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Extraction of Cu(II) Based on Tube Radial Distribution of Ternary Mixed Carrier Solvent in Microchannels

Naoya Jinno, Masahiko Hashimoto, and Kazuhiko Tsukagoshi*

Department of Chemical Engineering and Materials Science, Doshisha University, Kyotanabe, Kyoto 610-0321

(Received March 28, 2011; CL-110258; E-mail: ktsukago@mail.doshisha.ac.jp)

The extraction of Cu(II) as a model was examined based on tube radial distribution of a ternary mixed carrier solution of water–acetonitrile–ethyl acetate (2:3:1 volume ratio) in a microchannel in a microchip. A microchip incorporating microchannels in which one wide channel was separated into three narrow channels was designed and manufactured. When the ternary carrier solution was fed into the wide channel under laminar flow conditions, the carrier solvent molecules were radially distributed in the channel, generating inner (organic solvent-rich major) and outer (water-rich minor) phases. The Cu(II) dissolved in the carrier solution was distributed between the inner and outer phases due to its hydrophilic nature and then collected through the three narrow channels. The concentrations of Cu(II) in the two side narrow channels were greater than that in the center narrow channel through extraction.

Microchip technology is of major interest in analytical chemistry. For example, there are many advantages to the development of solvent extraction on miniaturized devices on microchips. A microchannel in a microfluidic device provides a large phase interface area to its inside volume, which is beneficial to chemical processes involving phase interface phenomena, such as solvent extraction. The effective solvent extraction of metal ions in the two-phase flow on microchips has been reported.[1–3]

Recently, our group reported the tube radial distribution of carrier solvents,[4–8] which we call the "tube radial distribution phenomenon (TRDP)". When a ternary carrier solution of water–hydrophilic/hydrophobic organic solvent mixture is delivered into a microspace, such as a microchannel or a capillary tube under laminar flow conditions, the carrier solvent molecules are radially distributed in the microspace, generating inner and outer phases. For example, when a carrier solution of water–acetonitrile–ethyl acetate (3:8:4 volume ratio) was fed into a fused-silica capillary tube (75 µm i.d.), an organic solvent-rich major phase was generated around the middle of the tube far from the inner wall as an inner phase, while a water-rich minor phase formed near the inner wall as an outer phase or capillary wall phase. A novel capillary chromatography system where the outer phase works as a pseudo-stationary phase under laminar flow conditions has been developed based on the TRDP. We call it "tube radial distribution chromatography (TRDC)".[4–8]

The TRDP creates a phase interface or kinetic liquid–liquid interface in a microspace under laminar flow conditions from a homogeneous solution of water–hydrophilic/hydrophobic organic solvent mixture in a vessel, although not necessarily with clear liquid–liquid interface. In this study we applied the phase interface created through the TRDP, i.e., inner and outer phases, to the extraction procedure in a microchannel in a microchip. Cu(II) as a model was dissolved in the homogenous carrier solution of water–acetonitrile–ethyl acetate mixture. The carrier solution was fed into a newly designed microchannel in a microchip to generate the inner and outer phases through the TRDP under laminar flow conditions. The Cu(II) was distributed between the inner and outer phases or was extracted to the side narrow channels due to its hydrophilic nature in this case.

Water was purified with an Elix UV 3 system (Millipore Co., Billerica, MA). All reagents used were obtained commercially and were of analytical grade. Copper(II) chloride, perylene, Eosin Y, acetonitrile, and ethyl acetate were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). A microchip made of quartz and incorporating microchannel lines was manufactured by Microchemical Technology (Kanagawa, Japan). Figure 1 illustrates the microchip designed in this study. The one wide channel (300 µm wide × 40 µm deep) was separated into the three narrow channels (each 100 µm wide × 40 µm deep) in the microchip. Here, we designate these channels as channel W and channels N1–N3, respectively, as shown in Figure 1.

A microchip incorporating the microchannels was set up for a fluorescence microscope–CCD camera system. The fluorescence in the microchannel was monitored around the combining point using a fluorescence microscope (BX51; Olympus, Tokyo, Japan) equipped with a Hg lamp and a filter (U-MWU2, ex 330–385 nm, em. >420 nm) and CCD camera (JK-TU53H). The organic solvent-rich carrier solution (water–acetonitrile–ethyl acetate; 3:8:4 volume ratio) contained 0.1 mM perylene and 1 mM Eosin Y. The carrier solution was delivered into the microchannel at a flow rate of 6.3 µL min^{-1} using the microsyringe pump.

Figure 2 shows the obtained fluorescence photograph of the dyes in the microchannels. The photograph shows that the

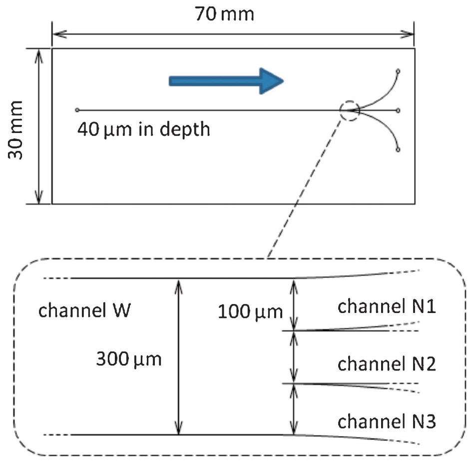

Figure 1. Illustration of the newly designed microchip incorporating microchannels.

