Journal of Colloid and Interface Science 388 (2012) 243–256

Contents lists available at SciVerse ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

A double layer model of the gas bubble/water interface

Philippe Leroy [a,*], Damien Jougnot [b], André Revil [c,d], Arnault Lassin [a], Mohamed Azaroual [a]

[a] BRGM, UMR BRGM/CNRS/ISTO 7327, 3 Avenue Claude Guillemin, 45060 Orléans Cedex 2, France
[b] University of Lausanne, Institute of Geophysics, CH-1015 Lausanne, Switzerland
[c] Colorado School of Mines, Green Center, Department of Geophysics, Golden, 80401 CO, USA
[d] ISTerre, CNRS, UMR CNRS 5275, Université de Savoie, 73376 Cedex, Le Bourget du Lac, France

ARTICLE INFO

Article history:
Received 10 May 2012
Accepted 10 July 2012
Available online 20 July 2012

Keywords:
Zeta potential
Gas bubble
Electrical double layer
Surface conductivity
Proton
Surface tension

ABSTRACT

Zeta potential is a physico-chemical parameter of particular importance to describe sorption of contaminants at the surface of gas bubbles. Nevertheless, the interpretation of electrophoretic mobilities of gas bubbles is complex. This is due to the specific behavior of the gas at interface and to the excess of electrical charge at interface, which is responsible for surface conductivity. We developed a surface complexation model based on the presence of negative surface sites because the balance of accepting and donating hydrogen bonds is broken at interface. By considering protons adsorbed on these sites followed by a diffuse layer, the electrical potential at the head-end of the diffuse layer is computed and considered to be equal to the zeta potential. The predicted zeta potential values are in very good agreement with the experimental data of H_2 bubbles for a broad range of pH and NaCl concentrations. This implies that the shear plane is located at the head-end of the diffuse layer, contradicting the assumption of the presence of a stagnant diffuse layer at the gas/water interface. Our model also successfully predicts the surface tension of air bubbles in a KCl solution.

1. Introduction

For an electrically charged gas/water interface, the zeta potential is defined as the electrical potential at the slipping plane that separates the stationary and mobile phases in tangential flow of the liquid with respect to the surface. In either distilled water or dilute 1:1 electrolytes (NaCl or KCl), gas bubbles (O_2, N_2, H_2) migrate in the opposite direction of an electrical field. This indicates that the surface of the gas/water interface is negatively charged, which in turn implies a negative zeta potential in both distilled water [1–4] and dilute 1:1 electrolytes [5–8].

Being able to predict the sign and the magnitude of the zeta potential of gas bubbles as a function of pH and salinity is of considerable importance in many fields including (i) industrial processes involving the presence of gas bubbles such as froth flotation, waste, and water treatment [4–6] and (ii) studies of contaminant transport in the vadose zone involving, for instance, ions, nanoparticles, and colloids sorbed onto the surface of the gas bubble (e.g., [9], [10]).

To date, few electrostatic surface complexation models have been developed to quantitatively predict the zeta potential of gas bubbles as a function of pH at low to medium salinities (10^{-5} to 10^{-1} M). Karraker and Radke [11], Manciu and Ruckenstein [12], and Gray-Weale and Beattie [13] considered surface adsorption of hydroxides ions OH^- to explain the negative surface charge of gas bubbles and used a Modified Poisson–Boltzmann (MPB) equation to compute the zeta potential of 1:1 dilute electrolytes (NaCl or KCl). The MPB equation accounts for ion free energies that are not described by the classical electrostatic Poisson–Boltzmann equation. These contributions to the Gibbs free energies of the ions explain image charge, dispersion, and solvation forces at the gas/water interface [14]. The image charge force theory [15,16] describes the electrostatic repulsive force acting on ions at the interface between two dielectric media. Indeed, a charge embedded in a dielectric is repelled by the charge density it induces on the dielectric boundary (Fig. 1). This force significantly influences the location of the ions near the surface at low ionic strengths (typically $\leqslant$0.2 M; [12]). Dispersion forces are estimated by calculating the change in the free energy of ion due to changes in the London-van der Waals interactions caused by the nearby interface [11,17]. Solvation or hydration forces describe the influence of the hydrogen bonding network of surface water molecules on the ion free energy [12,14].

There are, however, several drawbacks to using the MPB equation. The equation is non-linear and must be solved numerically. In addition, it requires the free energy values for each type of ion (to describe image, dispersion, and hydration forces), which are difficult to estimate a priori. Moreover, there is still no unified model

---

[*] Corresponding author. Address: BRGM, Water Division, 3 Avenue Claude Guillemin, 45060 Orléans Cedex 2, France. Fax: +33 (0)2 38 64 37 19.
E-mail address: p.leroy@brgm.fr (P. Leroy).

0021-9797/$ - see front matter © 2012 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.jcis.2012.07.029

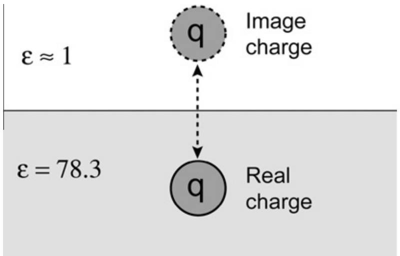

Fig. 1. The image charge force. The ion is repelled from the interface into the aqueous phase by an "image" charge of the same size and polarity (modified from Jungwirth and Tobias [18]).

based on the MBP equation to describe the electro-chemical properties of the gas/water interface.

