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Analytical Conditions and Separation Performance of Capillary Chromatography Based on the Tube Radial Distribution of Aqueous–Organic Mixture Carrier Solvents under Laminar-Flow Conditions

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We have developed a capillary chromatography system using an open capillary tube made of fused-silica, polyethylene, or poly(tetrafluoroethylene), and a water–hydrophilic–hydrophobic organic mixture carrier solution. This tube radial distribution chromatography (TRDC) system works under laminar-flow conditions. In this study, the following analytical conditions in the TRDC system using a fused-silica capillary tube and a water–acetonitrile–ethyl acetate mixture carrier solution were for the first time examined: tube temperature, 5 – 25°C; tube inner diameter, 50 – 250 μm; tube effective length, 100 – 200 cm; and flow rate, 0.2 – 1.5 μL min^{-1}. For example, the effects of temperature on the separation performance in the TRDC system were observed with an organic solvent-rich carrier solution; 1-naphthol and 2,6-naphthalenedisulfonic acid in a model mixture were eluted with baseline separation over the temperature range of 5 – 23°C. The resolution, theoretical plate number, and height equivalent to the theoretical plate were calculated from the experimental data obtained by examining the effects of the tube length. A mixture of 1-naphthol, Eosin Y, 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, and 1,3,6-naphthalenetrisulfonic acid was subjected to the present TRDC system, and the analytes in the mixture solution were eluted in this order with the organic solvent-rich carrier solution, providing good separation performance on the chromatogram.

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Introduction

Miniaturization is one of the most active research directions in analytical chemistry. Valuable investigations with respect to miniaturization have also been made in the field of liquid chromatography; *e.g.*, capillary liquid chromatography or capillary chromatography. Capillary chromatography is generally performed with fused-silica capillary tubes *ca.* 50 – 100 μm in inner diameter (i.d.), because of their superior mechanical and optical properties compared with other materials. Various capillary chromatography techniques, including capillary electrochromatography,[1,2] micellar electrokinetic capillary chromatography,[3,4] and high-performance liquid capillary chromatography using packed and monolithic columns,[5-7] have been investigated as powerful separation tools. Naturally, they require specific treatments or procedures, such as applying a high voltage, the addition of additives (gels, surfactants, *etc.*), and packing agents.

Capillary chromatography using open fused-silica capillary tubes has also been investigated, and the results have indicated interesting and unique characteristics. Most of these studies, however, used coated or modified capillary tubes. For example, the inner wall of the tube was coated with silicone grease (SE-30[8]) or modified with a monolayer particle phase.[9] Porous silica structures were also introduced on the wall by dynamic or static coating techniques,[10-12] and various polymeric siloxanes were immobilized on the walls.[13,14] We modified the inner walls with specific functional groups or molecules, such as phenylboronic acid, iminodiacetic acid, and antibodies for capillary chromatography to take advantage of specific interactions between the solutes and the modified walls.[15-18] Methods for the preparation of open capillary tubes coated with molecularly imprinted polymer[19] and cation exchange polymer[20] have also been reported for use in chromatography. Furthermore, such coating techniques have been applied to fused-silica capillary tubes less than 10 μm in i.d. to improve the separation performance.[21-23]

However, coating of the inner walls required for separation in chromatography is both a time-consuming and laborious procedure, and it is more difficult to introduce it to narrow-bored capillary tubes. Recently, capillary chromatography using open fused-silica capillary tubes that were not specially coated or modified were reported.[24-28] In one example, Tabata *et al.* developed an open tubular capillary chromatography method based on the microphase separation of mixed solvents, even though they used narrow-bored tubes of 10 μm i.d.;[27] when an acetonitrile–water mixture with a suitable salt concentration was pumped into a fused-silica capillary tube in which the inner wall was negatively charged due to the dissociation of its silanol groups, microphase separation occurred near the capillary wall, resulting in a water-enriched aqueous phase attached to the capillary inner wall. Furthermore, capillary chromatography

