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Short communication

Electroosmotic flow in poly(dimethylsiloxane) microchannels

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Abstract

This paper reports on the study of electroosmotic flow (EOF) in poly(dimethylsiloxane) (PDMS) microchannels on the basis of indirect amperometric detection method. Gradual increase of EOF rate in freshly prepared PDMS microchannels was observed with the running buffer of phosphate buffer solution (PBS). With the same concentration (10 mM) of PBS containing different cations and the same pH value (7.0) and, the time of the stable EOF in PDMS microchannels under the applied separation voltage of 1000 V was 49.8 s (Li^+-PBS), 57.1 s (Na^+-PBS), 91 s (K^+-PBS), respectively. Meanwhile, the different adsorption of cations (Li^+, Na^+ and K^+) on hydrophobic PDMS wall was observed through their separation in PDMS microchannels. Such experimental results demonstrated that the EOF in PDMS microchannels came from the cations and anions adsorbed on PDMS wall. This study would not only help us understand the surface state of PDMS, but also provide a useful guidance for establishing the effective surface modification methods in PDMS microchip CE.

Keywords: Electroosmotic flow; PDMS microchip; Inorganic ions; Indirect amperometric detection

1. Introduction

For microchip and conventional CE, EOF plays an important role in the separation of analytes, the transportation of solution and the optimization of electrokinetic procedures [1,2]. It is well known that EOF in fused silica capillary electrophoresis is generated due to the presence of acidic silanol (Si-OH) groups on the surface of silica or glass channels [3]. Although PDMS microfluidic systems have been applied and studied for several years [4,5], the generation mechanism of EOF in PDMS microchannels has not been explained clearly.

Van Wagenen et al. [6] reported that negative charges were presented on PDMS surface. Ocvirk et al. [7] demonstrated that the native PDMS microchannel supported EOF and the EOF was changed only when high concentrations of big organic ions, such as sodium dodecyl sulfate (SDS) were added. Ren et al. [8] proved the presence of silanol groups on oxidized PDMS surface but the silanol groups would easily disappear after the surface was exposed in air. Wang et al. [9] also reported the same EOF characteristics in microchannels fabricated with Sylgard PDMS (with fumed silica) and UCT PDMS (without fumed silica), respectively. Thormann and coworkers [10] observed the similarity between the electrokinetic data of PDMS microchannel and fused silica capillaries on the ionic strength and EOF dependence on pH. Zare and coworkers [11] demonstrated that EOF in PDMS channels was not influenced by the components in curing agent and the monomer. All above and other related studies [12,13] on the EOF in PDMS microchannels are full of interest to us due to the key role of EOF.

The above studies on EOF were mainly carried out on the basis of current monitoring; a simple and effective method to measure EOF was developed by Zare et al. [14] in 1988. The EOF rate can also be investigated on the basis of the migration time of the neutral markers [15,16]. It is also well known that the difference of concentration between the sample solution and running buffer is a good neutral marker for the measurement of EOF. Such a difference could be determined with conductivity detection method [17] for conventional but not microchip CE. In our previous report, we developed an indirect amperometric detection approach for PDMS microchip CE [18]. With this method, difference of concentration between the sample solution and running buffer can be accurately detected. Here, we report on the study of EOF in PDMS microchannels with different phosphate buffer solutions as the running buffers.

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2. Experimental

2.1. Reagents

All reagents were of analytical grade. Sylgard 184 (PDMS monomer and curing agent) was from Dow Corning (Midland, MI, USA). NaCl, LiCl, KCl, Na_2HPO_4, KH_2PO_4, Na_2HPO_4, K_2HPO_4, KH_2PO_4, LiOH and H_3PO_4 were purchased from Nanjing Chemical Reagents Factory (Nanjing, China). All solutions were prepared with doubly distilled water and passed through a 0.22 μm cellulose acetate filter (Xinya Purification Factory, Shanghai, China). Ten millimolars PBS consisting of Na^+ and K^+ was prepared with KH_2PO_4 and Na_2HPO_4 (1:1). Ten millimolars PBS consisting of only Na^+ was prepared with Na_2HPO_4 and NaH_2PO_4 (1:1). Ten millimolars PBS consisting of only K^+ was prepared with K_2HPO_4 and KH_2PO_4 (1:1). Ten millimolars PBS consisting of only Li^+ was prepared with 30 mM LiOH solution and neutralized with H_3PO_4. The pH value of all the PBS is equal to 7.0. The 10 mM bulk of KCl, NaCl or LiCl was prepared with doubly distilled water. Before use, they are diluted with the running buffer.

