Direct Observation of Extraction of Cu(II) into Microcapsules Containing 8-Quinolinol by Use of Capillary and Chemiluminescence Detection

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In order to observe extraction behavior of a metal ion into microcapsules containing an extraction reagent, a new method using a fused-silica capillary and chemiluminescence (CL) detection was developed. The microcapsules were prepared from hexamethylenediamine and terephthaloyl chloride by interfacial polymerization. 8-Quinolinol was used as an extraction reagent, with which Cu(II) was extracted into the microcapsules. An aliquot of Cu(II) aqueous solution in the emulsion including the microcapsules was delivered by siphoning through the capillary to CL detection cell. The extraction of Cu(II) into the microcapsules was directly observed by measuring the Cu(II) concentration with the CL intensity.

Microcapsules and microencapsulation techniques have been widely used in various fields involving pharmacy, agricultural chemistry, and the chemical industry. An application of microcapsules to the separation of metal ions has been reported by several groups.[1–4] They examined an availability of microcapsules as a supporting material of ligands for extraction of metal ions. Some advantages were demonstrated; for example, a large interfacial area was better for acceleration of extraction rate than that in other membrane extraction systems. However, in order to observe extraction behavior of a metal ion into the microcapsules containing an extraction reagent, the separation of the microcapsules must be done by means of a filtration or sedimentation method. As a devise of removing the troublesome separation process, incorporation of colloidal magnetic was shown to be effective for collecting microcapsules by use of external magnetic field.[5]

In this study, we developed a new method using a fused-silica capillary and CL detection for observing extraction behavior of a metal ion into the microcapsules. A direct observation could be performed without any pretreatments of the emulsion, such as filtrations and sedimentations.

All of the reagents used were of commercially available special grade. Ion-exchanged water was distilled for use. An interfacial polymerization was carried out as described below, essentially according to the procedure previously reported.[1,5] To 150 mL of aqueous solution containing 22.5 mM sodium carbonate and 3.0 mM hexamethylenediamine which was cooled below 4 °C, was added 15 mL of chloroform–benzene (1:4; v/v) dissolving 0.609 g terephthaloyl chloride and 0.145 g 8-quinolinol, stirring for 3 min. After the addition of 75 mL water to the emulsion, the polyproduct was washed with Tween 20 aqueous solution, 2-propanol, and water in this order. The obtained microcapsules were dried. The microcapsules were examined by SEM; the average diameters of them were 200–400 µm.

The schematic diagrams of the whole experimental system and CL detection cell are shown in Figure 1. Carbonate buffer (10 mM, pH 10) was fed by siphoning through the capillary (75 µm i.d. and 70 cm length). CL reagent (a mixture of 2.5 mM luminol and 25 mM H_2O_2 in the carbonate buffer) was also fed through Teflon tube. Microcapsules (0.01 g) were dispersed in 5 mL of the carbonate buffer containing 1×10^{-4} M Cu(II) and 1×10^{-4} M potassium sodium tartrate. The emulsion was stirred with 40 or 140 rpm at 20 °C. Sample (an aliquot of Cu(II) bulk solution in the emulsion) was injected into the capillary by siphoning for 10 s at height of 15 cm, after which the carbonate buffer was successively delivered through the capillary. The sample zone finally reached to the CL detection cell, and mixed with CL reagent at the tip of capillary to produce visible light. The CL was detected by the photomultiplier tube equipped in CL detector (Model EN-21, Kimoto Electric, Inc.).

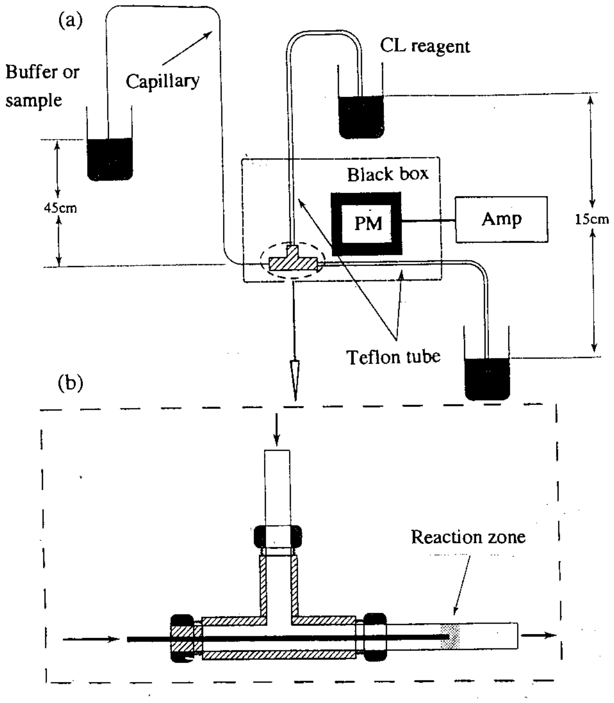

Figure 1. Schematic diagram of (a) the whole experimental system and (b) CL detection cell.

