

Ionic Recognition with Quinone-Derivatized Calixarenes in Solution and at Self-Assembled Monolayers

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Abstract : Redox-active calix[4]arenes with carboxylic acid and disulfide groups were prepared and spontaneous deposition on silver and gold surfaces was observed. Owing to their unusual structure, the calix[4]arenes exhibit selective affinity for alkaline earth metal ions in aqueous media. When annular ionophores are immobilized on the surface, voltammetric and spectroscopic studies show the entrapment of metal ions. Furthermore, it was possible to reversibly capture and remove the ions using strong chelating agents such as ethylenediaminetetraacetic acid (EDTA).

초 록 : 카르복시산과 이황화물 다리를 가지며 산화환원 활성이 있는 칼릭스[4]아렌을 합성하였고 그것이 은과 금 표면 위에 자발적으로 흡착하는 것을 관찰하였다. 칼릭스[4]아렌은 특이한 구조 때문에 수용액에서 알칼리 토금속 이온에 선택적인 친화력을 보인다. 한편 등그런 이온 수용체를 전극 위에 고정시켰을때 금속 이온을 포획하는 것을 전압전류법 및 분광학적인 연구를 통해 확인하였다. 아울러 EDTA와 같은 강한 킬레이트제를 이용하여 이온을 가역적으로 제거할 수 있음을 보였다.

Key words : Redox-active calixarene, Water-soluble calixarene, Self-assembled monolayer, Ionophore, Selective recognition

1. Introduction

Macrocyclic calix[4]arene compounds are known to act as selective ionophores especially for the Na^+ ion.¹⁾ Simple derivatization with quinone produces independent voltammetric data due to its electrochemical activity in addition to its physical size. Properly functionalized calixarenes can possess excellent ion-binding properties for the selective inclusion of inorganic or organic cations in aprotic solvents due to their rigid three-dimensional cavities.²⁻⁴⁾ Insufficient solubility of these compounds in water prevents them from having a wide application to aqueous media. Therefore, calix[4]arene with four carboxylic groups in the lower rim has attracted attention with respect to the selective analysis of electrochemically inactive cations such as alkali and alkaline earth metal ions in aqueous media.⁵⁾

Quinone moieties in the annular frame of the compound as ring members, where two or three carboxylic groups in the lower rim are unchanged, show very interesting characteristics such as well-defined redox behavior, selective complexation with Ca^{2+} and high solubility in water.⁶⁾ These factors make the electrochemical reduction of quinone very reversible in the presence of calcium ion and its behavior is not modified even by the presence of an one thousand-fold excess of alkali metal ions including the physiologically abundant Na^+ ion. This result indicates that the concentration of Ca^{2+} in body fluids can be measured without removing Na^+ , which is one of the most severe interfering ions. And thus

intallic monitoring of Ca^{2+} is possible, which is essential in phy- siology and neuroscience.

Self-assembled monolayers (SAM) of these compounds on silver and gold surfaces can be utilized as a heterogeneous sensing device for alkaline earth metal ions as well as a stationary phase for ions with different interactions in ion chromatography as seen in a few examples. In this paper, we present details of the electrochemical properties of monoquinone derivatized calix[4]arene with carboxylic acids and disulfide group. In addition, practical applications connected with selective detection of alkaline earth metal ions will be presented.

2. Experimental

Electrochemical experiments were performed with a Windows-driven electrochemical analyzer (BAS100B/W, Bioanalytical Systems, West Lafayette, IN) using positive feedback routines to compensate for resistance. The surface of the working electrodes, a glassy carbon and a polycrystalline silver disk BAS mini-electrode (area = 0.071 cm^2), were polished with 0.05 μm alumina (Buehler, Lake Bluff, MN) and then rinsed with plenty of deionized water. A Pt wire counter electrode and a $\text{Ag} | \text{AgCl}$ (in KCl 3 M) reference electrode were used for voltammetric experiments. Dissolved oxygen was removed by bubbling purified nitrogen gas. The voltammetry with modified working electrodes was carried out in pH 7.4, 0.05 M 4-(2-hydroxyethyl)-piperazine-1-ethanesulfonic acid (HEPES) buffer. All experiments were carried out in nitrogen atmosphere at room temperature. Synthesis and identification of the calix[4]arenes were described in the our preceding

