Environmental Management Science Program

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Optically-Based Array Sensors for Selective In Situ Analysis of Tank Waste

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Research Objective

The objective of this research program is to conduct the fundamental research necessary to develop an array of chemically selective sensors, based on highly selective molecular recognition agents and highly sensitive fluorescence and/or phosphorescence techniques, that can be coupled to fiber optics for remote analytical applications. These sensors will be of great value to DOE for the safe and cost-effective in situ characterization of high level waste tanks. Characterization of high level tank waste currently entails obtaining and analyzing core samples at the cost of about $1 million per sample. The ability to detect and measure specific chemicals and radionuclides directly inside a high level waste tank using a remote sensing device could result in considerable benefits with regard to both cost savings and safety issues. This multidisciplinary approach to the design of sensors will be to immobilize agents for selective molecular recognition, chosen from solvent extraction processes, in an organic polymer matrix that mimics the organic medium in an aqueous-nonaqueous extraction. In this manner the matrix will enhance both the separation and the achievement of chemical selectivity.

Research Progress and Implications

Good progress has been made in the first nine months of this project. Calix[4]bis-crown-6-ethers in the 1,3-alternate conformation have been shown to possess a high degree of selectivity for cesium over sodium (Cs/Na selectivity > 104 in selected diluents), and moderate selectivity over potassium (Cs/K selectivity of about 102 in selected diluents). Our work has involved the preparation of a new class of calixarene-based ionophores. Of particular interest within this class of compounds are various derivatives of calix[4]arene-crown-4, -crown-5, and -crown-6 ionophores, possessing high selectivities for sodium, potassium, and cesium, respectively. Our goal is to synthetically modify the ionophore by attaching a fluorescent probe molecule to the crown ring in such a manner that fluorescence is normally quenched by photoinduced electron transfer but becomes activated upon complexation of the metal ion. The concept has been evaluated by observing the fluorescence quenching (of the naphthylene group) following Cs+ complexation of the ligand calix[4]-bis-(2,3-naphtho-crown-6). We are investigating potential fluorescence turn-on groups in simple crown ethers as a model for the behavior to be expected in calix crowns. We have investigated the fluorescence enhancement following metal ion complexation for the 9-methylanthracene derivative of dibenzo-21-crown-7. The degree of enhancement was disappointing, and we are preparing the 9-methyl-10-cyanoanthracene derivative, which is expected to show a greater signal enhancement. Other attractive fluorescence turn-on groups are under investigation. N-1-pyrenylmethyl-monoaza-18-crown-6 and N-(1-pyrenyl-4-butyl)monoaza-18-crown-6 were synthesized by the reaction of the appropriate bromo-pyrene derivatives with aza-18-crown-6. The compound with one carbon atom separating the aza nitrogen and the pyrene shows relatively weak fluorescence in the absence of metal ion complexation. In the presence of K+ the fluorescence is enhanced by a factor of 4. The derivative with four carbon atoms shows little quenching or metal ion enhancement. The rate of photoincuced electron transfer quenching is apparently very sensitive to the number of carbon atoms separating the fluorophore and the quencher.

Planned Activities

The relationship between the length of the carbon chain and the degree of quenching/enhancement for the aza-crowns and pyrene will be further investigated. Likewise the quenching observed in benzocrowns substituted with cyano anthracene will be defined. A suitable fluorescence enhancement mechanism will be established with simple crowns prior to preparing more complex calix crown derivatives. We will also begin evaluation of the polymeric organic matrix that will be used to attach the ionophores to the fiber optic including the necessity of adding modifiers. This evaluation will initially use the fluorescence quenching following Cs^+ complexation of the ligand calix[4]-bis-(2,3-naphtho-crown-6). The objective is to maximize both selectivity and loading as a function of matrix variation. When the ligands with fluorescence turn-on upon metal ion binding have been characterized in solution, studies will begin with the materials embedded in the optimized polymeric matrix. At this stage pattern recognition analysis of the response to complex solutions will begin using an array of selective ligands attached to an imaging fiber optic bundle. If appropriate, different modifiers/ polymers will be utilized for different selectivities/loading. If the research proceeds as expected, the goal is to test an imaging fiber with an array of sensor sites selective for Cs, Na, and K.

Other Access To Information

Hai-Feng Ji, R.Dabestani, and G.M.Brown, “Fluorescence Probes for the Detection of Potassium Ions,” to be presented at the American Chemical Society National Meeting, Boston, MA.