MULTI-STEP MIXING IN EXTENDED NANOSPACE BY CONTINUOUS FLOW CHEMICAL PROCESSING WITH EFFECT OF ION HYDRATION ON LIQUID PROPERTY

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ABSTRACT

We report multi-step mixing of aqueous solutions of different ion concentration in a T-shaped nanochannel, where symmetry of mixing was broken by the ion hydration effect. When the ion species is K^+ of small hydration radius, the fluidic resistance was increased as pure water probably due to different liquid structure by loosely coupled water molecules by the confinement, while Na^+ and Li^+ of large hydration radius made the fluidic resistance same as the bulk. The present study will contribute to develop nanofluidic systems for integration of chemical processes.

KEYWORDS

Extended nanospace, mixing, ion hydration, pressure driven flow.

INTRODUCTION

Recent studies of extended nanospace (10-1000 nm) have suggested potential of new engineering field of integrated chemical systems by revealing specific properties of liquid and chemical reaction [1]. In order to develop fluidic systems by extended nanochannels, a methodology of system engineering for integration of chemical processes is strongly required. Our group has developed a concept of integration by connecting units of chemical process, e.g., mixing, reaction and separation, in parallel and series [2]. Although this method is expected to be applicable to extended nanospace, the specific liquid property must to be considered to design the fluidic network by extended nanochannels (Figure 1). Especially, since previous studies suggested a possibility that water molecules are loosely coupled from the surface and affect the liquid property [1], the ion hydration is an important factor to be considered. Therefore we investigated the effect of the ion hydration on the mixing in the nanochannel and proposed a concept of designing nanofluidic network.

EXPERIMENTAL SECTION

Figure 2 illustrates schematics of (a) an experimental setup and (b) a T-shaped nanochannel. The extended-nano and microchannels were fabricated on a glass substrate by electron beam lithography and plasma etching. The mixing in the T-shaped extended nanochannel of (1700 nm and 1200 nm widths and 600 nm depth) by pressure driven flow control was investigated. Mixing of pure water and electrolyte solution was conducted for KCl, NaCl and LiCl of a concentration of 1 M. These ions have different property of hydration: K^+ and Cl^- with hydration radius smaller than 3 Å don't have any effect on the orientation of water molecules, while Na^+ and Li^+ with hydration radius larger than 4 Å affect the orientation. A 20 μM Alexa Fluor 488 was dissolved into the electrolyte solution to evaluate the mixing. The mixing ratio was observed by a fluorescence microscope, based on an assumption that the fluorescent intensity is proportional to the concentration of fluorescent molecules. The fluorescent intensity normalized by that without mixing was used for the evaluation.

After the mixing in the T-shaped nanochannel, two-step mixing in extended nanospace was demonstrated. Pure water and 1M LiCl solution containing Alexa Fluor 488 were prepared. Considering results obtained from one-step mixing, values of applied pressure to the nanochannel were determined.

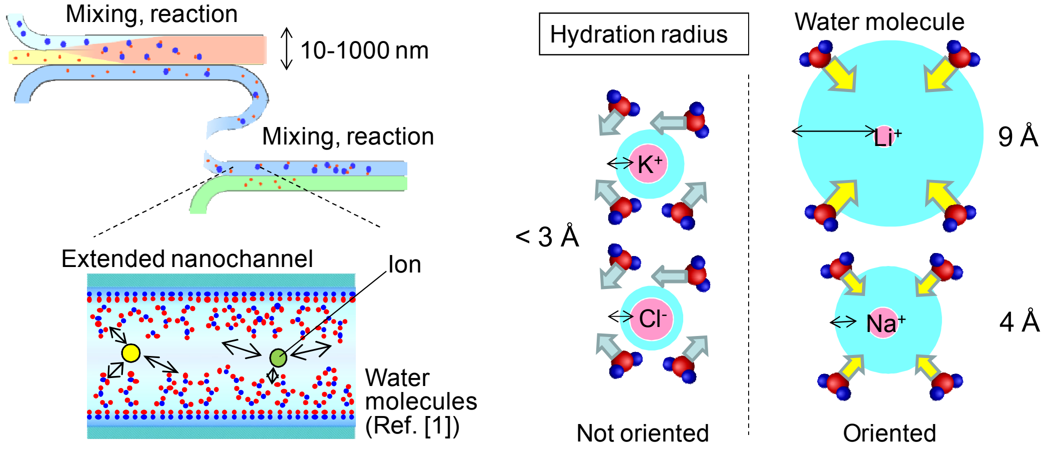


Figure 1. Schematic illustration of integration of chemical process into extended nanochannels considering an effect of ion hydration on a liquid property derived from loosely coupled water molecules from the surface.

