



Electrochemical recognition of Ca^{2+} ion in basic aqueous media using quinone-derivatized calix[4]arene

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Received 30 November 1998; received in revised form 10 May 1999

Papers received in Newcastle, 24 January 2000

Abstract

The voltammetric study on a water-soluble calix[4]arene (calix[4]arene-triacid-monoquinone, CTA) in basic aqueous solution in the presence of Ca^{2+} ion provided important information about the unique electrochemical behavior of Ca^{2+} -CTA complex. The redox behavior of CTA and voltammetric responses to Ca^{2+} ion are reminiscent of those of quinone-derivatized calix[4]arenes in aprotic media. Using CTA, Ca^{2+} ion in aqueous solution could be recognized quantitatively by voltammetric techniques. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Electrochemical recognition; Water-soluble calixarene; Ca^{2+} ion; Calix[4]arenemonoquinone tricarboxylic acid; Selective response

1. Introduction

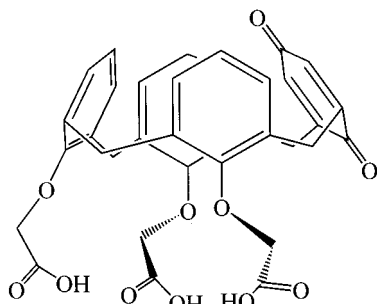
For the study of supramolecules, calixarenes are very attractive macrocycles because of their easy and diverse modification, intrinsic ion-selectivity and stability [1,2]. These advantages of calixarenes inspired many electrochemists to develop new redox-active ionophores and to examine their properties. It has been accepted that the redox-active calixarenes recognize certain ions selectively and electrochemical perturbation can change the binding ability markedly. Since it is possible to control the affinity constant for molecular shuttling and switching specific ions, much efforts on both synthesis of redox-active supramolecules and finding their new electrochemical behavior have been progressed [3–6].

Calixarenes with one or more quinone moieties as ring members have been reported since 1989 [7]. Apparently, quinones in the calixarene structure behaved like independent redox centers and each quinone followed well-known electrochemical mechanism in aprotic media [8]. The electrochemical reduction potential of free calixarenes shifted to the positive direction in the presence of cations depended on the size and charge of cations [9,10]. As an analytical application, this phenomenon provided a method to determine the concentration of alkali, alkaline earth and/or lanthanide ion selectively by voltammetry [9]. However, in our knowledge so far, no report has been published for the electrochemical behavior extended to the aqueous media.

We recently have synthesized a redox-active and water-soluble calixarene, calix[4]arene-triacid-monoquinone (CTA) as depicted in Fig. 1, for the first time and reported the novel response to Ca^{2+} ion as well as the electrochemical behavior in aqueous media [11].

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CTA

Fig. 1. Structure of CTA.

The present study reports interesting voltammetric responses of CTA to Ca^{2+} ion in basic aqueous solution, which is reminiscent of those observed in aprotic media. In addition, the quantitative increase of a new peak due to the addition of Ca^{2+} ion proposes a new voltammetric method for Ca^{2+} ion in aqueous media.

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 electrode, a glassy carbon BAS mini-electrode (area = 0.071 cm²) was polished with 0.3 μm alumina (Buehler, Lake Bluff, MN) and then rinsed with a plenty of deionized water. A Pt wire counter electrode and an Ag|AgCl (in KCl 3 M) reference electrode were used for voltammetric experiments. Dissolved oxygen was removed by bubbling purified nitrogen gas. All experiments were carried out in nitrogen atmosphere at room temperature. Synthesis and identification of CTA was described in the previous paper [11]. Tetraethylammonium hydroxide aqueous solution (TEAOH, 20 wt.% in aqueous solution, Acros Organic) was used as a base for controlling pH. Other reagents were purchased from Aldrich except CaCl_2 (Junsei Chemical, guaranteed grade) and used without further purification.

3. Results and discussion

In aqueous solution, CTA exhibits only a single reduction peak, in which two-electron transfer reaction is involved [11,12]. This behavior is also found in the case of most water soluble quinone derivatives including 1,4-benzoquinone (BQ) [13]. Considering that there

is no redox-active group in CTA structure except quinone moiety as shown in Fig. 1, it is not surprising that the electrochemical behavior of CTA is almost the same as that of BQ [11]. In well-buffered neutral solution, two protons are thought to be involved on the basis of the fact that the acid dissociation constants ($\text{p}K_a$) values of BQH^+ , BQH^- and BQH_2 are 4.1, 10.35 and 11.4. It is quite reasonable to assume that the $\text{p}K_a$ values of corresponding species of CTA are close to that of BQ even though there is a little structural difference between BQ and CTA [13,14].