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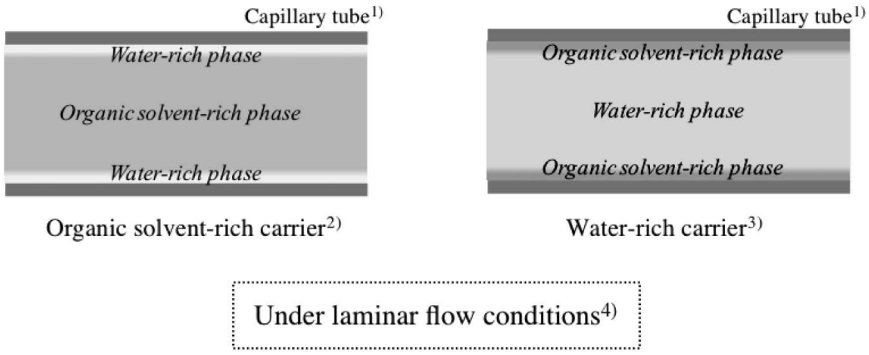

Fig. 1 Illustration of a tube radial distribution of the carrier solvents in the TRDC system that is drawn based on fluorescence photographs obtained by the fluorescence microscope-CCD camera.[34] 1) Fused-silica (50 µm i.d.), polyethylene (200 µm i.d.), and PTFE (100 µm i.d.) capillary tubes were available.[29,30] 2) For example, a water–acetonitrile–ethyl acetate (2:9:4 v/v/v) mixture solution was used as an organic solvent-rich carrier solution.[30] 3) For example, a water–acetonitrile–ethyl acetate (15:3:2 v/v/v) mixture solution was used as a water-rich carrier solution.[29,30] 4) The analytes that are delivered through the capillary tube are distributed between the inner and outer phases, undergoing chromatographic separation under laminar-flow conditions.

using wide-bored tubes of 50 µm i.d. was carried out together with an ionic liquid and a gel.[28]

We developed a capillary chromatography method using an open capillary tube and a water–hydrophilic–hydrophobic organic solvent mixture (homogeneous solution) as a carrier solution;[29–33] the system worked under laminar-flow conditions. We called this a tube radial distribution chromatography (TRDC) system. We have demonstrated the separation of a mixture of hydrophilic and hydrophobic molecules by capillary chromatography using open capillary tubes made of fused-silica, polyethylene, or poly(tetrafluoroethylene) (PTFE) (50, 200, or 100 µm i.d., respectively), and a water–acetonitrile–ethyl acetate mixture carrier solution (homogeneous solution).[29,30] The elution times of the analytes in the system can be easily reversed by changing the component ratio of the carrier solvents (or by using an organic solvent-rich carrier solution and a water-rich carrier solution) in all types of the capillary tubes. The first peaks nearly appeared with the average linear velocities, and the second peaks were eluted with smaller velocities than the average linear velocities under laminar-flow conditions with both of the organic solvent-rich and the water-rich carrier solution. In addition, the analytes were not separated with any water–acetonitrile mixture carrier solutions not including ethyl acetate. Based on our results, we proposed that separation in the capillary chromatography system was performed based on the tube radial distribution of the carrier solvents under laminar-flow conditions, known here as "a tube radial distribution chromatography (TRDC)" system.

The tube radial distribution of the solvents in the TRDC system is illustrated in Fig. 1 and phenomenologically described as follows. Aqueous and organic solvents in the carrier solution of a water–hydrophilic–hydrophobic organic mixture are dispersed non-uniformly in a specific flow in the capillary tube under laminar-flow conditions, generating an organic solvent-rich phase and a water-rich phase in the capillary tube. A major inner phase is formed around the center of the tube and away from the inner wall, while a minor outer or capillary wall phase is generated near the inner wall. An organic solvent-rich carrier solution generates an organic solvent-rich inner phase, while a water-rich carrier solution results in a water-rich inner phase, as shown in Fig. 1. The tube radial distribution of the solvent molecules in the carrier solution is thus caused in the flow in the capillary tube that features an extremely large specific surface area of the inner wall relative to the inside volume. Consequently, the analytes that are delivered through the capillary tube are distributed between the inner and outer phases, undergoing chromatographic separation under laminar-flow conditions. So far the tube radial distribution in the TRDC system has been supported by experimental data using polymer particles as analytes[31] and phenylboronic acid or iminodiacetic acid-modified fused-silica capillary tubes.[33] An illustration of the tube radial distribution of the carrier solvents (Fig. 1) is also drawn based on data of the fluorescence photographs and profiles obtained by a fluorescence microscope-CCD camera.[34]

Since our investigation of the TRDC system has just begun, it is important to examine the elution behavior under various analytical conditions in the system in order to expand our knowledge regarding its separation performance. In this study, we examined the analytical conditions of the TRDC system in detail, including tube temperature, tube inner diameter, tube length, and flow rate using fused-silica capillary tubes and a water–acetonitrile–ethyl acetate mixture as a carrier solution. Fused-silica capillary tubes with various inner diameters are commercially available and are economical, in contrast to polyethylene and PTFE capillary tubes. We demonstrated the separation and detection of a mixture sample solution including five analytes in the present TRDC system.