2.2. Apparatus

The homemade microchip holder made of plexiglass has been reported previously [18]. Briefly, a precisely three-dimensional adjustor (Shanghai Lianyi Instrument Factory of Optical Fiber and Laser, China) integrated on the holder was used to locate the working electrode fixed by a clip of optical fiber. The carbon fiber electrode reported previously was mounted into the end of the PDMS microchannel under a stereoscopic microscopy equipped with micro-ruler (XTB-1; Jiangnan Optical Instrument Factory, Nanjing, China). A straight separation PDMS microchannel of 50 μm width and 18 μm depth with cross sampling channels of 30 μm width and 18 μm depth was made on the basis of a master composed of a positive relief structure of GaAs plate microfabricated in No. 55 Electronic Institute (Nanjing, China). The length of the separation channel was 4 cm. A homemade power supply provides two outputs with voltage ranging from 0 to 5000 V for the injection and separation of PDMS microchip.

2.3. Procedure

Before use, the PDMS layer with microchannel and the PDMS flat were ultrasonically cleaned orderly with acetone, methanol and water for 10 min, respectively, and were then dried under infrared lamp. Then they were sealed together to form a reversible PDMS microchip. The working electrode was inserted into the electrode hole on the platform using the grease to prevent the leakage. The PDMS microchannel was conditioned for 1000 s after the PDMS microchip was fixed on the holder. After that, the working electrode was mounted into the end of the microchannel for 40 μm. A homemade computer program for the power supply was used to control the output voltage switching from injection to separation. Sampling mode was simple crossing without pinch. During the separation procedure, the sample and sample waste reservoirs were kept floating.

2.4. Indirect amperometric detection method

The indirect amperometric detection mode was performed with the carbon fiber micro disc electrode (diameter 8 μm) as a working electrode, an Ag/AgCl electrode as a reference and a Pt electrode as an auxiliary ones on an Electrochemical Workstation CHI660A (CH Instruments, USA). All experiments were performed at room temperature (25 °C). The principle of the indirect amperometric detection mode has been described previously [16]. Briefly, the dissolved oxygen is used as an electroactive indicator. With the in-channel mode, the change of the solution concentration passing through the working electrode results in the change of CE separation electric field. The change of potential between the working electrode and the reference electrode induced by the change of CE separation electric field brings about the change of the apparent reduction potential of dissolved oxygen. Thus, the small difference between the running buffer and sample solution can be used to measure EOF rate. Here, the 75% diluted running buffer was used as the neutral marker for the determination of EOF.

3. Results and discussion

3.1. Determination of EOF in PDMS microchannels

Fig. 1 shows the determination of EOF in freshly prepared PDMS microchannels with the running buffer of common PBS consisting of Na^+ and K^+. Under the applied separation voltage of 1000 V, for 10 mM PBS in ten times of successive measurement, the migration time of neutral marker decreased from 86.8 to 72.0 s (Fig. 1(I)). After the solutions in the reservoirs were all refreshed, the migration time becomes stable at 63.4 s (not shown). While with 25 mM PBS as running buffer, as shown in Fig. 1(II), the migration time in eight times of successive measurement decreased from 87.7 to 83.4 s. The migration time became stable at 80 s after all the solutions were refreshed (not shown). The slower EOF in 25 mM PBS is due to the thinner electric double layer in higher concentration buffers, and then less zeta potential. Such results indicated that in PDMS microchannels EOF was increased gradually in the beginning and the magnitude of the gradual increase was dependent on the concentration of the running buffer.