On the other hand, the electrochemical reduction of BQ is not affected by the presence of alkali and alkaline earth metal ions in aqueous media. But CTA forms complexes with some alkaline earth metal ions such as Ca^{2+} , Sr^{2+} and Ba^{2+} , which cause a significant change in the redox behavior of CTA [11]. In the presence of Ca^{2+} ion, for example, the redox behavior changes rather significantly at pH 8.2, as shown in Fig. 2(a). A symmetric couple of redox wave appears and this phenomenon is also found in the neutral solution. At pH larger than 9, the single peak splits into two peaks and the potential difference between the peaks is proportional to pH. Fig. 2(b) shows the cyclic voltammograms of CTA in the absence (dotted curve) and presence of 1.0 equivalent of Ca^{2+} ion at pH 10.4. Two new peaks, E_1 and E_2 , appear and the redox processes of both peaks seem reversible. Chronocoulometric data reveal that one-electron transfer reaction is responsible for both E_1 and E_2 where the step potentials are to -0.22 and -0.53 V from 0.20 V, respectively.

Fig. 3 shows the dependence of E_p on pH in cyclic voltammograms in the presence of excess Ca^{2+} ion in basic solution. The E_p of E_1 is independent of pH while that of E_2 follows a linear relationship with pH and the slope is found to be 55 mV/pH. The identical experiment in the presence of 1.0 equivalent Ca^{2+} ion gives the same results. These results indicate that no proton transfer takes place in the first one-electron transfer process of Ca^{2+} -CTA complex whereas one proton transfer step is coupled to the second one-electron transfer process in the range of pH 9–12.

The appearance of E_1 , which is independent of proton concentration, has a few implications. First, semiquinone ($\text{Q}^{\cdot-}$) in CTA structure is stabilized preferentially by Ca^{2+} ion, which is entrapped in the lower rim, rather than by proton. This phenomenon is quite unusual in a well-buffered aqueous solution. Because CTA is one of quinone derivatives with ionophoric cavity-like structure, CTA can form a complex with Ca^{2+} ion. Presumably, Ca^{2+} ion is placed so close to the quinone moiety, stabilizing $\text{Q}^{\cdot-}$ by electrostatic interaction, that the proton transfer is blocked. In neutral solution, however, unusually stable $\text{Q}^{\cdot-}$ due to Ca^{2+} ion was observed by *in situ* UV-visible spectroscopy during the electrolysis [11,12]. Although a few experimental evidences on the stabilization of $\text{Q}^{\cdot-}$ have