Experimental

Reagents and capillary tubes

Water was purified with an Elix UV 3 (Millipore Co., Billerica, MA). All reagents used were commercially available and of analytical grade. 1-Naphthol, 1-naphthoic acid, 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, 1,3,6-naphthalenetrisulfonic acid, Eosin Y, acetonitrile, and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Fused-silica capillary tubes were purchased from GL Science (Tokyo, Japan).

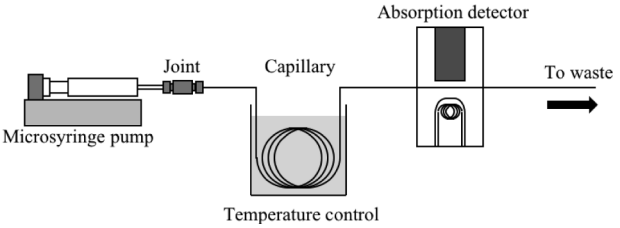

Fig. 2 Schematic diagram of the present capillary chromatography system.

Apparatus and procedures

A schematic diagram of the present capillary chromatography system comprised of an open fused-silica capillary tube, a microsyringe pump (MF-9090; Bioanalytical Systems, Inc., West Lafayette, IN), and an absorption detector (modified SPD-10AV spectrophotometric detector; Shimadzu Co., Kyoto, Japan) is shown in Fig. 2.

The tube temperature was controlled by dipping the capillary tube in water maintained at a definite temperature in a beaker with stirring. Water–acetonitrile–ethyl acetate mixtures with volume ratios of 3:8:4 and 15:3:2 were used as carrier solutions. Analyte solutions were prepared with the carrier solutions.

The analyte solution was introduced directly into the capillary inlet side by the gravity method. After analyte injection, the capillary inlet was connected through a joint to a microsyringe. The syringe was set on the microsyringe pump. The carrier solution was fed into the capillary tube at a definite flow rate under laminar-flow conditions. On-capillary absorption detection (254 nm) was performed with the detector.

Results and Discussion

Reversal of the elution times of the analytes in the TRDC system

Model mixture solutions of 1-naphthol and 2,6-naphthalenedisulfonic acid as well as 1-naphthoic acid and 1,3,6-naphthalenetrisulfonic acid were analyzed using the present TRDC system. The obtained chromatograms are shown in Fig. 3; the analytical conditions are described in the figure caption. Using an organic solvent-rich carrier solution of water–acetonitrile–ethyl acetate with a volume ratio of 3:8:4, mixtures of 1-naphthol and 2,6-naphthalenedisulfonic acid as well as 1-naphthoic acid and 1,3,6-naphthalenetrisulfonic acid were separated through the open capillary tube, and were detected in this order (Fig. 3a). On the other hand, using the water-rich carrier solution of water–acetonitrile–ethyl acetate with a volume ratio of 15:3:2, the two mixture solutions were separated and detected with inverse elution times, *i.e.*, 2,6-naphthalenedisulfonic and 1-naphthol as well as 1,3,6-naphthalenetrisulfonic acid and 1-naphthoic acid were detected in this order (Fig. 3b).

The components of the analytes on the chromatograms were confirmed from the individual absorption signals.

In both chromatograms, the first peaks were detected with elution times roughly corresponding to the average linear velocities under the laminar-flow conditions, and the second peaks were eluted with a velocity below the average linear velocity. When organic solvent-rich carrier solutions were used, the comparatively hydrophobic analytes were first eluted, while when the water-rich carrier solutions were used as carrier solutions, the comparatively hydrophilic analytes were eluted first. That is, the chromatograms clearly indicated the reversibility of the elution times by changing the component ratio of the solvents in the carrier solution. The results shown in Fig. 3 were consistent with the tube radial distribution behavior of the carrier solvents in the TRDC system that was proposed in our previous studies.[29-33]