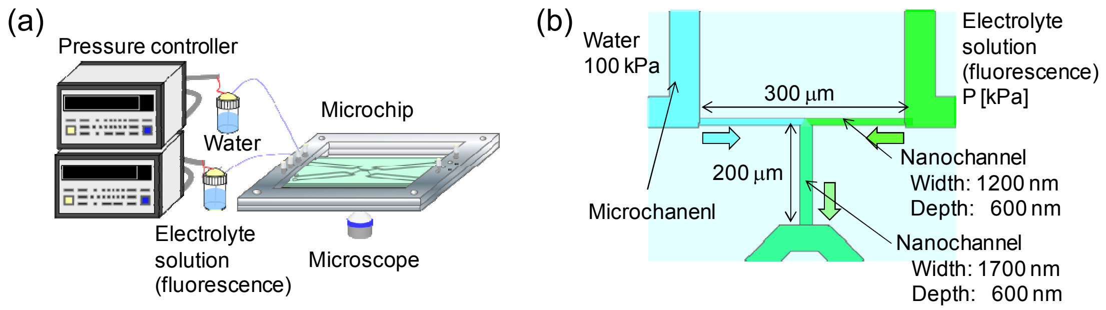


Figure 2. Schematics of (a) an experimental setup and (b) a T-shaped extended nanochannel for the mixing.

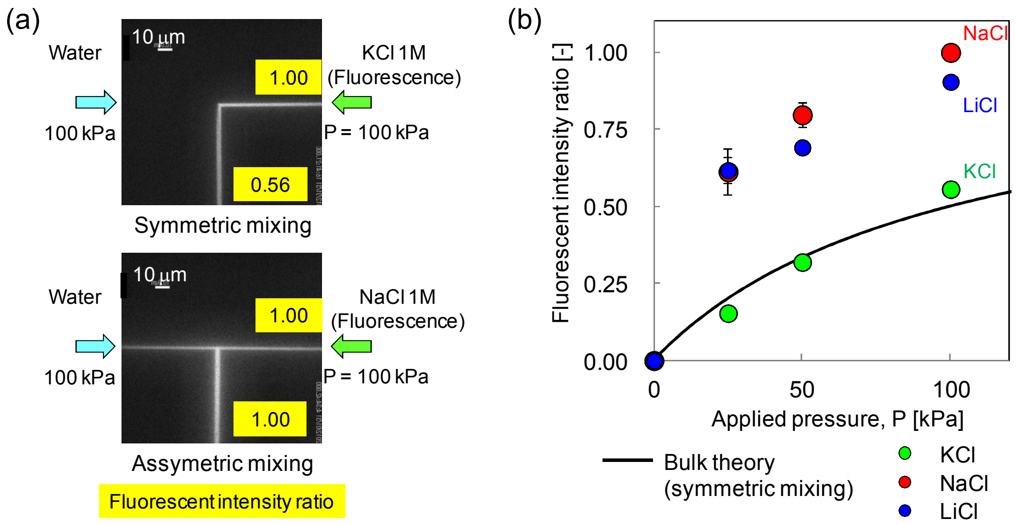


Figure 3. (a) Fluorescence images for mixing of KCl 1M and that of NaCl 1M. Applied pressures toward pure water and electrolyte solution were 100 kPa. (b) Ratio of fluorescent intensity (mixing outlet/mixing inlet) as function of applied pressure toward electrolyte solution for various ion species.

