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Zeta potential determination with a microchannel fabricated in solidified solvents

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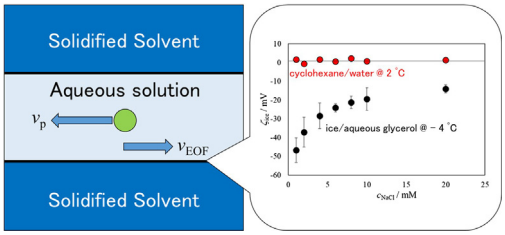
GRAPHICAL ABSTRACT



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ABSTRACT

This paper proposes a simple and versatile method for the determination of the zeta potential of a channel wall and discusses the values measured for the surface of frozen solvents, which are not only of scientific interest but also of potential use for microfluidic platforms. The zeta potential of the solid surface is an important parameter for discussing its electrokinetic properties, the distribution and reaction of ions in an electric double layer, and the fluidic behavior in the space surrounded by the surface. While the zeta potential of colloidal matters can be determined from their electrophoretic mobility, it is often difficult to determine that of a bulk material. In this paper, the zeta potential of a microchannel fabricated in a frozen solvent is determined by measuring the apparent mobility of microparticles as the probe. The electrophoretic mobility of the microparticles has been measured in advance using microchip electrophoresis under various conditions. This approach allows us to determine the zeta potential of water-ice and frozen cyclohexane. We discuss the pH dependence of the zeta potential of ice and also effects of the NaCl concentration on that of ice and frozen cyclohexane.

1. Introduction

The zeta potential is a useful measure of the electrostatic properties of interfaces widely employed to evaluate the stability of colloids, electrokinetic phenomena, and interactions of ionic solutes [1–4]. The zeta potential of colloids and particulate matter is often determined from their electrophoretic mobility. This principle is applied in commercially available instruments, i.e., zeta potential analyzers [5]. Another method is based on the ultrasonic vibration potential (UVP), which is generated when an ensemble of particles vibrates and is periodically polarized in an ultrasonic field [6–8]. UVP measurements are applicable to highly concentrated particle suspensions, in which electrophoretic measurements are difficult.

The zeta potential of a channel wall is also a critical parameter in microfluidics, in which a fluid is precisely manipulated in the nL–pL scale. An electroosmotic flow (EOF) instead of a pressurized flow is often employed to deliver a liquid to channels since high pressure resistance causes no practical problems in the former case [9–12]. The zeta potential of a microchannel wall should be quantitatively known for the prediction and precise control of the EOF in such systems, which is determined by the zeta potential

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of the channel wall. Direct observation of the EOF using a fluorescence dye is one of the common methods for zeta potential evaluation in microfluidics [13–15]. However, precise measurements are difficult, particularly at low EOF rates. Although streaming potential measurements can also be employed for the determination of the zeta potential of a microchannel wall [16,17], their applicability to highly viscous liquids is severely restricted. Thus, zeta potential determination in microfluidics is not straightforward in some cases.

We have recently proposed a new concept for a microfluidic device using a frozen solvent, such as water-ice, instead of glass and plastics [18–20]. This approach has several methodological advantages: (1) the channel dimensions can be varied in a wide range by controlling the temperature and concentration of the solution before freezing, (2) frozen-solvent devices can be repeatedly fabricated by thawing–freezing cycles, and (3) a liquid-core waveguide can be fabricated using ice cladding because water-ice has a refractive index lower than that of most liquids [18]. Although we have employed ice as the main material for the fabrication of frozen solvent microdevices, other materials can also be used for this purpose. Different surface characteristics would allow us to construct novel analysis and separation systems. The zeta potential of frozen device surfaces is an important parameter for the design of effective systems and their efficient operation. However, the determination of reliable zeta potentials is elusive. In this paper, we present a robust method for the measurement of the zeta potential of the surface of frozen solvents, namely water-ice and frozen cyclohexane as model solvents, using the migration of microparticles as the probe. The present method is applicable to systems with entirely different surface characteristics.