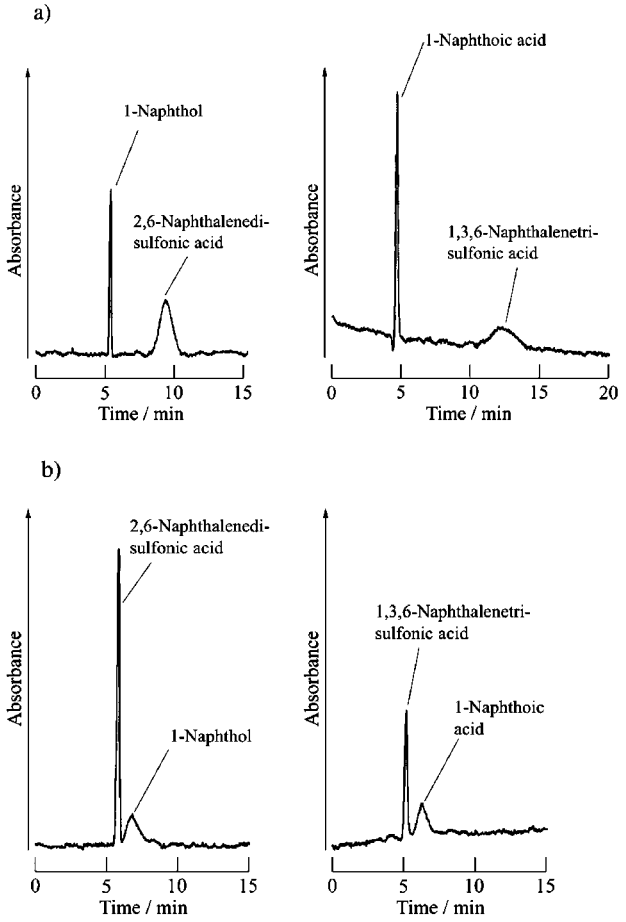

Fig. 3 Chromatograms of a mixture of 1-naphthol and 2,6-naphthalenedisulfonic acid as well as 1-naphthoic acid and 1,3,6-naphthalenetrisulfonic acid obtained by the present system. Conditions: capillary tube, 120 cm (effective length: 100 cm) of 75 μm i.d. fused-silica; carrier, a) water–acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution and b) water–acetonitrile–ethyl acetate (15:3:2 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 30 s; flow rate, 0.8 μL min^{-1}; tube temperature, 20°C; 1-naphthoic acid, 2,6-naphthalenedisulfonic acid, and 1-naphthol, 1 mM each and 1,3,6-naphthalenetrisulfonic acid, 2 mM.

Effects of tube temperature on separation

We examined the effects of tube temperature on separation in the TRDC system with a mixture analyte solution of 1-naphthol and 2,6-naphthalenedisulfonic acid as a model. The following experiments were performed with the organic solvent-rich carrier solutions, because the carrier solutions provided a better resolution on the chromatograms than the water-rich carrier solutions, as shown in Fig. 3.

The obtained chromatograms are shown in Fig. 4 together with the analytical conditions. As can be seen in Fig. 4, 1-naphthol and 2,6-naphthalenedisulfonic acid in the mixture solution were detected with baseline separation in the temperature range of 5 – 23°C, while they were not separated at all at a temperature of 25°C. In more detail, the resolutions

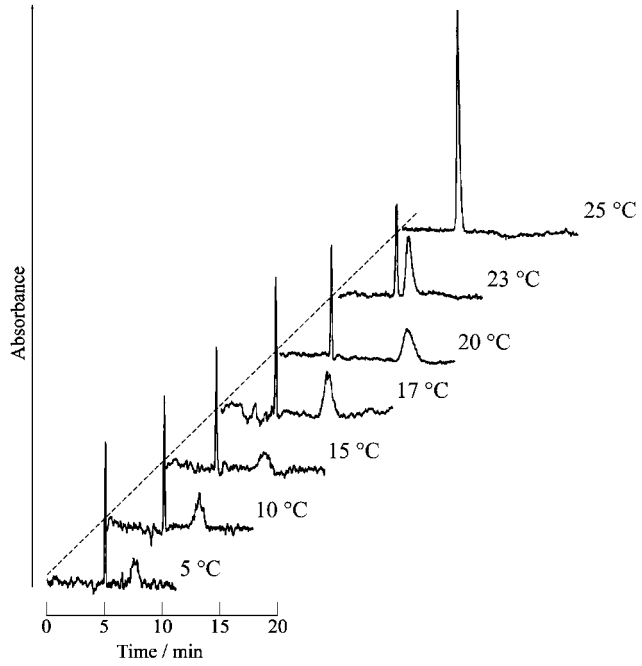

Fig. 4 Effects of the temperature on separation in the present system. Conditions: capillary tube, 120 cm (effective length of 100 cm, the part of it (*ca*. 80 cm) was dipped in the temperature-controlled water) of 75 μm i.d. fused-silica; carrier, water-acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 30 s; flow rate, 0.8 μL min^{-1}; tube temperature, 5 – 25°C; 2,6-naphthalenedisulfonic acid and 1-naphthol, 1 mM each.

