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A novel method of measuring electrophoretic mobility of gas bubbles

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Abstract

Accurate measurement of electrophoretic mobility for gas bubbles is a challenging task as it requires the creation of a desired number of very small air bubbles to ensure negligible rise velocities during the course of the measurement. Here, we report a simple and reliable method for generating stable dispersions of "nano-bubbles." Preparation of such dispersions relies on the nucleation of nano-bubbles in solutions supersaturated with gas. Electrophoretic mobility of these nano-bubbles is determined by the ZetaPALS technique (Brookhaven Instruments) using Uzgiris electrodes coated with palladium. The Smoluchowski limit is assumed in the calculation of zeta potentials. In regard to reproducibility and reliability, this novel method shows a clear advantage over other existing techniques of zeta potential measurement for bubbles.

Keywords: Bubbles; Electrophoretic mobility; Oil sand; Process water; Zeta potential

1. Introduction

Gas bubbles dispersed in aqueous media carry a surface charge whose value depends on the solution chemistry. The most common approach for determining the bubble surface charge is through electrophoretic mobility measurements, from which zeta potential values are calculated [1–6]. The main source of error in electrophoretic mobility studies stems from the high rise velocities of the bubbles in a gravitational field. The problem is especially severe for large (i.e., millimeter-sized) bubbles as the rise velocities are much higher than velocities due to electrophoresis. It is therefore of no surprise that researchers have attempted to devise techniques to either generate smaller bubbles to reduce the rising velocity or to somehow minimize the effects of buoyancy during electrophoretic mobility measurements. For example, Sherwood [5] used a rotating cell to counteract buoyancy effects with centrifugal forces. The bubble was kept in the center of a cylindrical rotating cell and was free to move along the cell axis in response to an applied field. The measured eletrophoretic mobility of the bubble was corrected for the Taylor column effect (centrifugal force effect). Li and Somasundaran [4] used a Buchner funnel connected to a glass frit with pores 2–2.5 µm in diameter to generate small bubbles. A peristaltic pump was used to keep the bubble-in-water dispersion in circulation and thus prevent bubble rises and coalescence. Periodically, a sample of the dispersion was directed into an observation cell for electrophoretic mobility measurement. Yang et al. [7] moved the camera at the same speed as the velocity of the rising bubble to trace the bubbles vertically. The horizontal velocity of the bubble, which is due to an applied electric field, was used to calculate the zeta potential with high precision. Despite the remarkable accuracy of the above-mentioned methods, they are very difficult to carry out and often require much practice and experimental skills.

Kubota et al. [6], and Okada and Akagi [1] used an interesting approach to generate small bubbles in surfactant solutions and measured their electrophoretic mobility. Air was dissolved in three aqueous solutions, each containing a different type of surfactant (sodium dodecylbenzene sulfonate, sodium dodecyl sulfate, and cetylpyridium chloride) under high pressure (∼5 atm). When the air-saturated solution was exposed to atmospheric pressure, air bubbles nucleated in the solution. Larger bubbles were allowed to float to the top while the small bubbles (microns in size) formed a dispersion that remained stable for several hours. A dispersion thus formed was intro-

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duced into a conventional electrophoresis cell and the velocities of the bubbles were measured at the stationary plane. Zeta potentials were calculated from electrophoretic mobilities using the Smoluchowski equation (presented later in this communication) and trends for zeta potential versus concentration and type of surfactants were determined. Takahashi [9] introduced another method for zeta potential measurements. This method for bubble generation was similar to what Li and Sumasundaran proposed except that vertically positioned electrophoresis cell and graphic data processing method were used to obtain zeta potential values. The study of the effect of alcohol on bubble zeta potential is one of the interesting aspects of Takahashi's study [9]. More recently, Kim et al. [8] used an ultrasonic dismemberator and palladium electrode to generate nano-sized bubbles. The authors reported that their bubble dispersions were of sufficient stability to conduct electrophoretic mobility measurements.

In this study, we follow the concept of nucleating nanobubbles in solutions saturated with gas molecules to produce bubble dispersions. Our approach is different from those proposed in the past [1,6] as it relies on changes in temperature, rather than changes in pressure, to initiate bubble nucleation. Generating bubbles by temperature control allows us to generate sufficient number of bubbles for the measurement. The nano-bubbles generated in the aqueous phase can remain dispersed for sufficient duration (several minutes) to allow for reproducible zeta potential measurements.

