Electrochemical Studies for Cation Recognition with Diazo-Coupled Calix[4]arenes

Bongsu Kim and Tae Hyun Kim

Department of Chemistry, Soonchunhyang University, Asan 336-746, Republic of Korea

Correspondence should be addressed to Tae Hyun Kim; thkim@sch.ac.kr

Received 2 October 2014; Revised 19 December 2014; Accepted 2 January 2015

1. Introduction

Macrocyclic receptors have been synthesized and received much attention to be endowed with superior molecular recognition properties used in chemical sensors [1, 2]. Calixarenes have been extensively used as macrocyclic hosts for a wide range of metal ions because they have unique structure of conformational adaptability toward hosting guests along with easy derivatization of the lower rim and upper rim and the possibility of locking a desired conformation (cone, partial cone, 1,2-alternate, and 1,3-alternate) [1, 3, 4]. Many have been utilized as optical sensors to monitor the target by UV/Vis and fluorescence spectroscopic measurements. Among them, azocalixarene bearing azophenol units acting as a chromogenic center are particularly attractive for their interesting aspects of complexation with alkali, alkaline earth, and transition metal ions disclosed by studying the optical behavior of chromophoric units [4–8]. Our group has been also interested in designing selective optical sensors toward metal ions based on azocalixarene derivatives [9, 10]. As one of our efforts, we have developed a simple qualitative analysis protocol to screen alkali, alkaline earth, and transition metal ions using azocalix[4]arene derivatives. To tune up the selectivity toward specific metal ions, we have also tried to perform the pH study of azocalix[4]arene bearing carboxyl group and to change the position or the numbers of substituents, which leads to enhancement of the selectivity for Pb$^{2+}$, Cu$^{2+}$, or Ca$^{2+}$ metal ions in the spectroscopic measurements.

Azophenols as electroactive groups in azocalixarene system can be studied by also electrochemical measurements [11–13]. Electrochemical sensors are quite interesting and useful because electrochemical changes such as current and voltage by recognition of guest molecule can be directly and immediately reported to electrical signal, which is not necessary to use other transducers. Thus, electrochemical techniques are suitable for the development of convenient, sensitive, selective, and low cost devices that could be utilized for a rapid monitoring, ultimately applicable to hand-held operation. However, only a few examples of electrochemical measurements using azocalix[4]arenes have been reported [10, 14–16]. Previously, our group reported colorimetric discrimination system towards alkali, alkaline earth, and transition metal ions using azophenylcalix[4]arenes bearing ortho-carboxyl group (o-CAC) and ortho-ester group (o-EAC) (Scheme 1) [9]. To the best of my knowledge, however,
voltammetric study of o-CAC and o-EAC has not been reported. Present study reports o-CAC exhibiting a selective response to alkaline earth and transition metal ions and o-EAC to transition metal ions in acetonitrile solution (CH₃CN) by electrochemical methods. One can discriminate almost all metal ions by simple electroanalytical methods.

2. Experimental

2.1. Synthesis. Synthesis and identification of o-CAC or o-EAC were described in the previous papers [9].

2.1.1. 5,11,17,23-Tetra[(2-benzoic acid)(azo)phenyl]calix[4]arene (o-EAC). A solution of 2-aminobenzoate (3.10 g, 18.7 mmol), NaNO₂ (5.1 g, 0.045 mol), and calix[4]arene (o-EAC) were described in the previous papers [9].

2.1.2. 5,11,17,23-Tetra[(2-benzoic acid)(azo)phenyl]calix[4]arene (o-CAC). A solution of 2-aminobenzoate (3.10 g, 18.7 mmol), NaNO₂ (5.1 g, 0.045 mol), and calix[4]arene (2.00 g, 4.70 mmol) in THF:pyridine (5:2) for about 24 hrs at room temperature. After removal of the solvent in vacuo, the resulting solid was dissolved in EtOAc (100 mL) and the organic layer was washed three times with water. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed in vacuo to give a reddish oil. Column chromatography using EtOAc:hexane (2:1) provided 2.4 g (45%) of I as a yellow orange solid. Mp: 158–162°C. IR (KBr pellet, cm⁻¹): 3220, 1735. H NMR (200 MHz, CDCl₃): δ 7.43–7.22 (m, 24H, Ar-), 3.42 (broad s, 4H, Ar-C-N), 0.82–0.75 (t, 12H, OCOCH₂), 7.33–7.02 (m, 8H, COC₃H₃), 0.82–0.75 (t, 12H, COC₃H₃), J = 6.9 Hz.

