Fiber-Optic Chemical Sensor for Alkali Metal Ion Using Calixarene as Ionophore

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Optical measurement of chemical species through an optical fiber has great advantage in remote sensing. Determination of alkali metal ions is a special interest in the industrial and clinical fields. Calixarenes have been reported as a novel ionophore for alkali metal ions in the electrochemical sensors. In this study, a fiber-optic sensor for alkali metal ions is constructed by using these calixarenes, and performance of the sensor is evaluated.

Sensing Membrane. First, a calixarene derivative (p-t-butyl-calix[6]arene ethoxycarbonyl-methyl ester) was synthesized from p-t-butyl-calix[6]arene and bromoacetic acid ethyl ester. This calixarene derivative was well known as an ionophore for cesium ion. Secondly, the calixarene derivative and an ion-exchanger were dissolved in dioctyl sebacate. Succeedingly, tetrahydrofuran and poly(vinyl chloride) were dissolved in the solution. A distal end of an optical fiber was dipped into the mixed solution to form a plasticized poly(vinyl chloride) membrane. Finally, this membrane was immersed into a solution of hexadecyl-acridine orange (fluorescent probe) in order to immobilize the probe on the membrane. An argon-ion laser was introduced into the optical fiber as an exciting source, and fluorescence from the membrane was collected through the same optical fiber.

Sensor Response. A sample solution containing cesium ion was prepared, and the sensor response to cesium ion was investigated. The constructed sensor reversibly responded to cesium ion in the concentration range of 10^{-3} - 10^{-1} M. The detection limit of cesium ion was 5 x 10^{-4} M, the response time being 35 s. A sensing membrane without containing the calixarene derivative was also prepared. However, the sensor showed no appreciable response to cesium ion. It implied that cesium ion in the sample solution was strongly extracted into the membrane by the calixarene derivative. The fluorescent probe of hexadecyl-acridine orange was highly hydrophobic, and leaching out of the probe from the membrane was not observed. It resulted the stable response of the sensor.

Selectivity. The sensor was applied to the measurement of sodium, potassium, and cesium ions, and the selectivity of the sensor was evaluated. The selectivity coefficients for sodium and potassium ions against cesium ion were 1.2 x 10^{-3} and 0.24, respectively, and high selectivity to cesium ion was obtained by using the calixarene derivative. These selectivity coefficients were comparable to those of the electrochemical sensors using a similar calixarene derivative.

Calixarenes were useful ionophores for alkali metal ions, and various calixarenes could be designed for selective extraction of metal ions. Thus the fiber-optic sensor with a different selectivity could be easily constructed by using such calixarenes.