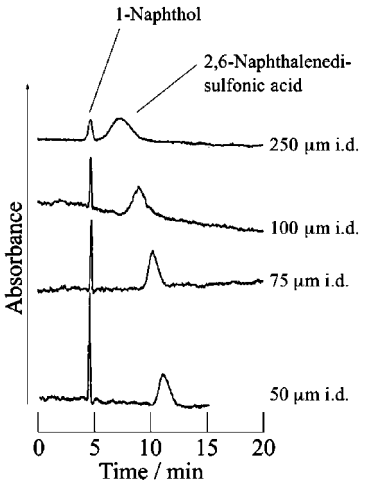

Fig. 5 Effects of the inner diameter of the tube on separation in the present system. Conditions: capillary tube, 120 cm (effective length: 100 cm) fused-silica; carrier, water-acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 2 – 45 s; flow rate, 0.5 – 8.0 μL min^{-1}; tube temperature, 20°C; 2,6-naphthalenedisulfonic acid and 1-naphthol, 1 mM each.

were improved with increasing temperature between 5 and 20°C, but the resolution decreased suddenly at 23°C. The data clearly indicated that the tube temperature had a significant and critical influence on the separation performance in the TRDC system. The formation of the inner and outer phases of the carrier solution in the tube due to the tube radial distribution of the solvents must change with the temperature.

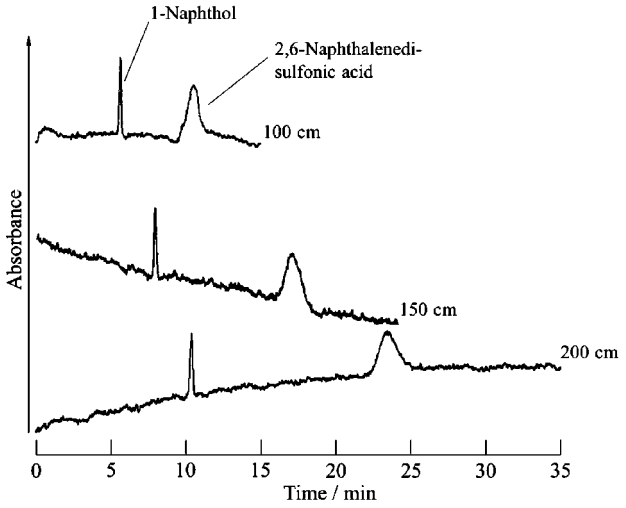

Fig. 6 Effects of the effective length of the tube on separation in the present system. Conditions: capillary tube, effective length (100 – 200 cm) of 75 μm i.d. fused-silica; carrier, water-acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 30 s; flow rate, 0.8 μL min^{-1}; tube temperature, 20°C; 2,6-naphthalenedisulfonic acid and 1-naphthol, 1 mM each.

Table 1 Resolution (R_s), theoretical plate number (N), and height equivalent to the theoretical plate (H)

Effective length of capillary tube/cm	R_s	N		H/mm	
		1-Naphthol	2,6-Naphthalene-disulfonic acid	1-Naphthol	2,6-Naphthalene-disulfonic acid
100	6.0	7800	900	0.13	1.10
150	8.0	10800	1200	0.14	1.29
200	9.7	12900	1600	0.16	1.24

Effects of tube inner diameter on separation

We examined the effects of the tube inner diameter on separation in the TRDC system with a mixture analyte solution of 1-naphthol and 2,6-naphthalenedisulfonic acid as a model. We attempted to use commercially available fused-silica capillary tubes with various inner diameters. However, since tubes with i.d. of more than 250 μm lacked flexibility, it was difficult to fix them in the present adsorption detector. In addition, since tubes of 25 μm i.d. generated severe backpressure in the tube, it was difficult to deliver the carrier solution into it constantly with the present microsyringe pump. Consequently, the capillary tubes with i.d. 50 – 250 μm were used here.