The voltammetric behavior of o-CAC or o-EAC is complicated because the reductions of the azo groups of o-CAC or o-EAC produce highly proton-sensitive intermediates so that azophenol itself acts as a proton source. The reductions of the azo groups involve two electrons and, however, if a proton source is rich enough to cleave the azo linkage...
to two –NH₂ during the electrochemical reduction process, cyclic voltammogram (CV) will give irreversible redox peaks involving four electrons all together [17]. On the other hand, the oxidation of phenol in CH₃CN shows only one oxidation peak, as shown in Figure 1(a).

Thus, more attention has been paid to the oxidation wave rather than reduction waves of o-CAC or o-EAC. Electrochemical properties of o-CAC or o-EAC were also investigated by voltammetry at glassy carbon electrode in 0.1 M TBAPF₆/CH₃CN, by taking advantage of the phenol moieties present at the lower rim. Electrochemistry of o-CAC or o-EAC based on the oxidation of phenols is different from that of phenol (Figure 1(a)). Phenol exhibits simple redox behavior so that an irreversible electron transfer process is observed as one oxidation peak around 1.2 V and calix[4]arene with only phenol functional groups also shows one irreversible oxidation peak [18]. Based on the electrochemistry of phenol, o-CAC or o-EAC is also expected to be oxidized around 1.2 V. Differently from our prediction, o-CAC or o-EAC shows two irreversible oxidation waves (Figure 1(a)). This result can be proved by the fact that o-CAC or o-EAC presents a mixture of the two tautomeric forms, namely, azophenol and quinone-hydrazone, as explained in previous papers by spectroscopic data of o-CAC or o-EAC [9, 10]. Phenol groups of calixarene with only phenol group are identical because it forms intramolecular hydrogen bonding array in the lower rim of calixarene. But in this case, intramolecular hydrogen bonding array distorts and even breaks by the tautomerization of o-CAC or o-EAC. Therefore, o-CAC or o-EAC shows two irreversible peaks at intervals. One peak is due to the ease of protonation of phenol and the other peak is due to the difficulty of oxidation of phenol by intramolecular hydrogen bonding. In order to get a better resolution, differential pulse voltammetry of o-CAC or o-EAC was also performed in the same condition of cyclic voltammetry. As shown in Figure 1(b), there are two irreversible waves and prewave in the oxidation process of both hosts, which is thought to be due to the tautomerization. Anodic potential of o-CAC and o-EAC is summarized in Table 1. The potential differences between two peaks (ΔEₚ = Eₚ₂ – Eₚ₁) of o-CAC and o-EAC are around 400 mV. These values reflect the strength of intramolecular hydrogen bonding. ΔEₚ of o-CAC from both CV and differential pulse voltammogram (DPV) are slightly smaller than those of o-EAC. This might be due to relatively longer distance between two oxygens of o-CAC than that of o-EAC caused by the relative degree of steric hindrance between o-carboxyl groups and o-ester groups.

The complexation behavior of o-CAC and o-EAC was also investigated in the presence of alkali, alkaline earth, and transition metal ions in CH₃CN by comparing the voltammetric behaviors of their phenols in differential pulse voltammetry with 0.1 M TBAPF₆ as the supporting electrolyte. A constant volume (10 μL) of each cation stock solution was injected successively into the electrochemical solution to make 0.5–1.5 equivalent of cation in the solution. DPVs were recorded after

| Table 1: Anodic peak potentials of o-CAC and o-EAC. |
|-----------------------------------|----------------|----------------|----------------|----------------|
|                                   | o-CAC          | o-EAC          | o-CAC          | o-EAC          |
|                                   | CV  | DPV | CV  | DPV | CV  | DPV | CV  | DPV |
| 𝐸_{pre}                          | —   | 460 | 424 | 376 | —   | 460 | 424 | 376 |
| 𝐸_{p₁}                           | 861 | 804 | 840 | 776 | 1277| 1212| 1262| 1204|
| 𝐸_{p₂}                           | 1277| 1212| 1262| 1204| 1277| 1212| 1262| 1204|
| Δ𝐸ₚ  (= 𝐸_{p₂} – 𝐸_{p₁})         | 416 | 408 | 422 | 428 | 416 | 408 | 422 | 428 |