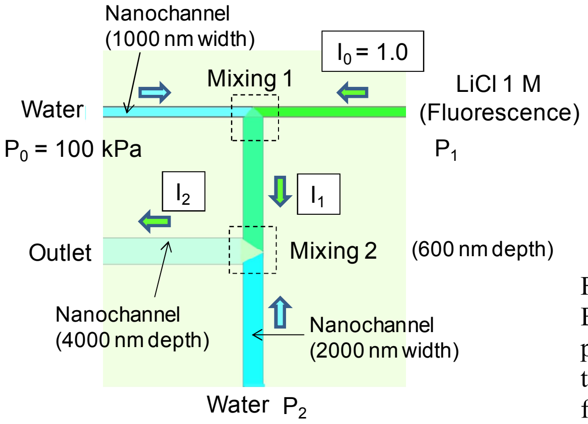
RESULTS AND DISCUSSION

Figure 3 shows results of the mixing in the T-shaped nanochannel. As shown in the fluorescence image (Figure 3(a)), almost symmetric mixing was observed for 1 M KCl solution at equivalent pressures of 100 kPa. On the other hand, in case of NaCl, the symmetry was broken, and only the electrolyte solution was injected into the nanochannel probably due to lower fluidic resistance of the electrolyte solution than water. Figure 3(b) shows mixing ratio, which is proportional to the fluorescent intensity ratio, as function of the applied pressure to the electrolyte solution for KCl, NaCl and LiCl. Mixing for KCl solution shows symmetric property, while mixing for NaCl and LiCl shows asymmetric property. Considering that ion hydration effect of K^+ and Cl^- on water structure is generally negligible due to hydration radii smaller than 3 Å, one possible reason for asymmetric mixing is ion hydration by Na^+ and Li^+ of hydration radii larger than 4 Å, which affects orientation of water molecules by hydrogen bonding. Our previous work suggests that water confined in extended nanospace has higher viscosity than the bulk due to specific liquid structure derived from loosely coupled water molecules by hydrogen bonding [1]. Based on this understanding, it is considered that the ion hydration with large hydration radii cancels the hydrogen bonding network of water molecules induced by the confinement in extended nanospace, and this results in the viscosity similar to the bulk and asymmetric mixing.

The results obtained from this work were applied to achieve two-step mixing of 1M LiCl with water (1/2 by first mixing, 1/4 by second mixing) as shown in Figure 4. The nanochannel of 600 nm depth was fabricated on fused-silica glass. For the first mixing, the widths of the branch channel and mixing channel were 1000 nm and 200 nm respectively, while those for the second mixing were 2000 nm and 4000 nm. A 100 kPa pressure was applied to water in the first mixing channel, and pressures applied to other two inlets, P_1 and P_2, were determined based on two cases, bulk theory and results shown in Figure 3. The result suggests that the pressure values determined based on the present study shows improvement in the two-step mixing toward the bulk theory which doesn't consider the ion hydration effect. The knowledge obtained from the present study suggests importance of the design of nanofluidic system considering the specific liquid property in nanospace.

CONCLUSIONS

Mixing of the electrolyte solution in extended nanospace was studied. Symmetry of the mixing by equivalent pressures was broken when the ion hydration radii is larger than 4 Å, where the ion hydration affects orientation of water molecules by hydrogen bonding. Results suggested that the specific liquid structure with loosely coupled



	P_1	P_2	I_1	I_2
Bulk theory	100 kPa	44 kPa	0.75	0.50
Present study	18 kPa	49 kPa	0.39	0.30
(Identical)	–	–	(0.50)	(0.25)

Figure 4. Results of two-step mixing of LiCl 1M solution. Experiments were conducted for values of applied pressure based on the bulk theory (symmetric mixing) and the results of the present study. *P*: applied pressure, *I*: fluorescent intensity ratio (mixing outlet/mixing inlet).

water molecules by hydrogen bonding, which is induced in extended nanospace, is broken by ion hydration effect, and results in the asymmetric mixing.

Two-step mixing in extended nanochannel was demonstrated considering the specific mixing property revealed in this study. The results showed improvement of mixing close to identical values compared with the case when the parameters were decided based on the bulk theory. The knowledge obtained from this study suggests an importance of specific liquid properties for designing nanofluidic system for various chemical applications.

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