

**BINDING PROPERTIES BETWEEN Ba²⁺ AND AT
SELF-ASSEMBLED MONOLAYER OF
CALIXARENEDISULFIDE ON GOLD**

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A macrocyclic calix[4]arene compound is known as a selective ionophore especially for Na⁺ ion [1]. Electrochemically active quinone moiety was introduced to calix[4]arenes to utilize sensitive voltammetry. Quinone-derivatized calixarenes show very distinct electrochemical behavior due to its interaction with guest ions such as alkali metal, alkaline earth and ammonium ions[2]. Electrochemical reduction of quinone is enhanced due to the stabilization of the anion radical of quinone with positive ions.

Since most of calixarenes are not soluble in water, its application was rather limited. Two or three carboxylic groups in the lower rim of the quinone-functionalized calixarenes show interesting characteristics such as well-defined redox behavior, selective complexation with Ca²⁺ and high solubility in water [3, 4]. It makes the electrochemical reduction of quinone very reversible in the presence of calcium ion and its behavior is not influenced even in the presence of one thousand-fold excess of alkali metal ions including physiologically abundant Na⁺. This result indicates that the concentration of Ca²⁺ in body fluids can be measured without removing Na⁺.

Self-assembled monolayer of quinone-derivatized calixarenedisulfide (CDS) was obtained through two thiolate linkages on gold. Different electrochemical behavior of the self-assembled monolayers were observed in the presence of alkaline earth ions in the media compared with those without any guest ion as in solution media. Therefore, it is possible to use the self-assembled monolayer surface as a heterogeneous sensing device for alkaline earth ions. Ba²⁺ instead of Ca²⁺ turned out to be more selective on solid surface, probably due to the configurational restrictions inherited from the surface. Metal bound self-assembled monolayers were refreshed either by electrochemical oxidation or chemical extraction of metal with EDTA. (Fig. 1)

Both upper and lower rims of calixarene were involved in metal binding. It was proved with different length alkane thiols that also form SAM on gold and block selectively one of those binding sites. (Fig. 2) Details of the electrochemical property of self-assembled monolayers with quinone-derivatized calix[4]arene disulfide, metal binding sites and selective detection of metal ions will be discussed.

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Fig. 1. Cyclic voltammograms of CDS-modified gold electrode. a) In the absence of metal ion from freshly made SAM, b) In the presence of Ba²⁺ ion and c) Treated in 0.01 M EDTA solution after b) is obtained.

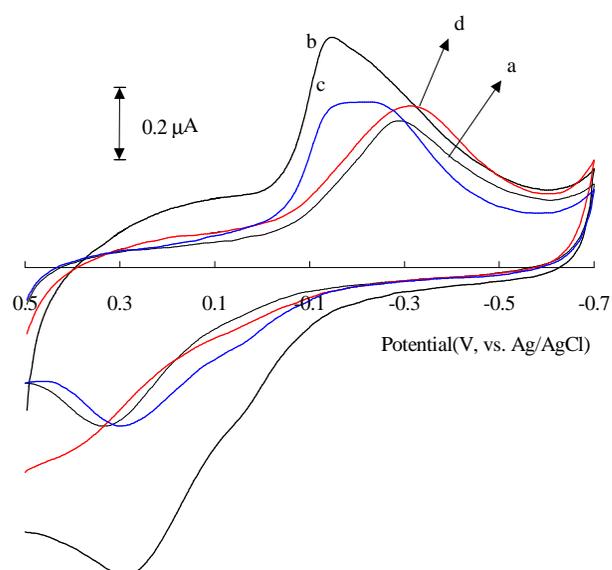


Fig. 2. Effect of different alkane thiols on the cyclic voltammograms of CDS-modified gold electrode. a) Mixed SAM of CDS and C12SH, no Ba²⁺, b) CDS SAM in the presence of Ba²⁺, c) Mixed SAM of CDS and C5SH with Ba²⁺, d) Mixed SAM of CDS and C12SH with Ba²⁺. Solution; 0.1 M HEPES buffer (pH=7.4), [Ba²⁺] = 10 mM, scan rate = 50 mV/s.

