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A Capillary Electrochromatographic Microchip Packed with Self-Assembly Colloidal Carboxylic Silica Beads

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An electrochromatographic microchip with carboxyl-group-derivatized mono-disperse silica packing was prepared from the corresponding colloidal silica solution by utilizing capillary action and self-assembly behavior. The silica beads in water were primed by the capillary action toward the ends of cross-patterned microchannel on a cyclic olefinic copolymer (COC) substrate. Slow evaporation of water at the front of packing promoted the self-assembled packing of the beads. After thermally binding a cover plate on the chip substrate, reservoirs for sample solutions were fabricated at the ends of the microchannel. The packing at the entrances of the microchannel was silver coated to fix utilizing an electroless silver-plating technique to prevent the erosion of the packed structure caused by the sudden switching of a high voltage DC power source. The electrochromatographic behavior of the microchip was explored and compared to that of the microchip with bare silica packing in basic borate buffer. Electrophoretic migration of Rhodamine B was dominant in the microchip with the carboxyl-derivatized silica packing that resulted in a migration approximated twice as fast, while the reversible adsorption was dominant in the bare silica-packed microchip. Not only the faster migration rates of the negatively charged FITC-derivatives of amino acids but also the different migration due to the charge interaction at the packing surface were observed. The electrochromatographic characteristics were studied in detail and compared with those of the bare silica packed microchip in terms of the packing material, the separation potential, pH of the running buffer, and also the separation channel length.

Key Words : Microchip, Silica packing, Capillary electrochromatography

Introduction

Recently, microchip-based analytical devices have attracted many research interests because of the promising advantages in instrumentation, minimized sample/reagent consumption, speed of analysis, and high throughput. Various analytical microfluidic devices such as DNA chips, clinical diagnostic chips, and capillary electrophoretic (CE) microchips have been developed and applied in the practical analysis. Among them, microchip CE platforms is an arena that has been extensively studied because of its simplicity, versatility, and efficiency in analytical separations. Numerous works on microchip-based CE separations have been published, ranging from their background information, chip designs and fabrications, sample pretreatments, injections, detections, and practical applications.[1-11] Nevertheless, many problems still remain to be solved, such as poor solution and chip handling issues, instability of electroosmotic flow (EOF) and difficulties in detection for miniaturized systems.

Recent works on fully packed microchips with a monolithic polymeric structure or a colloidal self-assembled silica packing structure showed improvements in EOF controls as well as in sample and chip handlings.[12-14] Particularly the colloidal self-assembled (CSA) packing structure provides promising chromatographic characteristics because of its well-defined nanoscale pore structure and the large surface area for the interaction with analytes. Therefore, it can be utilized as either excellent electrochromatographic stationary beds or electrophoretic matrix. For example, CSA packing structure has been used as molecular sorting template for continuous separation of DNA in pulsed field electrophoresis technique.[15] In addition, the utilization of CSA silica packing in microchip electrochromatographic separation was also demonstrated for amino acid separation in our laboratory.[14] Such technique provides many distinctive advantages over the ordinary CE microchips with hollow microchannels. For instance, the running buffer solution in the voids of crystalline packing can be held stable because of the extra strong surface interaction with the surface of the packed silica. Also the solution was only possible to flow through the packed microchannel by either capillary action or electroosmotic drive, resulting in the improved EOF control. Additionally the silica packing structure at the entrance of the microchannels in the reservoirs also served as built-in submicron filters. Therefore, neither chip cleaning process nor filtration of the solution was required. Subsequently the handling of the microchip and solution became much easier and simpler than with the ordinary microchips. The crystalline packing of submicron mono-disperse silica particles in the microchannels served as an excellent stationary bed and therefore made it possible to effectively separate the mixture of fluorescein isothiocyanate (FITC)-derivatized amino acids

with few mm-long separation channels. However severe irreversible adsorption of neutral molecules onto silica surface was one of the problems, which may deactivate the surface and affect the migration time of analytes due to the EOF change.[16] This irreversible adsorption is resulting from the relatively low polarity of the silica surface. Actually the green fluorescence microchannel pattern was observed due to the accumulation of fluorescein impurities in FITC adsorbed onto the silica surface as the chip was re-used. The adsorbed fluorescein impurities could be removed by prolonged washing with borate buffer solution of pH 9.5. In this circumstance the carboxyl group modified-silica particles were used to replace the bare silica in order to suppress the undesirable irreversible adsorption (of less polar molecules) by increasing the polarity of the silica surface. Through the microchip works with the carboxyl-derivatized silica packing, we could understand further regarding the electrochromatographic characteristics of the microchips packed with bare silica particles as well as with the modified silica particles. Hereinafter, we report their capillary electrophoretic characteristics studied with Rhodamine B and FITC-derivatized amino acids as probe molecules.

