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# Micro-electrode system designed to determine $H^+$ concentration distribution at particle-water interface

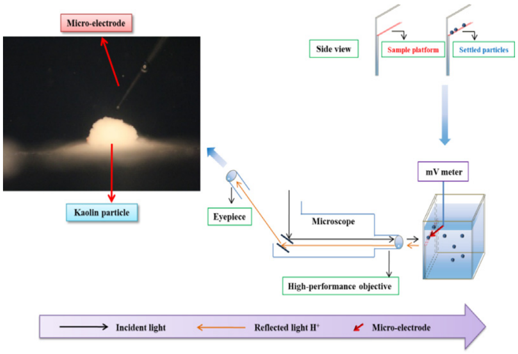
Liang Kuang [a,b], Huijuan Liu [b,c], Baiwen Ma [a,*], William A. Jefferson [a], Gong Zhang [a], Jiuhui Qu [a,b]

[a] Key Laboratory of Drinking Water Science and Technology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China
[c] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

## HIGHLIGHTS

- A designed $H^+$ selective micro-electrode instrument system was developed.
- $H^+$ concentration distribution at the particle-water interface was determined.
- The experimental results agree with general assumptions of EDL theory.
- Compressible effect of the electric double layer was verified.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The current understanding of the particle-water interface relies primarily on the use of electric double layer theory (EDL theory), in which the concentration distribution of ions with distance can be evaluated. However, although EDL theory provides a theoretical and mathematical basis, obtaining direct experimental results is also necessary. In this study, an instrument system set with a designed $H^+$ selective micro-electrode was developed for *in situ* determination at the particle-water interface, and a preliminary investigation of the $H^+$ concentration distribution at the particle-water interface was enabled using data collection at 1 nm/step. The experimental results agree with EDL theory and provide direct evidence to support its general assumptions. The compressible effect of the electric double layer with an increase in ionic strength is verified, and the defined length of the diffusion layer in this investigation is shown to have an approximately inverse proportion to the square root of ionic strength. The rise in $H^+$ concentration near the particle surface is also determined during interactions between trace $Fe^{3+}$ and particles. Results indicate that the method reported here can be applied to conduct dynamic *in situ* observations; based on its excellent performance, this innovative instrument system has great potential for interface mechanism research in the water environment.

## 1. Introduction

Solid matter is often present as dispersed particles in natural water; therefore, particle-water interface reactions play a major role in the water environment (Baier et al., 1968; Spaarnaay, 1972; Grahame,

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* Corresponding author.
*E-mail address:* bwma@rcees.ac.cn (B. Ma).

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1947; James and Healy, 1972; Lal, 1977), and such interactions at the particle-water interface include important aquatic chemical processes such as adsorption, coordination, and precipitation (Ji et al., 2015; Lykema, 1976a, b; Vicek et al., 2007). The particle-water interface is of central importance in colloid stability studies, where processes that occur effect the chemical fate of various kinds of substances, ions, and particles, and alter their chemistry speciation, stability, and toxicity (Boyle et al., 1977; Edzwald et al., 1974; Matjievic, 1977; Thuer and Stumm, 1978).

The most accepted and commonly applied methods to describe the particle-water interface are based on the electric double layer (EDL) hypothesis (Hayes et al., 1988), and related investigations have been primarily restricted to two perspectives (Ramanathn, 1988; Tao et al., 2000; Woelki and Kohler, 2000): (1) the use of calculation methods based on EDL theory, which has provided numerical simulations based on physical models and the new Triple-Layer Model (McCallum et al., 2017), where specifically absorbed ions are placed as partially solvated ions at the plane of closest approach; and (2) use of the determination method, which involves measuring the zeta potential (which is generally lower than the surface potential calculated in diffuse double layer theory). However, although the zeta potential reflects the potential difference between the plane of shear and the bulk phase, in reality, the distance between the surface and the shear plane cannot be defined. Other measurements of EDL properties have also been made, such as electrocapillarity using an electrochemical approach (Grahame, 1947), the specific adsorption of ions using X-ray photoelectron spectroscopy (XPS) (Brown et al., 2016; Kolb et al., 2010; Kolb, 2001; Wagner and Ross, 1983), and the potential drop using ambient pressure XPS (Favaro et al., 2016).

However, although both these perspectives emphasize the physical features in the particle-reaction process, the dynamic chemical factors are neglected to some extent and it is thus not possible to directly show the ion concentration gradient. In addition, zeta potential measurements require sampling from the reaction system, and this occurs on a timescale that may differ from that of the actual interfacial reactions.

