive Bubble Contact Angle, pH = 10.6, With Heating, Without Plasma Cleaning	MDS Sessile Drop Contact Angle
Quartz SiO₂	40°	0°	21° (001)
Sapphire Al₂O₃	51°	26°	20° (001)
Gibbsite Al(OH)₃	0°	0°	0° (001) relaxed surface state
Rutile TiO₂	46°	25°	64° *
Goethite FeOOH	0°	0°	10° (001)
Hematite Fe₂O₃	48°	0°	50° (001)

*Park and Aluru (2009, Table 2, Case D)

Further, the wetting characteristics depend on the procedure used to prepare the surface. For example, in some cases, when treated after polishing with acetone, ethanol, and water washing, followed by drying at 60° C, water contact angles of 40 – 60 degrees are obtained by captive bubble and sessile drop measurements at pH 5.5. The corresponding contact angles diminish significantly when measured at pH 10.6. The results are compared to results from MD simulation for rigid surfaces as shown in Table 2. In contrast, the same oxide surfaces prepared by argon plasma treatment at ambient temperature and pressure have significantly lower contact angles of 0 – 15 degrees. In the case of sapphire, our results presented in Table 2 can be compared with other experimental results, 25-37°, (Somasundaran, 2006) and with simulation results, 38°, as reported in the literature (Singh et al., 2010).

Specular hematite is an interesting example since the (001) surface exhibits a rather significant contact angle of about 50 degrees when prepared by polishing without plasma treatment. The kinetics of the hydroxylation/wetting reaction for the anhydrous (001) hematite surface depend on the pH of the solution. At pH 5.5 the hydrophobic character (~50 degrees) is sustained for a significant time, whereas at pH 10.6, hydroxylation/wetting occurs instantaneously. The hydroxylation reaction is expected since hematite is thermodynamically unstable with respect to goethite at room temperature, and the hydroxylated goethite surface is completely wetted by water, even at pH 5. In the absence of hydration and/or hydroxylation the surface exhibits a modest hydrophobic character.

The (001) hematite surface can be organized to conform to a surface state revealed by STM results reported in the literature (Hochella, 1995). In this case the (001) hematite surface consists of exposed oxygen atoms. MDS analysis of this (001) hematite surface confirms the hydrophobic state as reported in Table 2. Hydroxylation and wetting of the (001) surface of hematite has been established experimentally and the surface is expected to be similar to a goethite surface. For example, MDS sessile drop images for hematite and goethite are compared in Figure 2. Note that after hydroxylation the contact angle is reduced from 48° to 0°.

Figure 2. Snapshot of a water drop containing 1270 water molecules spreading at hematite (001) (top) and goethite (001) (bottom) surfaces. The simulation time is 1 ns. The color code for the atoms is as follows: green, Fe; red, O; white, H.

4. Layered Silicates (Phyllosilicates)

The wetting characteristics of layered silicate minerals (phyllosilicates), also known as clay minerals, are of interest from a number of perspectives and vary significantly with respect to composition. The layered silicate minerals consist of silica tetrahedral layers bonded to aluminum or magnesium octahedral layers, the gibbsite layer in the case of aluminum and the brucite layer in the case of magnesium. Classic examples are the bilayer silicates designated TO for the tetrahedral to octahedral bonding, and the trilayer silicates designated TOT for the sandwich structure having bonding of the octahedral layer between two silica tetrahedral layers. The layered silicate mineral particles are anisotropic having at least two surfaces, a face surface and an edge surface. The edge surfaces are hydrophilic with significant sites for H bonding of water molecules. On the other hand the silica face surfaces can have low polarity in some cases and exhibit a hydrophobic surface state. Properties of these surfaces have been established by traditional methods and most recently by atomic force microscopy (Miller and Liu, 2015; Yin and Miller, 2012; Yin et al., 2012). The layered silicates are also distinguished by their composition especially by the cation in the octahedral position, magnesium or aluminum for example. Beyond substitution in the octahedral position, substitution can also occur for silicon in the tetrahedral position and consequently the composition of these clay minerals can become quite complex with significant variation in their surface properties.