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paper.⁷⁾ All reagents were purchased from Aldrich, except for $\text{Ca}(\text{NO}_3)_2$ (Junsei Chemical Co., guaranteed grade), and used without further purification.

In order to record the reflection-absorption infrared (RAIR) spectra of calix[4]arene diquinone-diacid adsorbed on the silver substrate, a specular reflection attachment (Harrick VRA, Harrick Scientific Co., NY) was used in conjunction with a Harrick wire grid polarizer. The angle of incidence for the *p*-polarized light was at 80° . Each spectrum was obtained by averaging 2048 interferograms with 4 cm^{-1} resolution. All RAIR spectra are recorded with a parameter, $-\log(R/R_0)$, where R and R_0 are the reflectivity of the modified surface and the bare clean silver substrate, respectively. The substrates were prepared by evaporating silver at 10^{-5} - 10^{-6} torr in a thermal resistive evaporator on batches of thoroughly cleaned $2.5 \times 3.7\text{ cm}$ glass slides. The self-assembled monolayer was achieved by immersing the silver substrate and disk electrode in 10^{-4} M L1 and L2 in ethanol for 60 min at 25°C . In the case of L3, an analogous procedure was applied with dichloromethane instead of ethanol as the solvent.

3. Results and Discussion

3.1. Water-soluble calixarenes in homogeneous solution

Two quinone-functionalized calix[4]arenes, used in this study, have three (L1) or two (L2) carboxylic groups or disulfide linkage between two distal pendant arms (L3), as shown in Fig. 1. L1 and L2 are soluble enough in water up to 10^{-3} M at greater than pH 7 although the solubility decreases as the pH is lowered below pH 7. The redox behavior of these two compounds is very similar to that of 1,4-benzoquinone in aqueous media. In particular, L1 was reported to form a

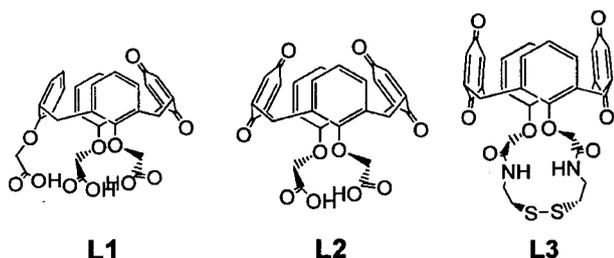


Fig. 1. Structures of the quinone-derivatized calix[4]arenes.

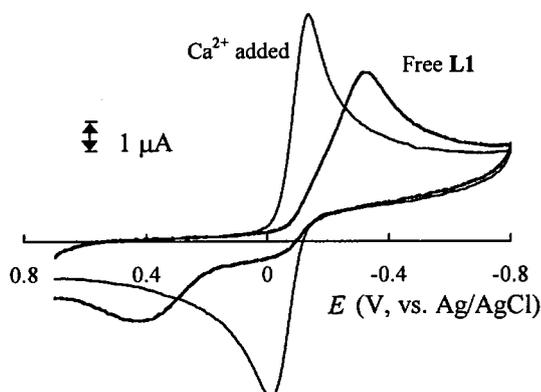


Fig. 2. Cyclic voltammograms of 0.5 mM L1 in the absence and the presence of 0.5 mM Ca^{2+} ion in 0.05 M HEPES buffer of pH 7.4