Figure 1: (a) Cyclic voltammograms (CVs) of o-CAC, o-EAC (1 × 10⁻⁴ M), and phenol (5 × 10⁻⁴ M) in 0.1 M TBAPF₆/CH₃CN. Scan rate: 50 mV/s. (b) Differential pulse voltammograms (DPVs) of o-CAC and o-EAC (1 × 10⁻⁴ M) in 0.1 M TBAPF₆/CH₃CN. Pulse amplitude: 50 mV.
adding stoichiometric equivalent of metal ions successively to the respective electrochemical solution. DPVs of 0.1 mM o-CAC and o-EAC in the presence of one equivalent of alkali and alkaline earth metal ions are shown in Figures 2–5.

Successive addition of an alkali metal ion to o-CAC or o-EAC, which is incapable of encapsulation, caused no significant change in the peak current or potential in accordance with previous spectroscopic data [9]. Figure 2 shows typical DPVs of o-CAC and o-EAC with the addition of one equivalent of alkali metal ions.

Very similar results are observed with o-EAC–alkaline earth metal complexation (Figure 3(b)). On the other hand, o-CAC in the presence of alkaline earth metal ions shows changes in peak currents and peak potentials (Figure 3(a)). Preoxidation wave around 0.5 V disappears and first oxidation peak shifts at more negative potential (Figure 3(a)). The presence of transition metal ions also alters both the oxidation peak potentials and currents of o-CAC or o-EAC, as in the voltammetric behavior of o-CAC–alkaline earth cation complexation (Figure 4). This result indicates that there is a subtle balance between metal complexation-induced release of proton from the azophenol to the quinone-hydrazone tautomer, and the ortho-carboxyl groups of o-CAC or ortho-ester groups of o-EAC can stabilize the quinone-hydrazone form in azocalix[4]arene after adding alkaline earth or transition metal ions.

The peak potential differences between o-CAC or o-EAC and o-CAC– or o-EAC–metal ion complexes are summarized
Figure 4: DPVs of ((a), (b)) \(\sigma\)-CAC \((1 \times 10^{-4} \text{ M})\) and ((c), (d)) \(\sigma\)-EAC \((1 \times 10^{-4} \text{ M})\) in the absence and presence of transition metal ions \((1 \times 10^{-4} \text{ M})\). Pulse amplitude: 50 mV, pulse width: 0.05 sec, sample width: 0.0167 sec, and pulse period: 0.2 sec.

Table 2: Anodic peak potential differences between \(\sigma\)-CAC or \(\sigma\)-EAC and \(\sigma\)-CAC– or \(\sigma\)-EAC–metal ion complexes in DPVs.

| mV | Li\(^{+}\) | Na\(^{+}\) | K\(^{+}\) | Rb\(^{+}\) | Cs\(^{+}\) | Mg\(^{2+}\) | Ca\(^{2+}\) | Sr\(^{2+}\) | Ba\(^{2+}\) | Cu\(^{2+}\) | Zn\(^{2+}\) | Co\(^{2+}\) | Pb\(^{2+}\) | Cr\(^{3+}\) | Fe\(^{3+}\) | Fe\(^{2+}\) | Ni\(^{2+}\) |
|-----|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| \(\sigma\)-CAC \(\Delta E_{p1}\) | -4 | 0 | -8 | 0 | -4 | -32 | -44 | -40 | -44 | -40 | -36 | -20 | -56 | -32 | -8 | -32 | -12 |
| \(\sigma\)-CAC \(\Delta E_{p2}\) | 12 | 4 | 4 | 4 | 8 | 12 | 16 | 16 | 4 | 12 | 12 | 20 | 12 | 24 | 24 | 8 |
| \(\sigma\)-EAC \(\Delta E_{p1}\) | -4 | -8 | -12 | -8 | -4 | -20 | -12 | -12 | -16 | -20 | -12 | -28 | -36 | -16 | -28 | -20 |
| \(\sigma\)-EAC \(\Delta E_{p2}\) | -4 | 0 | -4 | -4 | -4 | 0 | -4 | -4 | -4 | -4 | 0 | -8 | 0 | -4 | -4 | -4 | -4 |

in Table 2. The presence of alkaline earth and transition metal ions affects the oxidation peak potentials of \(\sigma\)-CAC, and transition metal ions influence the oxidation behavior of \(\sigma\)-EAC, whereas all alkali metal ions lead to no noticeable change in the voltammetric behavior of \(\sigma\)-CAC and \(\sigma\)-EAC. This result is in good agreement with previous spectroscopic experiments [9].

