closo-Dodecacarborane Anions as Novel Phase Transfer Catalysts for Ion-Selective Membrane-Based Sensors

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Phase transfer catalysts, such as tetraphenylborate salts, are commonly used in various electrochemical applications, including the study of interfacial ion transfer and phase partitioning, and for the development of membrane-based electrochemical sensors. Stringent criteria must be satisfied in order for an ion exchanger to be suitable for use in ionophore-based chemical sensors, such as sufficient lipophilicity, a delocalized monoanionic charge, suitable solubility in organic solvents, and chemical and electrochemical stability.

In addition to the criteria previously mentioned, ion exchangers used for radiochemical applications, such as liquid-liquid extraction and supported liquid membrane-based separations also require that the phase transfer catalyst is not susceptible to radiolysis. Cobalticarborane derivatives have successfully been employed as ion exchangers for radiocesium, ¹³⁷Cs and ¹³⁵Cs, for several decades, however they do not fulfill the requirement of a delocalized charge, which makes them unsuitable for sensor applications due to their ionophoric properties. Recently, chemical sensors containing halogenated *closo*-dodecacarborane derivatives have been reported that offer superior robustness in acidic samples, relative to lipophilic tetraphenylborate anions, which are readily hydrolyzed.

This class of compounds presents, for the first time, the opportunity to develop potentiometric sensors that are selective for radionuclides. In this work, ¹³⁷Cs was used as the target radionuclide due to its potential use in "dirty bomb" terrorist attacks. Several carborane-based ion exchangers were evaluated for their extraction efficiency and for their use as phase transfer catalysts in Cs⁺-selective electrodes. In addition to their use in radiochemistry, the inherent physical properties associated with these phase transfer catalysts make them suitable for most electrochemical applications.