

DEVELOPMENT OF DIELECTRIC CONSTANT MEASUREMENT METHOD FOR UNIQUE REACTION IN EXTENDED-NANO SPACE

Kyojiro Morikawa¹, Yutaka Kazoe¹, Kazuma Mawatari¹, Takehiko Tsukahara², Takehiko Kitamori¹

¹ Department of Applied Chemistry, School of Engineering, The University of Tokyo, JAPAN,

² Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, JAPAN

ABSTRACT

We developed a novel measurement method of dielectric constant of liquids in 10^1 - 10^3 nm space (extended-nano space). Using our streaming potential system [1], dielectric constant was measured by regarding an extended-nano channel as an electric circuit. We revealed that the dielectric constant of water in extended-nano space was dramatically decreased (approximately 1/4 in 580 nm channel compared to the bulk). The obtained unique results will be important information for unique reaction in extended-nano space, and this tool will contribute novel reaction analysis systems.

KEYWORDS

Dielectric constant measurement, extended-nano space, water property, streaming potential

INTRODUCTION

Recently, an extended-nano space has attracted much attention as new chemical reaction field due to its extremely high surface-to-volume ratio. For example, polymerizing reaction of hydrophobic molecules is accelerated in extended-nano space using hydrophilic glass surface [2]. Also in this space, uniquely structured water molecules with high proton mobility [3] are suggested. In order to utilize it as a new chemical reactions field, information of polar character of liquid depended on dielectric constant are strongly required. As a reason for this requirement, dielectric constant of solvent is very important parameter in chemical reaction with considering electrostatic force between reactants. In addition, electrostatic force between reactant and surface should be considered in surface-dominant extended-nano space. However, the measurement of dielectric constant of liquid in extended-nano space is difficult due to lack of analysis tools. For example, impedance measurements with AC [4] evaluate total capacitance which includes that of the surrounding material (glass in our case), electrodes and so on. In this study, we developed dielectric constant measurement method with DC by regarding an extended-nano channel as an electric circuit. With the electric circuit using Ohm's law and Coulomb's law, dielectric constant of liquids in extended-nano space were quantitatively evaluated. Obtained dielectric constant in extended-nano space was dramatically lower than that in bulk, and contribution of the unique dielectric constant to chemical reaction was discussed.

EXPERIMENT

Extended-nano channel for the measurement were fabricated on the synthetic quartz glass plate by electron beam lithography and plasma etching. Also, micro-meter-sized channels for the introduction of sample in the measurement channel on another plate, and they were thermally bonded at 1080 degree C [5]. Sample was filled in a chip and it was controlled by a pressure controller. The streaming potential is observed when the cation layer was moved by the hydrodynamic flow and the signal was detected by electrodes. Regarding the channel as electric circuit, the streaming potential depended on the channel electric capacitance C and the electric resistance R (Figure 1). All experiments were performed at room temperature (20 degree C).

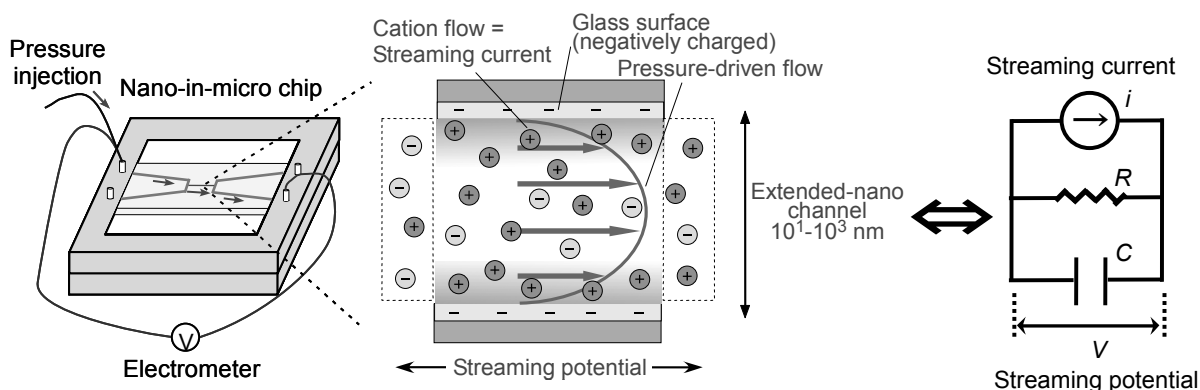


Figure 1. Concept of regarding electrokinetic phenomena in an extended-nano channel as electric circuit