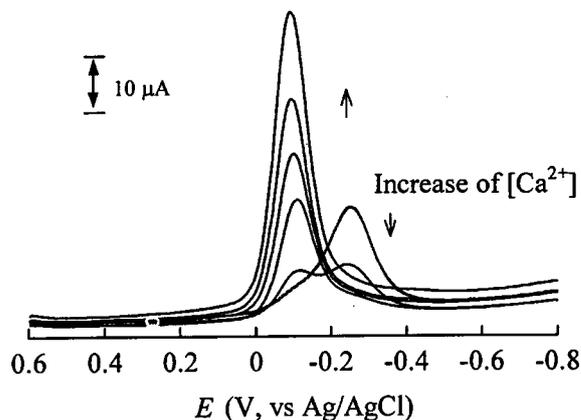


Fig. 3. Square-wave voltammograms of 0.5 mM L1 where the concentration of Ca^{2+} is 0, 0.05, 0.25, 0.50, 1.00 and 2.50 mM , respectively in the presence of 0.15 M Na^+ ion in 0.05 M HEPES buffer of pH 7.4. Step potential= 4 mV , frequency= 10 Hz and amplitude= 5 mV .

stable complex with Ca^{2+} in aqueous media.⁷⁾ Fig. 2 shows that the Ca^{2+} ion causes a drastic change in the voltammetric behavior of L1. According to a simulation study, the most probable scenario is that the Ca^{2+} ion, which is trapped by L1, effectively blocks subsequent proton transfer and electron transfer becomes highly reversible. As a result, redox peaks become more symmetric in the cyclic voltammogram in the presence of Ca^{2+} ion and also a new peak appears in the square-wave voltammogram as seen in Fig. 3. As the concentration of Ca^{2+} ion increases, the new peak grows proportionally. This is the first example of voltammetric Ca^{2+} assay with a redox-active calixarene. The unusual Ca^{2+} sensitivity of L1 implies applications for the voltammetric analysis of Ca^{2+} in aqueous media.

3.2. SAM on silver

If redox-active ionophores such as L1 and L2 are immobilized on the electrode surface without loss of ion-selectivity, the range of applications can be greatly expanded. It has been reported that simple hydrocarbons with carboxylic acid groups can adsorb to silver surface spontaneously through carboxylate anchoring and form a self-assembled monolayer.^{8,9)} With the aid of carboxylate groups in the lower rim, it is

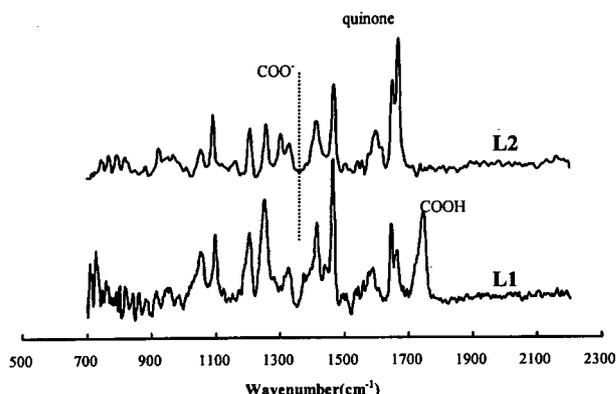


Fig. 4. Reflection-absorption infrared (RAIR) spectra of CTA and CDA adsorbed on Ag surface.

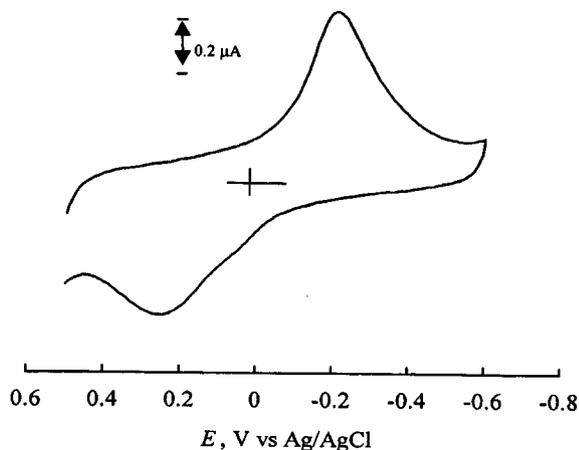


Fig. 5. Cyclic voltammogram of L3 on polycrystalline gold electrode. Scan rate = 50 mV/sec. 0.1 M HEPES buffer pH 7.4.