In order to investigate the influence of cations in running buffer on EOF, we measured EOF in PDMS microchannels with PBS consisting of different cations. For these buffer solutions, gradual increases of EOF were still observed (not shown). After reaching stable, as shown in Fig. 2, migration time of diluted running buffer was 49.8 s (Fig. 2, curve I for PBS consisting of Li^+), 57.1 s (Fig. 2, curve II for PBS consisting of Na^+), 91 s (Fig. 2, curve III for PBS consisting of K^+), respectively. Because EOF is rooted from the negative charges on inner surface of the microchannels, our experimental results obviously

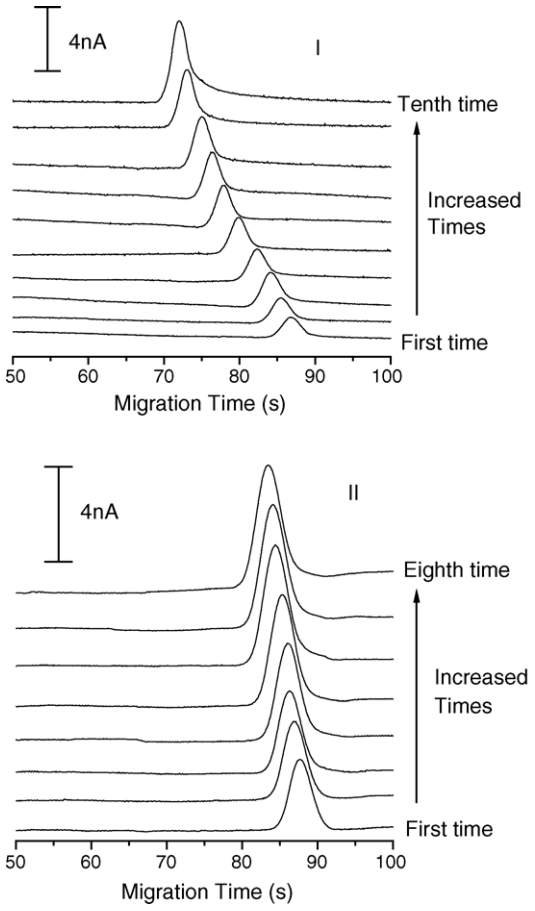

Fig. 1. Gradual change of EOF in PDMS microchannel with the injection times using 10 mM (I) and 25 mM (II) PBS as running buffer. Running parameters: sample 10 mM PBS (I) or 25 mM PBS (II); injection voltage 800 V; injection time 5 s; separation voltage 1000 V; detection potential 0 V.

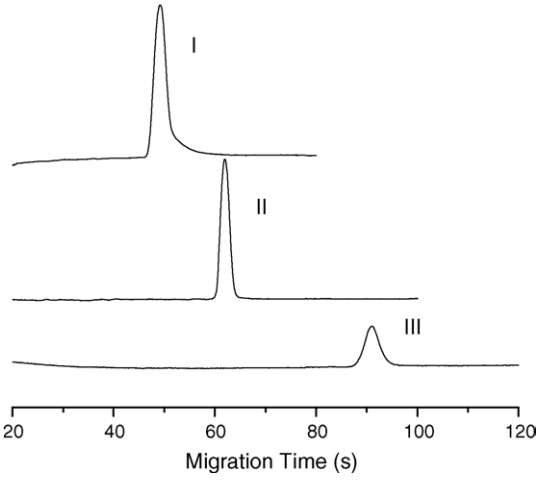

Fig. 2. EOF in PDMS microchannels using 10 mM PBS consisting of different cations as the running buffer. (I) Li^+; (II) Na^+; (III) K^+. Running parameters: sample diluted running buffers; injection voltage 800 V; injection time 5 s; separation voltage 1000 V; detection potential 0 V.

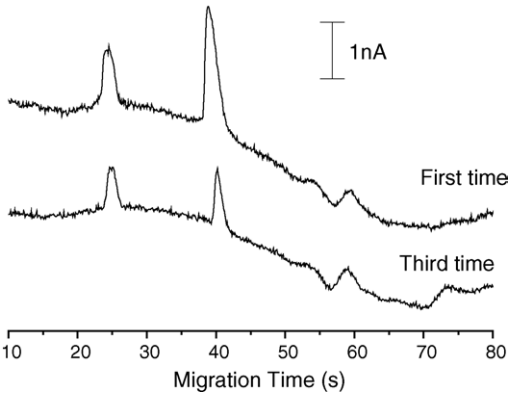

Fig. 3. Electrophoretograms of blank solution (running buffer) in PDMS microchannel that was used in the day before for the separation of Na^+ and Li^+ with 5 mM PBS as running buffer. Running parameters: sample 5 mM PBS; the others, same as in Fig. 1.

revealed that the cations in running buffer affected the rearrangement of the surface structure of negative charges on PDMS wall, i.e., the distribution of negative charges was greatly influenced by the different cations. It is clearly that the role of cations is essential in the structure of electrical double layer on PDMS wall.