RESULTS AND DISCUSSION

Streaming potential was gradually increased with applied pressure. From the circuit equation, streaming potential was functionalized by time t with the channel capacitance C , the resistance R , and the streaming potential in static state V_s .

$$V(t) = V_s \left[1 - \exp\left(-\frac{1}{CR}t\right) \right] \quad (1)$$

Streaming potential was fitted to equation 1 as shown in Figure 2. Using the result in Figure 2, the value of CR was obtained. Also, R was evaluated from current measurement with applying voltage. As shown in Figure 3, the current value and the applied voltage had good linear relationship corresponding Ohm's law, and R was obtained from its slope. With the results in Figure 2 and Figure 3, C was obtained. In the next experiment, cell constant of the setup was evaluated. Capacitance was expressed as a product of dielectric constant ϵ_r and cell constant. Relationship between capacitance and dielectric constant was evaluated by measurements using various solvent in Table 1. As shown in Figure 4, they showed linear relationship and cell constant was obtained from its slope. Thus, dielectric constant was obtained from measured capacitance and cell constant.

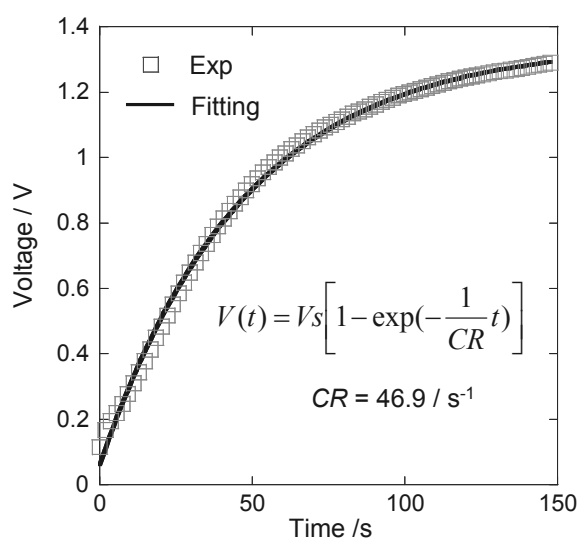


Figure 2. Time variation of streaming potential and its fitting result; channel size was 1190 nm, sample was DI water

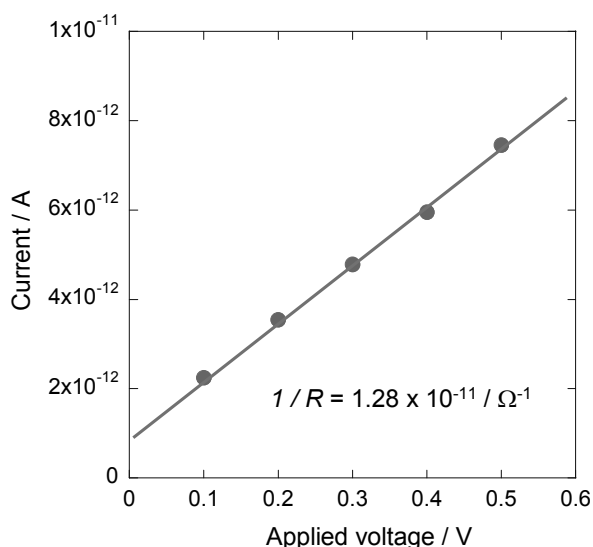


Figure 3. Relationship between current and applied voltage; channel size was 1190 nm, sample was DI water