As a preliminary experiment, Cu(II) solutions at various concentrations, not containing the microcapsules, were injected into the capillary and detected by the CL detector. The typical CL profile is shown in Figure 2. Cu(II) was detected at ca. 12 min. The calibration curve of Cu(II) was examined; it was determinable over a range of $6.0 \times 10^{-6} - 5.0 \times 10^{-3}$ M with a detection limit of 6.0×10^{-6} M (S/N = 3).

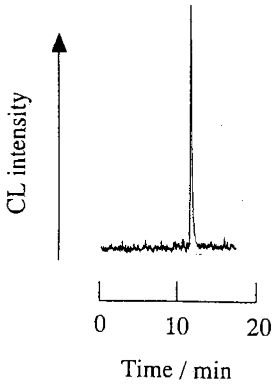

Figure 2. Typical CL profile of Cu(II). Sample was 1 × 10^{-5} M Cu(II).

Next, Cu(II) concentrations were controlled by means of a semi-batch reactor. The Cu(II) concentration (C) after the time of t is expressed by the following equation. $C = V_0 \cdot C_0 / (V_0 + v \cdot t)$; C_0, an initial concentration of Cu(II); V_0, an initial volume; and v, a flow rate. The Cu(II) solution, which was prepared by the semi-batch reactor under the conditions of C_0, 5 × 10^{-3} M, V_0, 50 µL, and v, 0.95 mL min^{-1}, was injected into the capillary as a sample and detected by the CL detector. Theoretical and experimental Cu(II) concentrations are plotted in Figure 3. The experimental values were obtained by use of the peak heights and the calibration curve of Cu(II). As shown in the figure, both values showed a good agreement. It was confirmed that Cu(II) concentrations in the emulsion, which gradually decreases with the time through extraction into the microcapsules, can be analyzed by use of the present system using a capillary and CL detection.

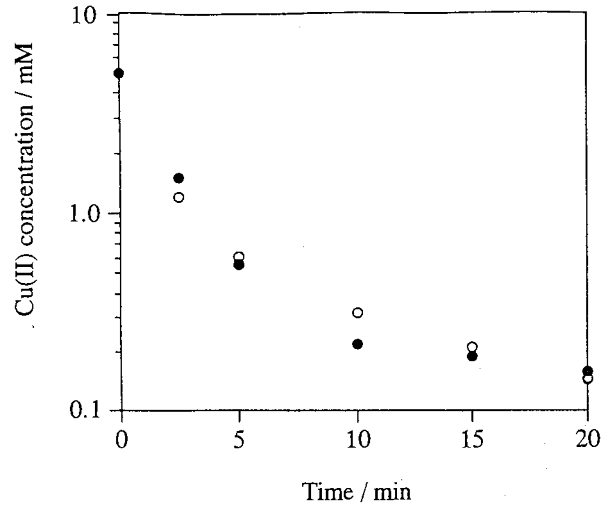

Figure 3. Relationship between the time and Cu(II) concentration. (○) Experimental and (●) theoretical value.

The extraction behavior of Cu(II) into the microcapsules containing 8-quinolinol was directly observed by the present system without any pretreatments such as filtrations and sedimentations. The relationship between the extraction time and the relative CL intensity is shown in Figure 4. The CL intensity of Cu(II) gradually decreased with the time. The extraction rate of Cu(II) at a stirring of 40 rpm was 66% at 30 min, 88% at 45 min, and 100% at 60 min. The extraction at 140 rpm accelerated the rate than at 40 rpm.

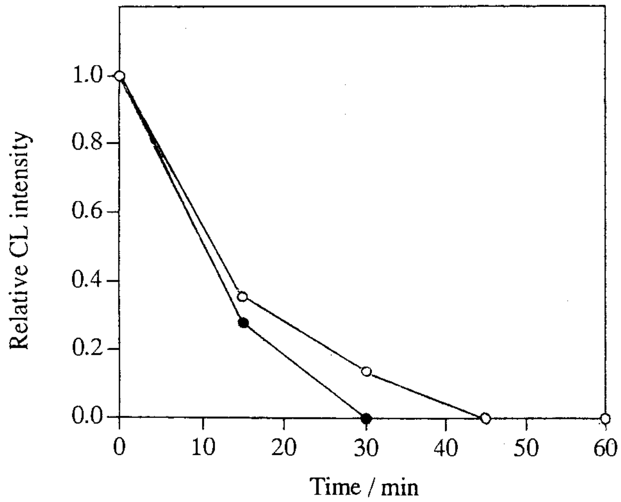

Figure 4. Relationship between the time and CL intesity. (○) 40 and (●) 140 rpm. Emulsion was a mixture of 0.01 g microcapsules and 5 mL of 1 × 10^{-4} M Cu(II) solution.

The present method will be useful for examining emulsion property, such as a permeability coefficient of membrane and a release rate of entrapped material.

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