In order to confirm this electrochemical recognition phenomenon, the electroactivities of \(\sigma\)-CAC or \(\sigma\)-EAC were measured in the presence of increasing substoichiometric amount of Sr\(^{2+}\), Zn\(^{2+}\), or Cr\(^{3+}\) cations, as representative models of alkaline earth or transition metal ions. The behavior observed in the oxidation process is shown in Figure 5. With a function of concentration of metal ion, preoxidation waves around 0.5 V of both \(\sigma\)-CAC and \(\sigma\)-EAC disappear and first oxidation peaks shift at more negative potential. While second oxidation peak of both \(\sigma\)-CAC and \(\sigma\)-EAC decreases, first oxidation peak of \(\sigma\)-EAC, however, increases and \(\sigma\)-CAC
Figure 5: DPVs of $\sigma$-CAC ($1 \times 10^{-4}$ M) upon the addition of increasing amount of (a) Sr$^{2+}$ and (b) Zn$^{2+}$, and (c) DPVs of $\sigma$-EAC upon the addition of increasing amount of Cr$^{2+}$. $[M^{2+}] = 0.5$, 1.0, and $1.5 \times 10^{-4}$ M. Pulse amplitude: 50 mV, pulse width: 0.05 sec, sample width: 0.0167 sec, and pulse period: 0.2 sec.

4. Conclusion

The electrochemical behaviors of azocalix[4]arene derivatives containing ortho-carboxyl or diethyl ester groups have been investigated in the absence and the presence of alkali, alkaline earth, and transition metal ions by electrochemical measurements. $\sigma$-CAC with the ortho-carboxyl groups preferentially binds with alkaline earth and transition metal ions over alkali metal ions, whereas $\sigma$-EAC with the ortho-diethyl ester groups shows selective complexation properties toward transition metal ions over alkali and alkaline earth metal ions. The complexation of metal ions gives rise to negative shifts of first oxidation peaks in the electrochemistry of the azocalix[4]arenes. This may be attributed to the metal complexation-induced release of protons from the azophenol to the quinone-hydrazone tautomer. With this system, one can screen metal ions to alkali, alkaline earth, and transition metal ions using simple electrochemical methods.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
Acknowledgment

This work was supported by the Soonchunhyang University Research Fund.

References

[1] F. Davis and S. A. Higson, Macrocycles: Construction, Chemistry, and Nanotechnology Applications, John Wiley & Sons, Hoboken, NJ, USA, 2011.

[2] Y.-W. Yang, Y.-L. Sun, and N. Song, “Switchable host-guest systems on surfaces,” Accounts of Chemical Research, vol. 47, no. 7, pp. 1950–1960, 2014.

[3] J. Vicens, J. M. Harrowfield, and L. Baklouti, Calixarenes in the Nanoworld, Springer, Dordrecht, The Netherlands, 2007.

[4] C. D. Gutsche, Calixarenes: An introduction, Monographs in Supramolecular Chemistry, Royal Society of Chemistry (Great Britain), Cambridge, UK, 2nd edition, 2008.

[5] O. Aleksiuk, S. Cohen, and S. E. Biali, “Selective hydroxyl replacement in calixarenes: amino-, azo-, and xanthenocalixarene derivatives,” Journal of the American Chemical Society, vol. 117, no. 38, pp. 9645–9652, 1995.

[6] H. Deligöz, “Azocalixarenes: synthesis, characterization, complexation, extraction, absorption properties and thermal behaviours,” Journal of Inclusion Phenomena and Macrocyclic Chemistry, vol. 55, no. 3-4, pp. 197–218, 2006.

[7] L. L. Lu, S. F. Zhu, X. Z. Liu, Z. Z. Xie, and X. Yan, “Highly selective chromogenic ionophores for the recognition of chromium(III) based on a water-soluble azocalixarene derivative,” Analytica Chimica Acta, vol. 535, no. 1-2, pp. 183–187, 2005.