The obtained chromatograms are shown in Fig. 5 together with the analytical conditions. The flow rates for all of the capillary tubes were adjusted to provide almost the same average linear velocity of *ca*. 22 cm min^{-1}. We observed well-separated peaks on the chromatograms; the first peaks were eluted with almost average linear velocity and the second peaks were eluted with a velocity smaller than the average linear velocity. Also, the elution times of the second peaks appeared earlier with increasing inner diameter, although the elution times of the first peaks were almost constant. The formation of the inner and outer phases of the carrier solution in the tube due to the radial distribution of the solvents must change markedly in the wider

tubes. We are now planning to examine the TRDC system using capillary tubes having wider inner diameters.

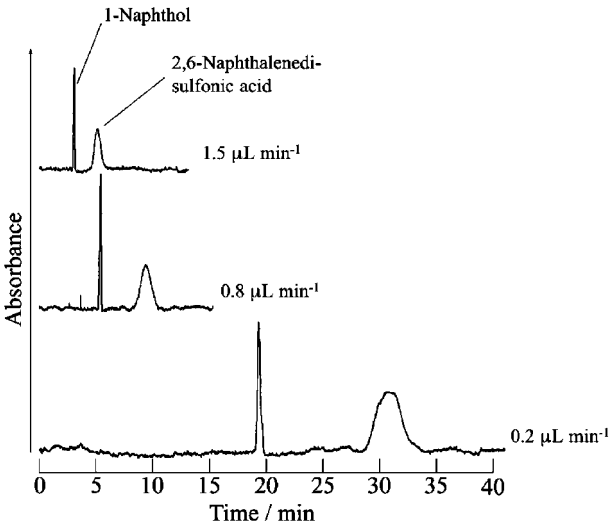

Fig. 7 Effects of the flow rate of carrier solution on separation in the present system. Conditions: capillary tube, 120 cm (effective length: 100 cm) of 75 μm i.d. fused-silica; carrier, water–acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 30 s; flow rate, 0.2 – 1.5 μL min^{-1}; tube temperature, 20°C; 2,6-naphthalenedisulfonic acid and 1-naphthol, 1 mM each.

Effects of tube effective length on separation

We also examined the effects of the tube effective length on separation in the TRDC system using the model mixture analyte solution. The obtained chromatograms are shown in Fig. 6 together with the analytical conditions. The first peaks were eluted with almost average linear velocity, and the second peaks were eluted with a velocity smaller than the average linear velocity. The resolution, theoretical plate number, and height equivalent to the theoretical plate were calculated in the usual manner; the obtained values are summarized in Table 1. As shown in Table 1, longer tubes showed better resolution and theoretical plate number. On the other hand, almost the same height equivalent to a theoretical plate of 0.13 – 0.16 mm for 1-naphthol or 1.10 – 1.29 mm for 2,9-naphthalenedisulfonic acids was observed for all tube lengths. From the data, separation in the TRDC system seemed to be performed based on the usual chromatographic separation procedure at least under the present analytical conditions.

Effects of flow rate on separation

The effects of the flow rate (0.2 – 1.5 μL min^{-1}) on separation were examined in the TRDC system. The obtained chromatograms are shown in Fig. 7 together with the analytical conditions. The first peaks were eluted with almost the average linear velocity, and the second peaks were eluted with a velocity smaller than the average linear velocity. Although the second peak showed a broadening at lower flow rates, they showed almost Gaussian peaks with good separation. That is, Fig. 7 means that the tube radial distribution of the solvents in the capillary tube was performed even at the minimum flow rate of 0.2 μL min^{-1} in the present system.