Experimental

Reagents and Materials. Unmodified mono-disperse colloidal silica and carboxyl group-derivatized silica having uniform sizes (0.80 and 0.97 mm in diameter, respectively) were purchased from Bang's Laboratories, Inc. (Fisher IN, USA). Rhodamine B, fluorescein isothiocyanate (FITC) and amino acids (L-arginine, D,L-phenylalanine, L-glutamic acid, glycine) were from Sigma-Aldrich. FITC-derivatized amino acids for fluorescence detection were prepared a day before CEC experiments, and stored in a refrigerator as described elsewhere.[14] 'Arg', 'Phe', 'Gly' and 'Glu' denote the FITC-derivatives of arginine, phenylalanine, glycine, and glutamic acid respectively in this work. Solutions used in CEC experiments were neither filtered nor degassed for convenience. Cyclic olefinic copolymer (COC) resins (Topas 8007, 5013) were obtained from Ticona (Summit, NJ, USA).

Chip Fabrications. The fabrication process of the fully packed microchip is described elsewhere.[14] The COC plastic microchip substrate patterned with simple cross microchannels was prepared by hot press molding technique using an electroformed nickel mold.[17] The patterned separation channel was 30 mm long, and all the other channels were 5 mm long from the channel cross. All channels were 100 μm in width and 50 μm in depth. The microchannel-patterned COC substrate was made from the COC resin having high glass transition temperature (T_g = 134 °C). After packing the microchannels with silica beads by self-assembly technique described below it was covered with a plain COC plate having low T_g (78 °C), and sealed using a homemade hot embossing machine. To avoid any possible disruption and destruction of the silica packing due to the pressure applied, the temperature of the hot embossing machine was thus maintained at 115 °C until the cover plate was softened. The plate was kept still at this temperature for about an hour without pressing and then it was squeezed from the top with the weight of the hot plate of the embossing machine for thirty minutes. The pressing was maintained until it cooled down to room temperature. Three reservoirs for sample, sample waste, and buffer solutions were drilled with a milling bit (2.4 mm in diameter), each at 6.2 mm from the cross center. A waste reservoir at the end of the separation channel was formed at the position of desirable length of the separation channel. Figure 1 is a schematic diagram of the packed microchip.

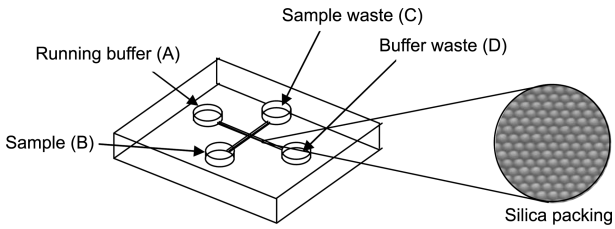

Figure 1. Structure of the silica-packed microchips.

Silica Bead Packing. The microchannels were packed with modified or unmodified silica colloidal beads as the self-assembly packing process previously reported.[14] After cleaning with piranha solution and deionized water, a cross-patterned COC chip substrate was pretreated with air plasma to make the microchannel hydrophilic. The end of the separation channel was dipped cautiously into the aqueous colloidal silica solutions (0.1 wt %, 40 °C) in a polyethylene beaker with gentle stirring to prevent the aggregation of the slowly precipitated silica particles. Capillary action of the hydrophilic microchannel caused the silica colloidal solution to move toward the ends of the microchannels. Subsequently the spontaneous three-dimensional crystalline packing of silica beads started from the end of the microchannels due to the slow evaporation of water. The self-assembly packing process continued slowly toward the end of empty microchannel at the bottom. After reaching the desirable length, the dipped area was washed with plenty of deionized water to remove any excess silica particles, and it was dried at room temperature. Then, it was subjected to cover bonding and further fabrications as described earlier.

