

Electrochemical Sensor for Aqueous Anions. Immobilized-Ferrocene Potential Shifts up to 700 mV in the Presence of Different Anions

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Thin films or monolayers of tetraalkylferrocenes, or functionalized tetraalkylferrocenes, were prepared on ITO and gold electrodes. Two examples of the ferrocenes were 1,1',3,3'-tetra(2-methyl-2-nonyl)ferrocene and 1,1',3,3'-tetra(2-methyl-2-nonyl)-4-(11-thiolundecanoyl)ferrocene. The Fe(III)/(II) reduction potentials for these sterically demanding ferrocenes in aqueous 0.1 M potassium chloride depended strongly on the presence of 0.001 M potassium salts of nitrate, perrhenate, and *closo*-1-carbadodecaborate(1⁻). The Fe(III)/(II) potential shifted by an unprecedented 700 mV from chloride to the carborane anion. The potential shift is due to the differences in hydration energy across the series of anions. The extremely large value of the potential shift is due to the large size of the ferrocenium cation that is formed by one-electron oxidation of the ferrocenes.

The large potential shift suggests that an electrochemical sensor based on the relative hydration energies of anions can be developed. The electrochemical behavior of a series of ferrocenes with alkyl groups with four to ten carbon atoms in the presence of a constant electrolyte salt was compared with liquid-liquid extractions of the same salt using the nitrate salt of the ferrocenium cations as the extractant.¹⁻⁴ There was a linear correlation between the

electrochemical selectivity and the ion-exchange selectivity over the series of ferrocenes. Other anions of environmental concern that were investigated include perchlorate, perfluorooctanoate, perfluorododecanoate, and perfluorooctanesulfonate.

References

1. Clark, J. F.; Clark, D. L.; Whitener, G. D.; Schroeder, N. C.; Strauss, S. H. *Environ. Sci. Technol.* **1996**, *30*, 3124.
2. Chambliss, C. K.; Odom, M. A.; Morales, C. M. L.; Martin, C. R.; Strauss, S. H. *Analyt. Chem.* **1998**, *70*, 757.
3. Chambliss, C. K.; Odom, M. A.; Martin, C. R.; Moyer, B. A.; Strauss, S. H. *Inorg. Chem. Communications* **1998**, *1*, 435.
4. Chambliss, C. K.; Strauss, S. H.; Moyer, B. A. *Solvent Extr. Ion Exch.* **1999**, *17*, 553.