Consider the sequence of the trilayer silicate minerals with aluminum in the octahedral position. The sequence is well known; pyrophyllite, illite, and muscovite mica as shown in Figure 3. Note that the common TOT structure is evident. The difference between these minerals is the degree of substitution of aluminum for silicon in the tetrahedral layer. In the case of pyrophyllite the TOT structure is ideal with no substitution in the tetrahedral layer. The pyrophyllite structure is neutral with balanced charges. In contrast, muscovite has the same TOT structure except aluminum substitutes for every fourth silicon in the tetrahedral layer, the charge being balanced with interlayer potassium as shown in Figure 3. Although the structures are similar, the wetting properties are quite different with the basal plane of pyrophyllite, the pyrophyllite face, being hydrophobic while the basal plane of muscovite mica has a hydrophilic face surface. Of course, the edge surfaces of all layered

silicates are hydrophilic. Experimental contact angle measurements are confirmed by results from MD sessile drop simulations. See Figure 4. Based on MDS, the effect of aluminum substitution for silicon in the tetrahedral layer of TOT structures has been established and the results are shown in Figure 5. It is evident that the contact angle is reduced significantly from 70 degrees to 30 degrees with only 5% isomorphous substitution in the tetrahedral layer and the face surfaces on illite and muscovite are completely wetted by water as evidenced by a contact angle of zero.

Figure 3. Variation in crystal composition for trilayer silicate minerals (TOT). Open circles represent oxygen atoms, black circles represent silicon atoms, gray circles represent hydroxyl, small open circles represent aluminum.

Figure 4. Snapshot of water drop containing 500 water molecules spreading at the pyrophyllite (001) (left) and muscovite (001) (right) surfaces. The simulation time is 1 ns. The color code for the atoms is as follows: green, Al; pink, K; red, O; white, H; yellow, Si.

Figure 5. Water contact angle calculated from MDS results as a function of the percentage of isomorphous substitution of aluminum in the silica tetrahedral surface of layered silicates (Yin et al., 2012).

Talc is another TOT layered silicate, similar to pyrophyllite except that magnesium is in the octahedral position rather than aluminum. Like pyrophyllite, the talc face surface is naturally hydrophobic due to the low polarity of the siloxane rings formed by the silica tetrahedral layer. The interfacial water structure at the talc silica surface has been examined by MDS and is characterized by the presence of a water exclusion zone, interfacial water dipoles parallel to the surface, a short residence time for interfacial water molecules (usually less than 10 ps) and incomplete wetting based on MDS contact angle simulations with an MDS sessile drop contact angle of 70 degrees. In contrast, the talc edge surface is wetted by water as shown experimentally and by MDS (Nalaskowski et al., 2007; Yin et al., 2012). See Figure 6.

Figure 6. Snapshot of equilibrated water-talc basal plane (left) and water-talc edge (right) surfaces. The color code for the atoms is as follows: green, Mg; red, O; white, H; yellow, Si. (Du and Miller, 2007a)

So it is evident for the TOT structures that the low polarity of the silica tetrahedral layer accounts for the hydrophobic state of the face surfaces for both pyrophyllite and talc. Substitution in the tetrahedral layer increases the polarity of the face surface and results in a hydrophilic surface state for illite and muscovite.

More recently the wetting characteristics of bilayer clay nanoparticles (TO structure) have been established by AFM, specifically the kaolinite surfaces (Yin and Miller, 2012; Yin et. al., 2012). Note that a kaolinite particle has 3 surfaces; silica face surface, alumina face surface, and an edge surface. Again, as in the case for the trilayer silicates, the silica face for kaolinite is hydrophobic, whereas the alumina face (gibbsite surface) and the edge surface are hydrophilic. These AFM results were confirmed by results from MDS which reveal the exclusion zone for interfacial water molecules at the hydrophobic silica face surface of kaolinite. See MDS snapshots in Figure 7 which also reveal the hydrophilic surface (gibbsite surface) of kaolinite. Finally, an MDS contact angle of 40 degrees has been found for the kaolinite silica surface (Miller and Liu, 2015).

Figure 7. Snapshot of equilibrated water-kaolinite silica face (left) and water-kaolinite alumina face (right) surfaces. The color code for the atoms is as follows: green, Al; red, O; white, H; yellow, Si (Miller et al., 2007).

5. Salt-Type Minerals

It is expected that the salt mineral surfaces, both semi-soluble and soluble salt mineral surfaces, will be well wetted by water. Generally this is the case but interestingly there are some salt minerals that exhibit a small degree of hydrophobicity. Analysis is complicated because of the dynamic equilibrium with the solution involving dissolution and recrystallization at the salt surfaces. In this regard, the interfacial water structure is influenced by the hydration characteristics of ions present in solution and at the salt surface.