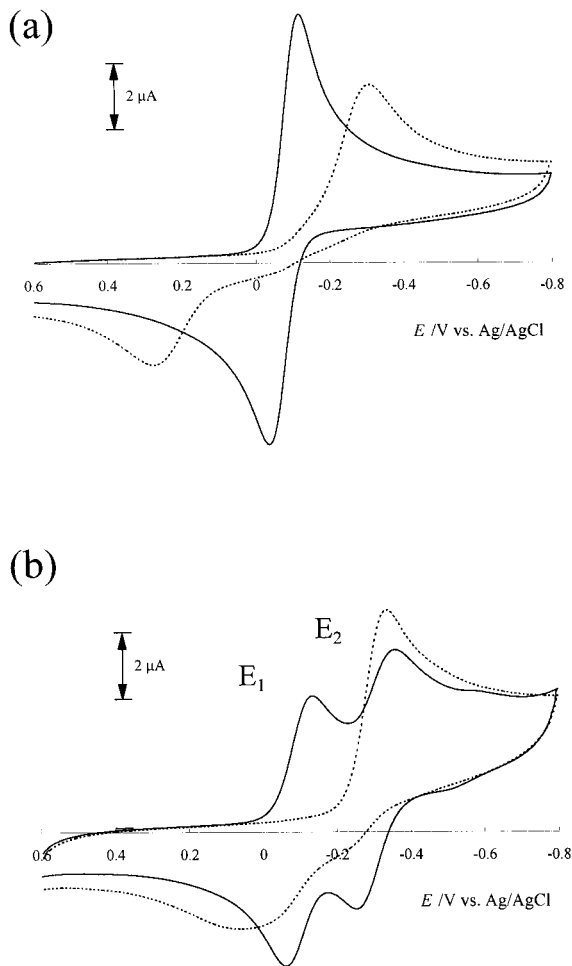


Fig. 2. Cyclic voltammograms of CTA in the absence (dotted line) and presence (solid line) of 1.0 equivalent of Ca^{2+} ion at pH 8.2 (a) and at pH 10.4 (b). The concentration of CTA is 0.5 mM in 0.1 M borate buffer and pH was adjusted by adding aqueous TEAOH stock solution. Scan rate was 50 mV/s.

been reported in the basic aqueous solution, no corresponding voltammetric behavior is presented [15,16]. Fig. 2(b) clearly shows that the stable $\text{Q}^{\cdot-}$ is produced electrochemically in the basic aqueous solution.

Second, although E_1 and E_2 are well separated in basic media, two peaks become close and eventually merged to each other as the pH decreases. When the pH is low enough for E_1 and E_2 to be very close to each other or to invert the order of the $E_{1/2}$ values, Ca^{2+} -CTA complex is predicted to exhibit a single redox wave, in which a two-electron transfer process is involved. This prediction is consistent with the result in Fig. 2(a).

The peak current of E_1 is directly proportional to the concentration of Ca^{2+} ion. Fig. 4 shows that the peak height of E_1 grows quantitatively until the concentra-

tion of Ca^{2+} ion reaches 1 equivalent. Meanwhile, E_2 exhibits very complicated behavior because E_2 overlaps with the peak due to free CTA and also proton transfer is involved in both peaks. The inset in Fig. 4 implies that the stoichiometry of 1:1 complex is formed between Ca^{2+} and CTA at pH 10.4. A little decay in the presence of more than 1.0 equivalent of Ca^{2+} ion stems from the decomposition of CTA. The decomposition rate becomes faster as the pH increases and any measurement is impossible at pH > 12. UV-visible spectrophotometric data indicate that 3.8, 4.9 and 5.4% of CTA are decomposed when 1, 2 and 3 min have elapsed at pH 10.4, respectively. Since all measurements were completed within 100 s, the error due to the decomposition is expected to be < 5%.

The behavior of E_1 , which is depicted in Fig. 2(b) and Fig. 4, is reminiscent of that of quinone-derivatized calix[4]arenes in aprotic media. Calix[4]arene-monoquinones (CMQ) with very similar structure to CTA exhibit typically two well separated reduction peaks due to successive one-electron transfers in aprotic media [17]. Calixarenediquinones (CDQ) show basically the same voltammetric behavior as that of CMQ except the number of electrons involved in corresponding two respective peaks [18–20]. As the concentration of Ca^{2+} ion increases, the new peak due to the complex is highly reversible and grows quantitatively [9]. The peak height reflects directly to the concentration of Ca^{2+} ion. Consequently, E_1 of Ca^{2+} -CTA complex in basic aqueous media behaves like those of CMQ or CDQ in aprotic solvent. This behavior can be utilized for the voltammetric analysis of free Ca^{2+} ion in aqueous media.

4. Conclusions

A water-soluble calix[4]arene, calix[4]arene-triacid-monoquinone, has a special structure that both quinone moiety and ionophoric cavity-like macrocycle are present. Ca^{2+} ion is entrapped by CTA and significantly stabilizes $\text{Q}^{\cdot-}$ which is produced by the electrochemical reduction in aqueous media at pH 10.4. As a result, no subsequent proton transfer accompanies the first heterogeneous electron transfer reaction that is independent of pH and highly reversible. On the other hand, the second reduction depends on pH and thus two one-electron transfer processes are merged into one peak when the pH is lower than 8.2. This phenomenon offers some insights for elucidating the redox behavior of Ca^{2+} -CTA complex in neutral solution. The voltammetric responses of CTA in the presence of Ca^{2+} ion at high pH are similar to those of quinone-derivatized calix[4]arenes in aprotic media. And they can be utilized for the Ca^{2+} ion analysis in aqueous solution. Detailed study on electrocatalytic reaction mechanism of Ca^{2+} -CTA in neutral solution and its