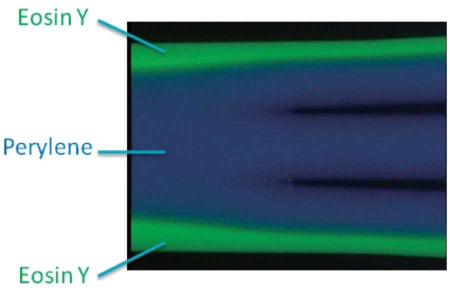

Figure 2. Fluorescence photograph of the fluorescent dyes dissolved in the ternary mixed carrier solvent in a microchannel. Conditions: Carrier, water–acetonitrile–ethyl acetate (3:8:4, v/v/v) mixture, including 0.1 mM perylene and 1 mM Eosin Y; and flow rate, 6.3 µL min^{-1} for channel W.

hydrophobic perylene molecule (blue) was distributed around the center of the wide channel (channel W) away from the channel inner wall, while comparatively hydrophilic Eosin Y (green) was distributed near the channel inner wall. The distribution phenomena of the carrier solvents fed into the microchannels clearly existed under laminar flow conditions in the wide channel. Only perylene molecules seemed to flow in the center of the three narrow channels (channel N2), and both perylene and Eosin Y, which were kept in the outer phases in the wide channel, flowed in the side narrow channels (channels N1 and N3). The distribution of the fluorescent dyes observed in the microchannels suggested the possibility of extraction taking advantage of the phase interface created through TRDP in these channels.

The homogenous carrier solution of water–acetonitrile–ethyl acetate mixture (2:3:1 volume ratio) including 2.0 mM Cu(II) was delivered into the wide microchannel (channel W) at a flow rate of 40 µL min^{-1}. The solution in each narrow channel (channels N1–N3) was collected through PTFE tubes into the corresponding vessel until 100 µL. The solution was dried under vacuum and to the residue was added 0.5 M aqueous ammonia (100 µL) for absorption measurement. The redissolved solution was subjected to absorption measurement at 600 nm. The Cu(II) concentrations of the center channel (channel N2) and the two side channels (channels N1 and N3) were 0.8, 2.3, and 2.8 mM, respectively (Figure 3). As a reference, the Cu(II) concentrations were examined with the water–acetonitrile (2:3 volume ratio) carrier solution in a similar way. The Cu(II) concentrations of channels N1–N3 were 2.1, 2.1, and 2.0 mM, respectively. The experimental data indicated that the Cu(II) was extracted to the water-rich solution in the side narrow channels from the homogeneous solution through the creation of a phase interface in the microchannel. We call this "tube radial distribution extraction (TRDE)" for convenience.

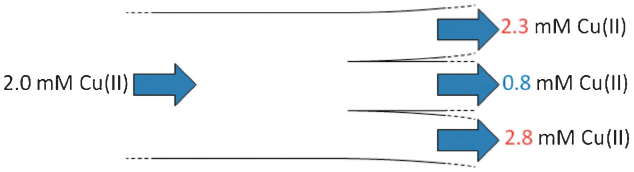

Figure 3. Extraction of Cu(II) from the homogeneous ternary mixed solution into the outer phases in the side narrow channels through TRDP. Conditions: Carrier, water–acetonitrile–ethyl acetate (2:3:1, v/v/v) mixture; flow rate, 40 µL min^{-1} for channel W; initial Cu(II) concentration, 2.0 mM.

In conclusion, when the homogeneous ternary mixed carrier solution (organic solvent-rich carrier solution) was delivered into the wide microchannel under laminar flow conditions, the carrier solvents were radially distributed in the channel according to the TRDP, generating the organic solvent-rich inner phase and the water-rich outer phase. The Cu(II) was clearly extracted from the homogeneous solution into the water-rich outer phase solution, although the detailed analytical conditions, including microchannel design, remain to be examined in the future. We will also examine the TRDE together with an extraction reagent for metal ions.

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References

1 H.-B. Kim, K. Ueno, M. Chiba, O. Kogi, N. Kitamura, *Anal. Sci.* **2000**, *16*, 871.
2 P. Kuban, J. Berg, P. K. Dasgupta, *Anal. Chem.* **2003**, *75*, 3549.
3 T. Maruyama, T. Kaji, T. Ohkawa, K. Sotowa, H. Matsushita, F. Kubota, N. Kamiya, K. Kusakabe, M. Goto, *Analyst* **2004**, *129*, 1008.
4 N. Jinno, M. Itano, M. Hashimoto, K. Tsukagoshi, *Talanta* **2009**, *79*, 1348.
5 N. Jinno, K. Tsuji, K. Shikatani, M. Hashimoto, K. Tsukagoshi, *J. Sep. Sci.* **2009**, *32*, 4096.
6 N. Jinno, M. Murakami, M. Hashimoto, K. Tsukagoshi, *Anal. Sci.* **2010**, *26*, 737.
7 N. Jinno, M. Murakami, K. Mizohata, M. Hashimoto, K. Tsukagoshi, *Analyst* **2011**, *136*, 927.
8 N. Jinno, M. Hashimoto, K. Tsukagoshi, *Anal. Sci.* **2011**, *27*, 259.