Fixing Packed Silica Structure. To prevent erosion of the packing structure at each entrance of microchannels resulting from the exposure to buffer solution or sudden polarity change of driving voltage, the packing at the entrances was fixed by the electroless silver-plating technique.[18,19] After filling the microchannels and reservoirs with 10 mM phosphate buffer solution (pH 7), the microchips were left to stabilize overnight. After removing the buffer solutions from the reservoirs, each reservoir was filled with a drop of 0.1% $SnCl_2$, and allowed to stand for 30 sec. Then the $SnCl_2$ solution was removed using a micropipette. To activate the surface of the packing structure at the entrance of the microchannels, each reservoir was filled with a drop of 0.12 M $AgNO_3$ in 0.75 M $(NH_4)_2SO_4$, and then 2.0 M NH_3. After 150 sec, the solutions were removed. The reservoirs were re-

filled with drops of a fresh 1:1 mixture of 0.12 M $AgNO_3$ in 0.75 M $(NH_4)_2SO_4$ and 2.0 M NH_3, and 2.0 M $CoSO_4$ in 0.75 M $(NH_4)_2SO_4$ and 2.0 M NH_3. The solutions were allowed to undergo electroless silver plating reaction for 150 sec. Then the reacting mixtures in the reservoirs were washed off thoroughly with distilled water. This electroless plating process was sufficient to fix the packing structure at the very ends of the microchannels without clogging the voids of the silica packing. The microchips were then kept in pH 7 phosphate buffer solution until their use.

Capillary Electrochromatographic Experiments. A multichannel high voltage power supply from Lab Smith (HVS 448-3000V) was used for the EOF drive of solutions. A CCD multichannel spectrometer (S2000 PCI, Ocean Optics) was connected to a fluorescence microscope (Olympus BMX 51) through a camera port using optical fiber for the detection of analytes. A 75-W Xe lamp was used as an excitation light source. A filter block with band pass of 400-440 nm and barrier filter of > 475 nm was used for the selection of the excitation and detection wavelength. A bandwidth of 100 nm for detection was set at 520 nm and 580 nm for FITC-amino acids and Rhodamine B respectively. The signal was integrated for every 100 ms. The detection zone was defined by controlling the size of the focusing slit on the microscope. An objective lens of 20X magnification was used for the fluorescence detection. A small USB-interfaced CCD camera was mounted on an eyepiece of the microscope to monitor the band movement of the fluorescing probe molecules. Rhodamine B, FITC and four FITC-derivatized amino acids (Arg, Phe, Gly, and Glu) were used as probe molecules. The reservoirs were filled with five to ten μL of solutions using a micropipette without any special levelling structure to prevent the hydraulic pressure caused by the height difference between the solutions in the reservoirs, which is very important in ordinary CE microchips with hollow channel structure. These solutions required no filtration because of the built-in silica filter at the entrances of the microchannels. A positive high voltage was applied to the sample reservoir (B), or the running buffer reservoir (A) with the sample waste reservoir (C) or waste reservoir (D) grounded as required for the separation. Pinching technique for sample loading and back-pushing technique for separation were applied using a programmable high-voltage power supply. Such a voltage program was varied from chip to chip depending on the packing quality. Typically in the migration experiment for Rhodamine B with 5 mm separation. 500 V was applied to the sample reservoir for sample loading with a grounded sample waste reservoir on the opposite side, while 380 V were applied to both the running buffer reservoir and also the waste reservoir to squeeze the sample stream. Separation voltage was varied from 200 V to 600 V with 50 V for back-pushing at both the sample reservoir and the sample waste reservoir. To separate the FITC-derivatized amino acids with 8 mm separation channel 200 V was applied for the sample loading with 180 V at the running buffer reservoir and 220 V at the waste reservoir for squeezing typically. Additionally the separation voltage was varied to achieve the optimum separation at the given studies.

Safety Considerations. The high voltage power supply should be handled with extreme care to avoid possible electrical shocks. The piranha solution is extremely corrosive and it should be used in a fume hood with proper protections for the eyes and skin.

Results and Discussion

Effect of Packing Materials. One of the objectives of this work is to explore the separation behavior of the carboxylic group-modified silica packing compared to that of the bare silica in fully packed microchips. Since the surface carboxylic groups can be ionized much easily compared to the silanol groups on the bare silica surface in basic solution, the EOF should be faster than the bare silica packing at the same driving conditions, resulting in faster migration of analytes.