3.2. Residue of cations on PDMS wall

In order to understand the interaction between the cations and PDMS, the residue of cations on PDMS wall was studied through the separation of cations in PDMS microchannels using the indirect amperometric detection method. Firstly, Na^+ and Li^+ were separated with 5 mM PBS as the running buffer. Then the injection channel was rinsed with the running buffer. When the running buffer was used as the sample, the peaks of the two anions still appeared (not shown). The PDMS microchip was then taken apart and washed orderly with acetone, methanol and water, respectively. After being dried under infrared lamp, the PDMS microchannel was re-constructed. Then using the 5 mM PBS as the running buffer, separation of the blank sample (the running buffer) in the washed PDMS microchannels was performed. It can be observed from Fig. 3 that there are still two peaks. Meanwhile, with the increasing of running times, the heights of the two peaks were decreased. Such results showed that the cations (Na^+ and Li^+) were strongly adsorbed on the PDMS wall. Under the same experimental conditions, no peak for the residue of K^+ in PDMS microchannels was observed. Such experimental results showed that the adsorption of different cations on PDMS surface is competitive. The adsorption of K^+ on PDMS wall was weaker than that of Na^+ and Li^+.

3.3. Mechanism of EOF generation in PDMS microchannels

It should be noted that usually the cations could not be easily adsorbed on the solid surface but stay in the solution because they are prone to be hydrated. For this reason, the influence of the

hydrated cations on EOF in PDMS microchannels was largely neglected. However, on the basis of our experimental results about the adsorption of cations on PDMS surface, it is necessary to investigate the interaction between water and PDMS due to the hydration of cations in water. It was previously reported that the exposure of PDMS to water for a period would cause the PDMS surface more hydrophilic [19]. This hydrophilicity would be easily transferred to hydrophobicity if PDMS were exposure to air. This phenomenon could not be easily explained because the PDMS surface is hydrophobic. More recently, Chen et al. [20] studied the surface properties of several PDMS copolymers in air and water by sum frequency generation (SFG) vibrational spectroscopy. Their experimental results revealed that the methyl groups on PDMS surfaces were prone to orient along the surface normal when PDMS was contacting with air. While contacting with water, PDMS surface was restructured and the methyl groups tilted more toward the surface due to the unfavorable interaction between the methyl groups and the molecules of water. Such results proved the strong interaction between water and PDMS from the microscopic dynamic point of view.

After the PDMS surface is restructured in water, cations would be prone to be adsorbed on PDMS surface due to the existence of oxygen on PDMS surface. The adsorption of different cations is dependent on the interaction between the cations and oxygen due to the different size of the cations and other factors. This interaction can be understood from the hydration of cations in water. For Li^+, Na^+, K^+, to our knowledge, the hydration of Li^+ is largest because of its small radius, and hydration of K^+ is the smallest due to its large radius. Thus, the interaction of Li^+ with oxygen exposed on PDMS wall would be the strongest and that of K^+ with oxygen would be the weakest. For the PDMS surface modified with different cations, the adsorption of anions (such as OH^-, $H_2PO_4^-$, HPO_4^{2-}, etc.) on its surface is dependent on the adsorption of cations. There would be more anions on PDMS surface modified with Li^+ so that the EOF rate would be biggest. While for PDMS surface modified with K^+, the EOF rate would be smallest. On the other hand, there is a process for establishing equilibrium between the interactions of cations with oxygen exposed on PDMS wall and that of cations with oxygen in water molecules. So, gradual increases of EOF could be observed in Fig. 1. Thus, the influence of cations on EOF in PDMS can be understood. That is said, EOF in PDMS microchannels generated from the cations and anions adsorbed on PDMS surface.

4. Conclusion

Based on the study of EOF in PDMS microchannels with different PBS as the running buffers by the indirect amperometric detection mode, it can be concluded that the cations in the running buffer has a great impact on the EOF rate in PDMS microchannels and it is clearly that EOF generation from the cations and anions adsorbed on PDMS wall. This study could not only provide a useful guidance to establish new surface modification methods in PDMS microchip CE but also help us to understand the surface chemistry of PDMS in more details.

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