EDL theory states that there should be variation in the charge distribution (concentration of positive and negative ions) with distance from the surface. This means that the ion concentration near the particle surface is different from that in the solution phase. However, direct *in situ* observations of the ion concentration distribution have not been achieved to date, and a better understanding of the structure of the double layer is required to push the boundaries of current aquatic interfacial studies (Lei et al., 2017; Loux and Anderson, 2001; Loux, 2006). Therefore, to solve this standing issue, we have designed a micro-electrode system to directly measure the $H^+$ concentration distribution at the particle-water interface. In addition, the $H^+$ concentration (pH value) is an aquatic parameter of unmistakable significance in the conformation and transformation of many chemical species, and as it is a positive ion, it is considered that its concentration distribution could be an indicator of the profile of the diffusion layer.

In this study, an instrument system set was developed that contains particles sedimentation submit, micro electrode displacement control submit, optical submit, data acquisition submit, and other subsystems. The instrument system can realize the subsidence and immobilization of mono-particles, present the edge of particles clearly in an optical field, move the micro-electrode in a range of nm (40 nm/step in coarse, 1 nm/step in fine), and can be controlled automatically. In this study, the *in situ* concentration distribution at the particle-water interface was measured, and results were compared with those of EDL theory. Subsequently, additional experiments were conducted to study changes in the $H^+$ concentration distribution at the interface in response to ionic strength variations and certain specifically absorbed processes.

## 2. Materials and methods

### 2.1. Micro-electrode preparation

The micro-electrode is the core component of the experimental device. However, currently available commercial micro-electrodes are not sufficiently fine and sensitive for the investigation of the particle-water interface, and we thus developed a new $H^+$ micro-electrode using a laser drawing process and an ion selective liquid filling process. The laser drawing process was conducted using a laser drawing instrument (Sutter P-2000, USA), in which the drawing heat, velocity, time, and pull strength were set to ensure that the tip diameter and shape of the micro-electrode met investigation requirements. The parameters of the Sutter P-2000 are as follows: HEAT = 320–350, FIL = 4, VEL = 75, PULL = 75–100. The $H^+$ selective liquid and electrolyte were then filled, and the electrode was connected to a mV meter with a reference electrode to indicate the pH value determined (Schulthess et al., 1981).

### 2.2. Preliminary observation platform of particles

It is difficult to directly observe particles when they move in a suspended state. Therefore, we designed a preliminary platform for the *in situ* observation of particles using optical vision. The system comprises a metallurgical microscope (Nikon IM4, Japan) and a square reactor that holds a settlement platform on one side, which is made from 0.17 mm ultra-thin glass and is roughly the size of a glass slide cover (as shown in Fig. 1). The platform is designed to capture particles and is a natural place for them to settle. The line of sight of the observer is horizontally aligned with the observation sample and is thus distinguished from the vertical optical path of the conventional microscopic observation mode. The sample platform on which particulate matter is settled can thus be placed vertically, and the side of the sample platform can be used as the angle of observation.

In the process, a metallurgical microscope is firstly used to determine the position of the captured particles on the settlement platform, and it particularly identifies the edge of particles in the optical field resolution. The tip of the micro-electrode is then slowly moved toward the particle surface in very fine increments, to limit any disturbance to the settled particles.

### 2.3. Displacement control of the micro-electrode and pH determination

The displacement of the micro-electrode is controlled by a micromanipulator with a resolution of 40 nm (MP285, Sutter, USA) and a piezo positioning system with a resolution of 1 nm (P-363 PicoCube scanner and E-563 PicoCube controller, PI, Germany). The control interface of the piezo positioning system is shown in Fig. S1. The displacement of the micro-electrode is recorded using a combination of these two pieces of equipment. The distance between the tip of the micro-electrode and the surface of the particle is analyzed by recording changes in the $H^+$ concentration from the micro-electrode feedback. As the pH near the surface of the particle is different from the $H^+$ concentration of the bulk solution, a certain gradient is evident. The reading point notes continual changes in the $H^+$ concentration of the micro-electrode up to a certain point at which a constant value of the micro-electrode is achieved. This position is then regarded as being the zero position, and the distance of the tip from the surface of the particle is zero. The micro-electrode is then withdrawn, and the $H^+$ concentration of the surface micro-environment is measured by using the $H^+$ concentration at different distances of 1 nm, 2 nm, and 3 nm, respectively. All measurements are determined under $N_2$ protection, and all equipment is placed on an air-floating optical platform to reduce disturbance from vibration.