Lutzenkirchen et al. [19] used a Four Layer Model (FLM) to describe the electro-chemical properties of hydrophobic media (gas, oil, diamonds, Teflon, and ice) in contact with 1:1 electrolytes. Their model corresponds to the classical Gouy–Chapman–Stern–Grahame model (commonly called the Triple Layer Model, TLM) with an additional plane located near the surface to represent the positive surface charge due to the preferential orientation of surface water molecules. Their work was inspired by the MD simulations of Zangi and Engberts [20] for the hard (hydrophobic) hydrocarbon wall/water interface and showed a great increase in hydroxides anions close to the surface. With this model, Lutzenkirchen et al. [19] successfully predicted the zeta potential data of the H_2/water interface. However, their surface complexation model needs nine parameters with a very high surface site density of 17.3 water molecules nm^{-2} and a significant and salinity-dependant distance between the head-end of the diffuse layer and the slipping plane. For example, these authors defined an empirical thickness of the "stagnant diffuse layer" of 22 nm at 10^{-4} M NaCl. This cannot be explained from a physical standpoint.

Another problem with previous studies is that their analyses are based on electrophoretic mobility measurements that are converted into apparent zeta potential data using the well-known Smoluchowski relationship [6]. However, this relationship does not consider the influence of surface conductivity on the electrophoretic mobility of the gas bubbles, and the ability of this approach to provide reliable estimates of the zeta potential is, therefore, questionable [13].

To the best of our knowledge, there has been no attempt to date to model the zeta potential of the gas/water interface taking into account surface conductivity in order to obtain intrinsic zeta potential values from electrophoretic mobility data. We propose here a unified and consistent model of the electro-chemical properties of the gas/water interface for 1:1 aqueous electrolytes like NaCl or KCl and at low ionic strengths (between 10^{-4} and 10^{-1} M). Our electrostatic surface complexation model is inspired of the traditional "one site/two *pK*" model applied to describe protonation/deprotonation at the surface of oxide minerals [21]. After a brief description of the possible mechanisms regulating the negative surface charge density of the gas/neat water interface, the interfacial model is presented and validated by comparison with corrected zeta potentials and surface tension data.

2. Theoretical background

2.1. On the origin of the negative electrophoretic mobility

The most likely charging mechanism of the gas/water interface involves the asymmetric dipoles of the surface water molecules, which are distributed to maximize their hydrogen bonding network in the under-coordinated environment. Vibrational Sum-Frequency Spectroscopy (VSFS) measurements for the vapor/water interface imply at least two different types of water layers within an interfacial region 6–9 Å thick [22–24]. Directly adjacent to the surface, these authors observed a thin layer in which water dipoles are oriented slightly into the bulk and possess "free" dangling OH (Fig. 2). This layer is called the "depletion layer" because the water molecules in this layer have fewer and weaker hydrogen bonding interactions than the tri- and tetrahedrally coordinated water molecules in the second layer. The hydrogen atoms of the water molecules in the second layer point toward the water phase. This leads to a positive electrostatic potential at the interface.

An explanation for the negative zeta potential of gas bubbles is related to an excess of hydroxide anions near the vapor/water surface [1,25]. Healy and Fuerstenau [26], Lutzenkirchen et al. [19], and Beattie et al. [25] considered the increased autolysis of surface water molecules. This increase results in a large excess of hydroxides, which compensates for the strong electrical field due to the preferential orientation of the water molecules. This was confirmed by MD simulations of the uncharged hydrocarbon wall/water interface [20,27]. However, the accumulation of hydroxides disappears in MD simulations with softer and less attractive hydrophobic media like vapor [28]. Moreover, for the vapor/water interface, selective spectroscopic techniques [23] and recent MD simulations [29] reported that H_3O^+, as opposed to OH^-, exhibits a relatively high affinity for the surface.

Consequently, the surface propensity of hydroxide anions and the chemical origin of the negative electrophoretic mobility of gas bubbles observed at neutral pH is still a subject of debate. Vacha et al. [30] recently used Sum-Frequency Spectroscopy measurements to characterize the oil/water interface and observed no sign of specific adsorption of hydroxides at this interface. They suggested that surface water molecules become partially charged due to a lack of balance between the number of donating and accepting hydrogen bonds. This can be responsible for the negative interfacial charge. We use this last hypothesis and consider the presence of negative surface sites "X^-" originated from charged surface water molecules.

2.2. Surface complexation model

We propose the following surface complexation reactions at the gas/water interface using the traditional "one site/two *pK*" model of Davis et al. [21] for oxide minerals:

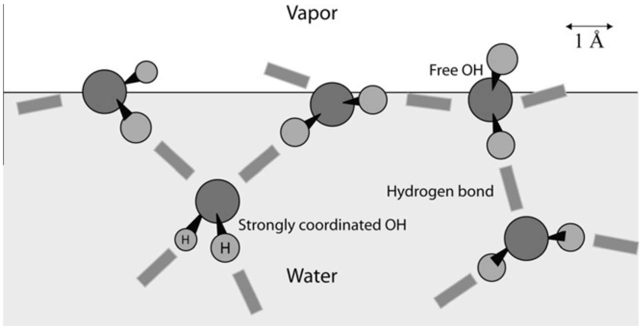

Fig. 2. The first two water layers with their hydrogen bonding network at the vapor/water interface according to Sum-Frequency Spectroscopy measurements (from Tarbuck et al. [23]). The topmost water layer is a thin depletion layer where water dipoles are oriented slightly into the bulk and possess "free" dangling OH. Water molecules in this layer have fewer and weaker hydrogen bonding interactions than tri- and tetrahedrally coordinated water molecules in the second layer where hydrogen atoms point preferentially toward the aqueous bulk phase, thus creating a positive electrical field.