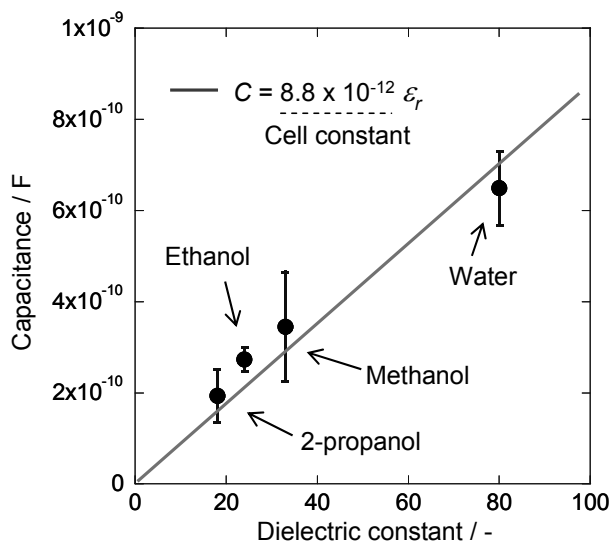


Figure 4. Relationship between dielectric constant and capacitance; channel size was 1190 nm

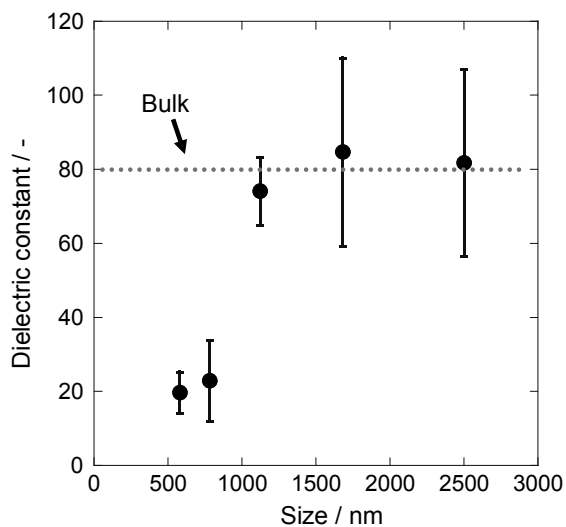


Figure 5. Size dependency of dielectric constant; sample was DI water

Table 1. Used samples and their dielectric constant in bulk

Sample	Dielectric constant ϵ_r
Water	80
Methanol	33
Ethanol	24
2-propanol	18

Table 2. Sizes of channels used in measurements

Channel size	Channel width	Channel depth
580 nm	610 nm	560 nm
770 nm	750 nm	790 nm
1190 nm	1380 nm	1050 nm
1650 nm	1580 nm	1730 nm
2500 nm	2500 nm	2500 nm

Finally, size dependency of dielectric constant of water was evaluated (Figure 5). Sizes of the channels used in measurements were shown in Table 2. In the space over 1000 nm, same dielectric constant as bulk ($\epsilon_r = 80$) was obtained. This showed that water in micro space can be treated as normal water in bulk. However, in extended-nano space, it was dramatically decreased compared to the bulk (approximately 1/4). Lower dielectric constant means that water molecules are more oriented. Considering proton transfer phase model in reference 3, water molecules in extended-nano space are loosely structured near the surface. Such water structure like network is considered to have high orientation, and our results have good agreement with its model. From these results, due to lower dielectric constant of water in extended-nano space, electrostatic shielding is considered to be weaker in this space. We expect that reaction using electrostatic interaction between reactants or between reactant and surface is accelerated in extended-nano space.

CONCLUSION

We developed novel dielectric constant measurement method by regarding an extended-nano channel as an electric circuit. Measured streaming potential signals were fitted in the electric circuit equation, and electric capacitance values with various solvents were obtained. Thus, applicability of our setup was shown and our method can be applied to various reaction systems. We also revealed that water in extended-nano space has lower dielectric constant compared to the bulk. This result had good agreement with proton transfer phase model. Due to lower dielectric constant of water in extended-nano space, electrostatic shielding is considered to be weaker in this space. We believe that unique chemical reaction can be performed using unique dielectric constant, and novel analysis systems for reaction using extended-nano channels can be achieved using our system.

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CONTACT

Takehiko Kitamori +81-3-5841-7231 or kitamori@icl.t.u-tokyo.ac.jp