expected that the deposition of L1 and L2 on silver electrode is a favorable process. The experiment shows that both compounds can successfully deposit on silver surface by immersing a silver electrode into the solution in ethanol. Blockage of the redox current of anthraquinone dicarboxylic acid reveals nearly full coverage. Moreover, the amount of the deposited compounds obtained from the area of the reduction peak indicates formation of a monolayer. Fig. 4 shows two reflection-absorption infrared (RAIR) spectra after immersing silver-deposited glass electrode into L1 and L2 solution in ethanol. The symmetric stretching band of the carboxylate group appears at $1400\text{--}1420\text{ cm}^{-1}$, which is in good agreement with the literature.⁸⁾ When comparing between L1 and L2, L1-modified silver surface exhibits strong absorption at $1740\text{--}1750\text{ cm}^{-1}$ due to carboxylate groups, which do not participate in chemisorption. It seems that the symmetric structure of L2 is favorable for the formation of a stable monolayer.

L2-modified silver electrode in the absence of Ca^{2+} shows similar electrochemical behavior to that in the homogeneous media as predicted. Owing to proton transfer following electron transfer, the corresponding oxidation peak is not observed in the potential window. When the monolayer is formed in the L2 solution in the presence of Ca^{2+} , SAM of L2 is also formed reproducibly. Its voltammogram shows that new symmetric redox waves appear at a more positive potential than that of the reduction wave of L2. The same symmetric voltammogram is obtained by adding Ca^{2+} to the HEPES buffer solution in which L2-modified silver electrode is immersed. Accordingly, the new peak does not depend on whether the complexation occurs in the solution or on the surface. In addition, Ca^{2+} in the SAM on the electrode can be extracted by EDTA in the solution and this phenomenon is confirmed by voltammetry. Therefore, the modified electrode acts as Ca^{2+} probe for multiple use. The results strongly suggest applications to a miniaturized Ca^{2+} -selective sensor and the stationary phase of columns for ion chromatography.

3.3. SAM on gold surface

L3 spontaneously deposits on gold surface through sulfur-

gold bond. The amount of monolayers was confirmed both by electrochemical and electrochemical quartz crystal microbalance (EQCM) techniques. EQCM shows that the deposition process is completed within a few minutes. This rapid chemisorption is of great interest in conjunction with the report on the SAM of cyclodextrin.¹⁰⁾ L3 film exhibits a very similar electrochemical behavior of the SAM of quinone with that of alkylthiolates, as displayed in Fig. 5. The voltammetric behavior undergoes dramatic change upon the addition of calcium ions. The reduction of L3 on gold surface is catalyzed and the peak potential appears at a less negative potential. The increase in reversibility results in the growth of the corresponding oxidation peak and the appearance of a new peak in the square-wave voltammogram. The new peak exhibits a systematic influence upon the alkaline earth metal ions in solution. It is notable that the Ba^{2+} ion gives rise to the largest new peak, which is independent of the 100-fold concentration of alkali metal ions.

4. Conclusions

Redox-active calix[4]arenes were successfully immobilized on an electrode surface and the repeated capturing/releasing of alkaline earth metal ions was made possible. Electrochemical and spectroscopic methods showed the formation of a monolayer and entrapment of metal ions. The present study suggests a few interesting applications, for example, the use of the self-assembled monolayer surface as a heterogeneous sensing device for Ca^{2+} or Ba^{2+} as well as its use as a stationary phase for ions with different interactions in ion chromatography.

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