Figure 2 shows the electrophoretic migration behavior of less polar Rhodamine B for both microchips. When a pure aqueous borate buffer solution was used as a running buffer, strong adsorption of Rhodamine B was observed on the bare silica surface which prevented the electrophoretic elution. On comparison, weaker adsorption occurred on the carboxylic silica surface, but this was not enough for the elution owing to the incomplete carboxylic derivatization on the residual silanolic surface. Unfortunately the coverage or acid concentration of the carboxylated silica was not available from the manufacturer. So a portion of ethanol was added to the borate buffer until the electrophoretic elution was possible in the microchannel packed with bare silica. It was 50% in ethanol content. The migration rates of Rhodamine B were twice higher in the carboxylated silica packed microchannel. The driving voltage was in a linear correlation to the migration rate for the caboxylated silica packing except at 200 V. Electrophoretic behavior was dominant in the carboxylic

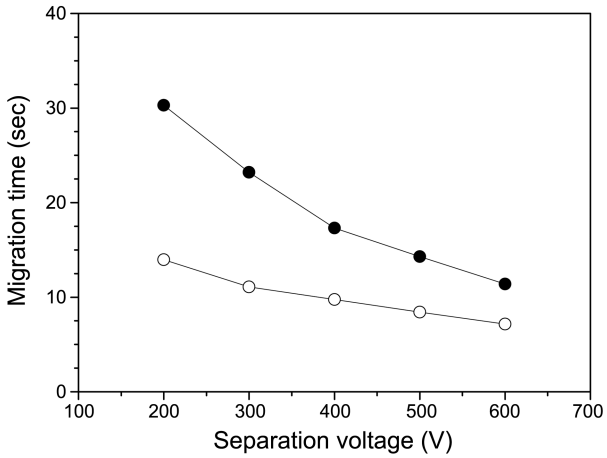

Figure 2. Effect of the separation voltage on the migration time of Rhodamine B. Solid circle: bare silica-packed microchip, open circle: carboxylic group-modified silica-packed microchip. 75 mM Rhodamine B in 1:1 ethanol and borate buffer (10 mM, pH 9.2), running buffer: 1:1 ethanol and borate buffer (20 mM, pH 9.2), separation voltage 500 V, detected at 3 mm from the channel cross.

silica packed microchannel. However, the migration rate was not linear in the bare silica packed microchannel. This is likely due to the reversible adsorption/desorption on the bare silica surface affecting the electrophoretic migration. Because of the large surface area the adsorptive electrochromatographic behavior of the less polar Rhodamine B was dominant in the silica packed microchannel compared to the electrophoretic behavior in ordinary CE microchips or CE employing fused silica tubing. The calculated surface area for the bare silica microchannel was briefly 90 times larger when compared to an empty channel with the same dimension, assuming the silica beads were in their closest packing. Although the interaction between the analytes and the capillary surface usually can be ignored in ordinary CE microchips, it is not the case in the colloidal silica packed microchip. The surface interaction plays an important role in the chromatographic elution in the packed microchip, which leads to the non-linear migration for the less polar molecules such as Rhodamin B. In contrast surface derivatization with carboxylic group allows higher EOF as well as suppresses the surface adsorption of neutral molecules. If the residual silanol group on the surface with the carboxyl group was capped properly, it would be much clearer. Similarly it is thought that the charge interactions between the analytes and the surface would also play certain roles in the separation using the microchip packed with the carboxyl-derivatized silica, unlike ordinary CE microchips.

Separation of Amino Acid Derivatives. To explore the migration behavior of analytes in the microchannel packed with the carboxyl derivatized silica, separation of FITC-derivative mixture of amino acids was carried out in various conditions. Figure 3 shows electrochromatographic behaviors of the bare silica packed microchip and the carboxyl derivatized silica packed microchip. Table 1 is the migration time data with the isoelectric points (pI) of their mother amino acid for Figure 3.[20] Generally the migration rates of the derivatives in the carboxyl derivatized silica packing were faster than in the bare silica packing at same driving conditions. It may be thought it is due to the increase of EOF resulting from the larger surface charges of ionized carboxyl group. However, assuming the same electrophoretic mobility, μ_{ep} of the derivatives and FITC in both cases, the change in migration time should be almost same for all analytes if the change was caused only by the change of EOF. But the migration rate of Arg, the derivative of a highly basic amino acid (pI = 10.76) was not changed. Moreover the rate change increased gradually from FITC to Glu as the isoelectric point, pI, decreased. Only ~10% increase for FITC was observed while it was doubled (20%) for Glu with the carboxyl derivatized silica packing. This observation cannot be explained with only EOF increase. Such observations suggested the possibility of surface charge interactions of the analytes. The elution behavior of the analytes in the silica packed microchannel is expected to be different from that in the hollow capillary channel of ordinary CE microchips. This is because the two systems have very different surface area, and the surface area (approximately 85 times) is not only responsible for the electrical double layer generation for EOF but probably also contributing to the surface-