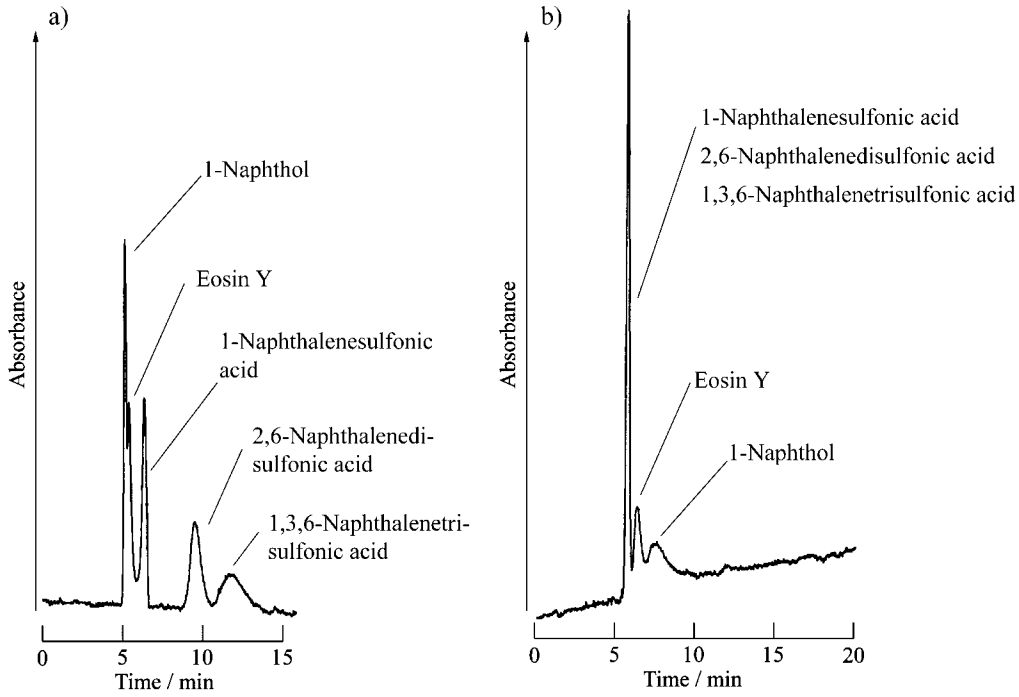

Fig. 8 Chromatograms of a mixture analyte solution of 1-naphthol, Eosin Y, 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, and 1,3,6-naphthalenetrisulfonic acid obtained by the present method. Conditions: capillary tube, 120 cm (effective length: 100 cm) of 75 μm i.d. fused-silica; carrier, a) water–acetonitrile–ethyl acetate (3:8:4 v/v/v) mixture solution and b) water–acetonitrile–ethyl acetate (15:3:2 v/v/v) mixture solution; sample injection, 20 cm height (gravity) × 30 s; flow rate, 0.8 μL min^{-1}; temperature, 20°C; 1-naphthol, 1-naphthalenesulfonic acid, and 2,6-naphthalenedisulfonic acid, 1 mM, 1,3,6-naphthalenetrisulfonic acid, 2.0 mM, and Eosin Y, 0.1 mM.

Separation of mixture solution including five analytes

We examined a mixture analyte solution of 1-naphthol, Eosin Y, 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, and 1,3,6-naphthalenetrisulfonic acid using the present TRDC system with an organic solvent-rich carrier solution and a water-rich carrier solution. The obtained chromatograms are shown in Fig. 8 together with the analytical conditions. The elution times of the analytes were reversed when using the organic solvent-rich and the water-rich carrier solutions in a similar way to other reported chromatograms in the TRDC system.[29,30] 1-Naphthol, Eosin Y, 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, and 1,3,6-naphthalenetrisulfonic acid were eluted in this order, leading to good separation with the organic solvent-rich carrier solution (Fig. 8a). The elution order seemed to be consistent with the hydrophilic character. With the water-rich carrier solution, the comparatively hydrophilic compounds 1-naphthalenesulfonic acid, 2,6-naphthalenedisulfonic acid, and 1,3,6-naphthalenetrisulfonic acid were not separated, but were eluted together with almost average linear velocity, while the hydrophobic compounds Eosin Y and 1-naphthol were eluted in this order with the velocity smaller than the average linear velocity (Fig. 8b), indicating reverse elution order compared to that of the organic solvent-rich carrier solution.

Conclusion

We have developed a capillary chromatography system using an open capillary tube made of fused-silica, polyethylene, or PTFE and a water–hydrophilic–hydrophobic mixture carrier solution. We call the system the tube radial distribution chromatography (TRDC) system, where the inner and outer phases are formed in the tube based on the radial distribution of solvents under laminar-flow conditions. The analytical conditions, such as temperature, tube inner diameter, tube length, and flow rate, were for the first time examined in the TRDC system. The resolution, theoretical plate number, and height equivalent to the theoretical plate were calculated based on the experimental data. The analytes that were delivered through the capillary tube were distributed between the inner and outer phases, undergoing chromatographic separation under the laminar-flow conditions. Separation of the mixture solution including five analytes indicated that the TRDC has a potential that should be examined further in future studies.

Acknowledgements

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