In the case of semi-soluble salt minerals, surface hydration of oxyanion salts is usually observed and minerals such as calcite, magnesite, apatite, bastnaesite, monazite, and gypsum generally have a small or zero contact angle and are well wetted by water. An exception is fluorite which is reported to have a distinct water contact angle of 20 degrees (Zawala et al., 2007; Zhang et al., 2015). In fact, wetting of the fluorite surface by water depends on the crystallographic surface considered. It was found that only the (111) surface of fluorite had modest hydrophobicity with a water contact angle of about 20 degrees (Zhang et al., 2015). These results were confirmed from MDS contact angle simulations. The corresponding analysis of interfacial water features showed a water

exclusion zone at the (111) surface and a water residence time significantly less than at other crystallographic surfaces. The MDS interfacial water results were complemented by SFVS measurements which indicated the presence of the water exclusion zone at the surface by the presence of a small $\sim 3700\text{ cm}^{-1}$ peak in the SFVS spectra. Other crystallographic surfaces of fluorite, (100) and (110), were well wetted by water with a zero contact angle determined experimentally and by MDS. The SFVS spectra of the (100) surface showed no evidence of the $\sim 3700\text{ cm}^{-1}$ peak. These surfaces were well hydrated and few if any free OH vibrations were detected, thus indicative of good H-bonding with many of the interfacial water molecules in tetrahedral coordination at the (100) and (110) surfaces. Finally it is interesting to note that the (100) and (110) surfaces are unstable and given sufficient time will recrystallize to the low energy (111) surface of fluorite. In this case the new (111) surfaces become hydrophobic with the expected contact angle of ~ 20 degrees (Zhang et al., 2015).

With respect to the soluble salt minerals, wetting of a soluble salt surface by its corresponding brine seems to depend on how the salt ions influence the water structure. For example, in the case of sylvite (KCl) wetting by brine is not complete and a contact angle of a few degrees (12 – 15 degrees) is found (Hancer et al., 2001). In contrast, wetting of halite (NaCl) by its brine is complete with a contact angle of zero. These and other results have been explained by the fact that some salts are water structure makers and other salts are water structure breakers. A water structure maker is a salt that promotes H-bonding and short range order of water molecules whereas a water structure breaker is a salt that tends to destroy short range order. The classification is demonstrated by comparing the viscosity of salt solutions. Structure maker salts cause an increase in viscosity with an increase in salt concentration. On the other hand structure breaking salts cause a decrease in viscosity with an increase in salt concentration. Basically for univalent ions the classification is determined by ionic size. The smaller ions are structure makers while the larger ions are structure breakers. NaCl is a water structure maker, while KCl is a water structure breaker. Although MDS interfacial water structure has been reported (Du and Miller, 2007b; Du et al., 2012) for KCl (sylvite), the experimental sessile drop contact angle of 12 – 15 degrees has not been confirmed by MD sessile drop simulation of KCl brine at a KCl surface.

6. Summary

Interfacial water structure is described by characteristic features including H-bonding, dipole orientation, exclusion zone thickness, and residence time. In contrast to polarized hydrophilic surfaces with oriented water dipoles, MDS analysis of water at hydrophobic surfaces reveals that these water molecules are not oriented; rather, the water dipoles are separated from, and parallel to, the surface.

Sulfide mineral surfaces are found to be hydrophobic under anaerobic conditions and become hydrophilic upon oxidation and hydrolysis. The hydrophobic sulfide surface is characterized by a “water exclusion zone” of $\sim 3 \text{ \AA}$, water residence times of less than 10 ps, and reduced H-bonding.

Oxide mineral surfaces have a modest hydrophobicity depending on how the surface is prepared. However, given sufficient time and an appropriate pH, surface hydroxylation occurs and the surfaces become hydrophilic.

In the case of layered silicates, the silica face surface of the anisotropic clay minerals exhibits a hydrophobic character in the absence of isomorphous substitution in the silica tetrahedral layer, examples include pyrophyllite, talc, and kaolinite. Of course, the edge surfaces are well wetted by water.

Salt-type minerals are generally well wetted by water, but some salt surfaces appear to have a lower level of polarity such as the (111) surface of fluorite (CaF_2) and the surfaces of structure breaking alkali halide salts such as sylvite (KCl).

Information on interfacial water structure should help to explain film rupture during bubble attachment in the flotation process, and such research is in progress.

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