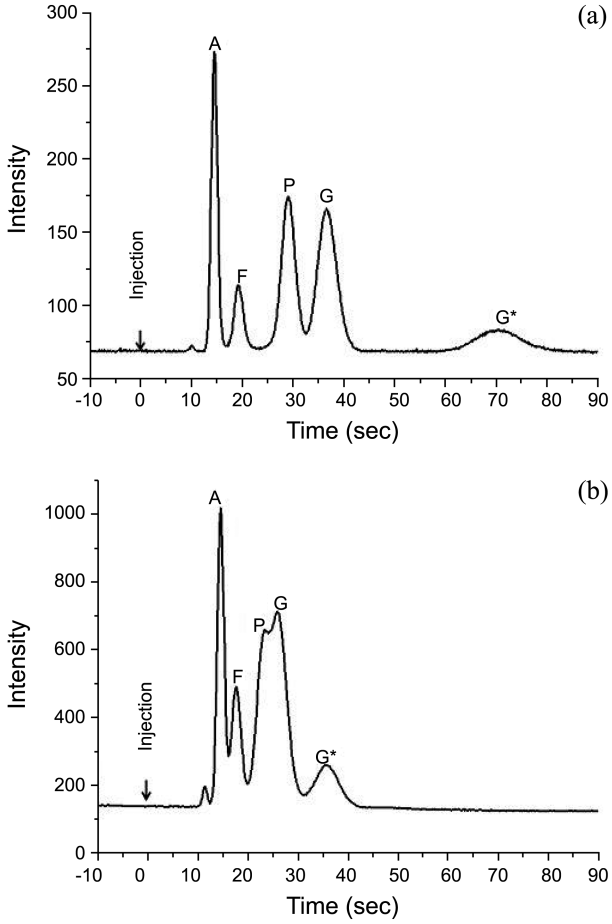

Figure 3. Electrochromatograms of a bare silica-packed microchip (a) and carboxylic group-modified silica-packed microchip (b). A: Arg, F: FITC, P: Phe, G: Gly, G*: Glu, running buffer solution: 20 mM $Na_2B_4O_7$ (pH 9.2), separation voltage: 200 V, detected at 2 mm from the channel cross.

Table 1. Migration time data of FITC-derivatives and the effect of separation voltage

Silica packing (Separation voltage)	Migration time in sec (relative migration time to FITC*)				
	Arg (pI** = 10.76)	FITC	Phe (pI = 5.48)	Gly (pI = 5.97)	Glu (pI = 3.22)
Bare (200 V)	14.4(0.75)	19.3(1.00)	29.0(1.91)	36.6(1.91)	70.2(3.68)
Carboxyl-modified (200 V)	14.4(0.82)	17.5(1.00)	23.0(1.47)	25.5(1.47)	35.1(2.04)
Carboxyl-modified (300 V)	11.4(0.80)	14.3(1.00)	19.4(1.57)	22.5(1.57)	32.5(2.26)

*: Relative migration time is in parenthesis. **: pI denotes the p-value of the isoelectric point of their mother amino acids.

analyte interactions. This might be surface adsorption or electrostatic charge interaction. Since more surface charge interaction with the analytes is expected for the carboxyl derivatized silica packing, the migration of Arg can be retarded by charge interaction although the electroosmotic mobility, μ_{eo} was increased. In contrast Glu would have repulsive interaction and move along with EOF resulting in the distinctively short migration time.

However, the situation was different with the increase of driving voltage. When the voltage was changed from 200 V to 300 V, the migration time of all analytes decreased by approximately 3 sec. Assuming constant electrostatic interactions of the derivatives to the carboxylic surface, the effect of EOF change owing to the increase of the separation voltage should be almost same for all analytes. Nevertheless the interpretation of the data in Figure 3 is not clear yet as explained above, because the surface concentration of the carboxyl group is not known and the free silica surface is not capped. Further studies on the surface derivatization with capping of underivatized silica surface have been carried out in our laboratory.

