Design and Synthesis of Highly Sodium Ion Selective Ionophores and the Preparation of High Performance Optical Sodium Ion Sensor Based on the Ionophore

Koji Suzuki and Noriko Yamamoto

(Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223, Japan)

Summary

In order to develop a highly selective ionophore for sodium ion for an excellent Na^+-sensor, we proposed a model based on 16-crown-5 which has a cavity size to fit the ionic size of Na^+ and has a "block" sub-unit to prevent the complex formation of ions of larger size than that of Na+. Based on this molecular model, eight kinds of 16-crown-5 derivatives have been synthesized and their structural ion selectivity was evaluated in detail. The 16-crown-5 derivatives having two bulky "block" subunits showed high Na+-selectivity relative to K+. Especially, the derivative with two decalino-subunits (DD16C5) exhibited the highest Na+-selectivity among all ionophores examined. When a phosphate ester-type membrane plasticizer, tris(ethylhexyl) phosphate (TEHP), was used as the membrane solvent (plasticizer) for the ion-sensing membrane based on poly(vinyl) chloride (PVC), the Na^+-sensor (Na^+-electrode) using DD16C5 exhibited a Na+-selectivity of over 1000 times relative to alkali metal and alkaline earth metal ions including K+ which is the most serious interferant.

Flow-through type fiber-optic Na^+-selective optodes based on the newly synthesized Na^+-ionophore and a lipophilic anionic indicator dye have been developed. Pellicular octadecylsilica (ODS) beads were coated with a lipophilic organic liquid containing the Na^+-ionophore (a highly lipophilic 16-crown-5 derivative, C18-DD16C5) and a dephenylamine type color changeable indicator dye (LAD-3). The optode system was constructed by packing this color changeable ion sensing beads in a flow-through optical cell (cell volume, 7 μ l) having a quartz window attached directly to the distal end of a bifurcated optical fiber. This optode could detect Na^+ in concentrations ranging from 10^{-5} to 10^{-1} M by measuring the absorbance change in the sensing beads at 510 nm. This optode showed a highly selective response to Na^+ without any interference from other metal ions except for K^+ up to 10^{-2} M.