2. Methods and materials

The electrophoretic mobility of microparticles (μ_P) in various solutions was determined by microchip electrophoresis by controlling the temperature on a Peltier unit (Fig. S1). This method provides reliable data even under harsh conditions where commercially available zeta potential analyzers are not applicable, e.g., low temperatures, highly viscous media, and high salt concentrations. A glass-made microchip having a crossed channel with 50 μm in width and 20 μm in depth (Micronit Co.) was used. The length of the separation and injection channels were 35 mm and 10 mm, respectively. The microchip was placed on a Peltier unit (Takagi Manufacturing Co., Ltd.), which was driven by a Peltier controller (Model TDC-2030R, Cell System). Polypropylene pipette chips, which were fitted to solution introduction holes of the microchip, acted as solution reservoirs. The microchannel was filled with the running solution, which was water-glycerol or aqueous NaCl. Carboxyl-modified polystyrene (PS) particles with 1 μm diameter (Polyscience Inc.) was injected to the channel as a probe with rhodamine B as the EOF marker. MCE was performed by applying voltages to Pt electrodes inserted in reservoirs. As an injection process, the negative-pressure pinched injection method was employed because the viscosity of the running solution was very high for the high glycerol concentrations. The sample solution was introduced to the injection channel, by negative pressure, which was applied to the sample waste reservoir. After the channel was completely filled with the sample, a voltage of 3.0 kV was applied to the reservoirs at both ends of the separation channel using a high voltage power supplier (HCZE-30P, Matsusada Precision Inc.). A small volume of the sample was introduced in the separation channel. The PS particles were stained with Yellow Green dye (λ_{ex} = 441 nm; λ_{em} = 486 nm) so that fluorescence detection of the particles was possible. The EOF and probe migration were observed with a laser confocal microscope (FV1200, Olympus). The velocities of EOF and probes were determined from captured movies.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcis.2018.07.137.

Fig. 1 schematically illustrates the fabrication of a microchannel in bulk ice. A polystyrene foam cell (3 cm width × 3 cm depth × 1 cm height) was placed on a Peltier unit. The bottom of the cell was sealed with a PTFE sheet. Half of the cell was filled with 4.5 mL of purified water, which was then completely frozen (Fig. 1A). A fused silica capillary (outer diameter, 150 μm; inner diameter, 75 μm; GL Sciences Inc.) was placed on the ice surface (Fig. 1B). The end of the capillary was connected to a microtube, which was fitted to a syringe. At the same time, a thermocouple was placed near the capillary to monitor the temperature. Another 4.5 mL of purified water was poured into the cell; thus, the capillary and thermocouple were immersed in water. The temperature was then set to

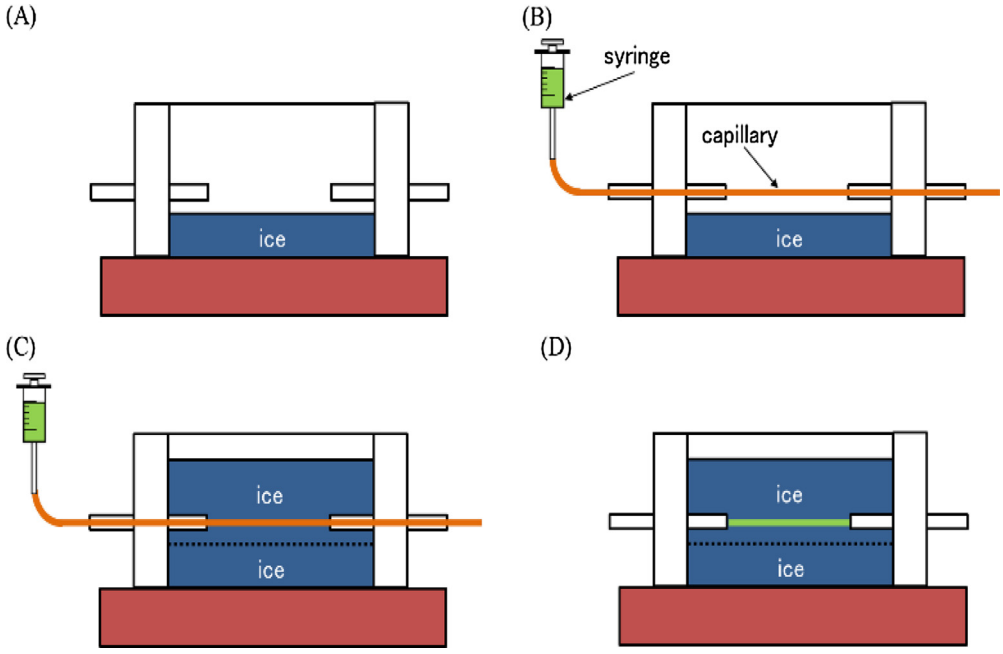

Fig. 1. Schematic illustration of the ice microchannel fabrication process.