Effect of pH on Separation. Figure 4 shows the effect of pH for the running buffer on the separation of the derivatives. The pH of the running buffer solution is expected to affect the degree of neutralization of the surface carboxylic group despite the exact pKa value of the carboxylic group is not known. Lowering the pH would cause the reduction of the negative surface charge, and subsequently slows the EOF down in the separation channel. Therefore, the migration time for the derivatives clearly increased with decreasing pH. The peak heights for Gly and Glu were low relative to the other peaks in the case of pH 8.0. It is due to the insufficient sample loading time for the steady state flow of all analytes, especially Gly and Glu. The sample loading time for pH 8.0 was kept same to the case for pH 8.5 and 9.0. For the quantitative analysis careful selection of the sample loading time is required. Although the relative migration time of Glu and Gly increased abruptly, the resolution did not increase much because of the band broadening by longitudinal diffusion. However, higher pH is not applicable due to the instability of the surface carboxylic group.

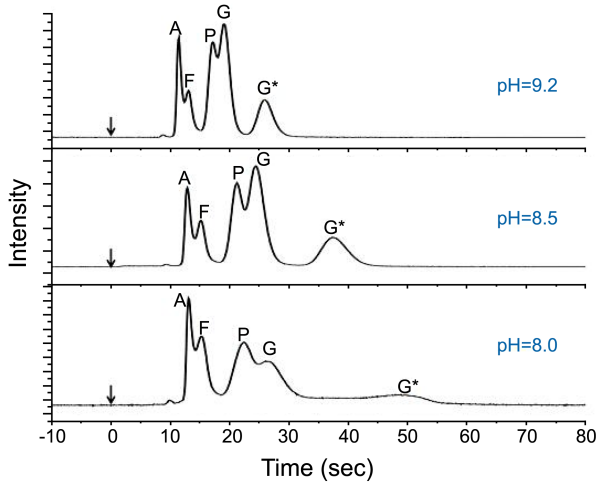

Figure 4. Effect of the pH of running buffer. A: Arg, F: FITC, P: Phe, G: Gly, G*: Glu, running buffer: 10 mM $Na_2B_4O_7$, separation voltage : 200 V, detected at 3 mm from the channel cross.

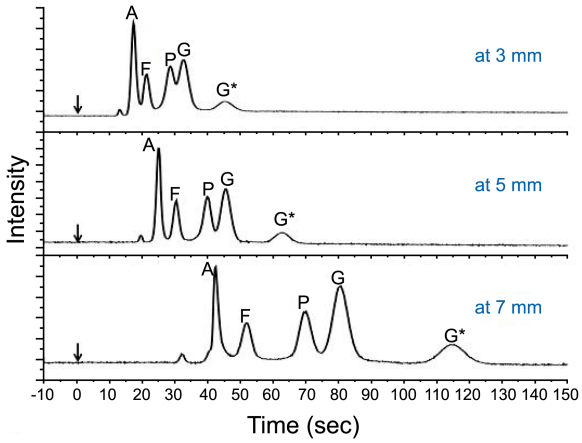

Figure 5. Effect of separation channel length (detection point from the channel cross). A: Arg, F: FITC, P: Phe, G: Gly, G*: Glu; running buffer: 20 mM $Na_2B_4O_7$ (pH 9.2), separation voltage: 300 V.

Effect of Separation Channel Length. Improvement in the resolution of the mixture was achieved by increasing the length of the separation channel, as shown in Figure 5. However with 4 mm separation channel, similar separation to that of the bare silica packed microchip with 2 mm separation channel was achieved. Nevertheless the relative migration time of the analytes to Arg became shorter than those in the bare silica packing. This is likely due to various interactions between analytes and the packed surface during the migration, which was mentioned earlier. Since the surface interactions between the analytes and the packing material are critical to the migration behavior, extra treatment, such as the capping of unreacted silanol group on the silica surface, is required. Such treatment would certainly provide further understanding about the analytical characteristics of the fully packed microchips.

Conclusions

In summary, we have demonstrated the electrochromatographic characteristics of the carboxyl derivatized silica packed CEC microchip compared to the bare silica packed microchip. In the fully packed microchips, it is possible to change the relative migration rates of analytes by modifying the surface properties, for example, using carboxylic group-derivatized silica packing instead of the bare silica packing. Since the anionic carboxylate groups on the silica surface formed at high pH can bind to FITC-derivatized amino acid derivatives through electrostatic interactions, the relative migration rates of analytes would therefore be altered. However, studies on the derivatization techniques and capping of the free surface are required to prevent surface adsorption of less neutral molecules and understand the effects of the surface derivatization clearly. Studies on the future application of the carboxylic group-modified silica packed microchips, and the possibility to modify the silica packing with

various functional groups are currently under investigation in our laboratory.

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