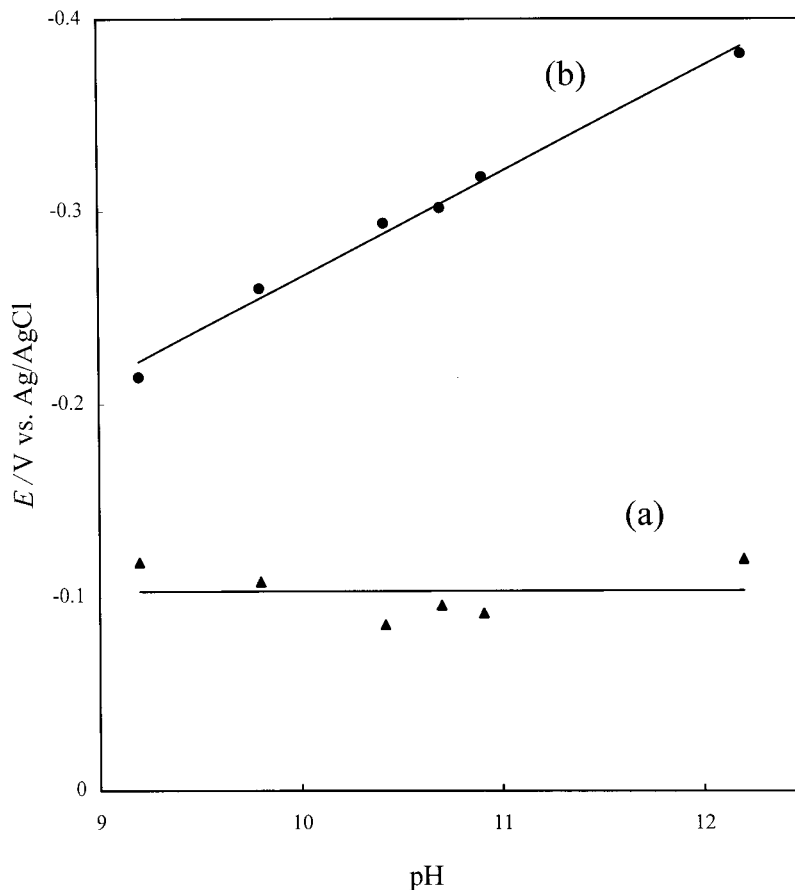


Fig. 3. Dependence of E_p on pH. (a) E_1 and (b) E_2 . E_p values were obtained from cyclic voltammograms of 0.5 mM CTA solution in the presence of ten equivalents of Ca^{2+} ion. Other experimental conditions are the same as those in Fig. 2.

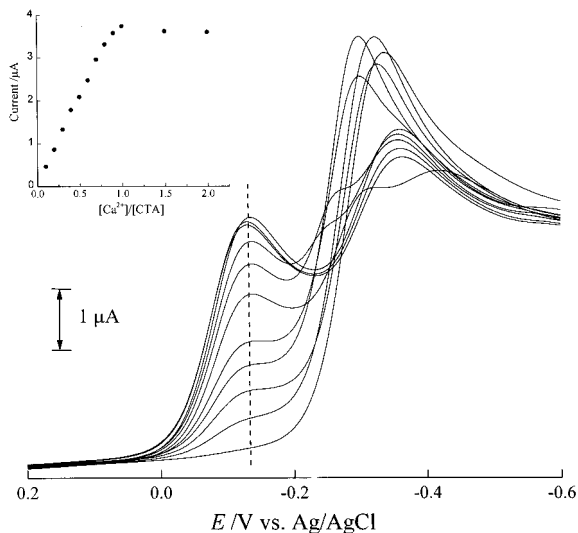


Fig. 4. Linear sweep voltammograms of CTA in the presence of various amounts of Ca^{2+} ion. Inset indicates the correlation between the relative quantity of Ca^{2+} ion and peak current at -0.12 V.

analytical applications are in progress and will be reported in a separate paper.

Acknowledgements

Financial supports from the Korea Science and Engineering Foundation through 95-0501-05-01-3 and the Center for Molecular Catalysis at Seoul National University and BSRI 98-3413 are gratefully acknowledged.

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