2. Novel approach for generation of small air bubbles

In this study, a simple and reliable method is proposed to generate dispersions of gas nano-bubbles, for which electrophoretic mobility can be measured using conventional means. Preparation of dispersion is based on the concept of bubble nucleation in a gas-supersaturated solution. The method is similar to the approach by Kubota et al. [6] and Okada and Akagi [1] in the sense that gas bubbles are nucleated in gas-saturated aqueous solutions. The nucleation of bubbles, however, is controlled here by temperature rather than pressure. Without the need for high pressure equipments, this method of preparing gas bubble dispersions is much easier to adopt in the laboratory and has better control for desired number of bubbles.

2.1. Gas dissolution in liquid

The effects of temperature on the dissolution of gases in liquids have been studied for many years and there are several empirical equations that can be used for determination of gas concentration in liquids [10–12]. As an example, we analyze here the dissolution of air in water.

Air is composed of several different gases, including nitrogen, oxygen, argon, carbon dioxide and others; the relative amounts of gases in air are shown in Table 1. Because oxygen and nitrogen are the dominant components of air, their dissolution in liquids is more often analyzed than for other gases.

Table 1
Composition of air [11]

Component	Symbol	Volume (%)
Nitrogen	N_2	78.08
Oxygen	O_2	20.95
Argon	Ar	0.94
Other gases		0.03

Oxygen dissolution in water obeys Henry's law with the dissolved amount roughly proportional to the partial pressure of oxygen in air; i.e.,

$$p_{O_2} = K_{O_2} \times x_{O_2}, \tag{1}$$

where p_{O_2} is the partial pressure of oxygen in air, x_{O_2} is the mole fraction of O_2 in oxygen-saturated water, and $K_{O_2}(T)$ is the Henry's law constant for oxygen in water.

Although Henry's law is important in the analysis of gas solubility in liquids, it does not describe the effect of temperature on dissolved gas molecules—at least not directly. Many empirical equations are now available in the literature to estimate oxygen solubility in liquids as a function of temperature, pressure, and humidity [10–12]. Here we present only a few of such equations.

The concentration of oxygen in air saturated water can be determined from the following empirical equations [11]:

(i) for $0\,^\circ\mathrm{C} < T < 30\,^\circ\mathrm{C}$,

$$C_{O_2} = \frac{0.678(P-p)}{35+T}, \tag{2}$$

(ii) for $30\,^\circ\mathrm{C} < T < 50\,^\circ\mathrm{C}$,

$$C_{O_2} = \frac{0.827(P-p)}{49+T}, \tag{3}$$

where C_{O_2} is the concentration of oxygen in water ($\mathrm{mg\ O_2/L}$), P is the barometric pressure Torr ($1\ \mathrm{Torr} = 133.32\ \mathrm{Pa}$), p is the vapor pressure of water (Torr), and T is the temperature (°C).

The concentration of nitrogen, neon and argon in aqueous salt solutions under atmospheric pressure can be calculated from the empirical correlation introduced by Garcia and Gordon [11]:

$$\ln(C) = A_0 + A_1 T_S + A_2 T_S^2 + A_3 T_S^3 + S\big(B_0 + B_1 T_S + B_2 T_S^2\big), \tag{4}$$

where $T_S = \ln(\frac{298.15-T}{273.15+T})$.

In the above expression, C is the gas concentration in the liquid at atmospheric pressure (nmol/kg for Ne and μmol/kg for N_2 and Ar), T is the temperature (°C). All coefficients are listed in Table 2 and definition of salinity S (PSS, Practical Salinity Scale) are provided in Ref. [11].

Fig. 1 shows the concentrations of oxygen, nitrogen and air in gas-saturated water at temperatures ranging from 0 to 50 °C calculated by Eqs. (2)–(4). As shown, the dissolution of all three gases can be increased by reducing the temperature of water.

2.2. Generation of nano-bubbles

A liquid can easily be saturated with a gas by bubbling the gas through the liquid at a low temperature. Then, according to