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Electrochemistry of Calixarene and its Analytical Applications

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Abstract. The electrochemistry of calixarene as a redox-dependent ionophore and its structural dependence are described. One or more redox-centers such as quinone, ferrocene, cobaltocenium and ruthenium bipyridine moieties have been introduced into the calixarene frame of the lower or upper rim. Although the electrochemical behavior depends mainly on the inherent redox property of these electrochemically active groups, the structural effect and solvent also play important roles, especially, in the presence of charged guests. When cationic species such as metal ions and ammonium ion are added to a quinone-functionalized calixarene solution, electron transfer to quinone is enhanced by the electrostatic effect or the formation of hydrogen bonds. In addition to redox-active hosts for voltammetric use, a number of calixarenes with novel structures have been developed as ionophores for potentiometric analysis and found to be successful for some target ions. In terms of Na^+, Cs^+ and Ca^{2+} selective ionophores for ion-selective electrodes, calixarenes are found to be excellent compared to crown ether derivatives or cryptands. Calixarenes can be also utilized to construct chemically modified electrodes, which are sensitive to gas species and biologically important compounds. The sophisticated design and synthesis of calixarenes are essential to specific potential applications to diverse fields.

Key words: calixarene, redox-dependent ionophore, electrochemistry, sensory device.

1. Introduction

A redox-dependent receptor is a receptor that undergoes a reversible redox process that changes the binding properties of the receptor [1]. Among such receptors, the molecules which recognize and bind specifically to a certain ion, can be classified and named separately as redox-dependent ionophore (RDI). As numerous biomimetic macrocycles with diverse structures and physical properties were reported, the idea of RDI was suggested and started to be realized on the basis of well known macrocycles such as crown ether derivatives in the early 1980s [2].

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Most of artificial RDIs are ionophoric macrocycles with one or more electrochemically active sites. RDIs can recognize ionic species by virtue of characteristic structures and cause a change in electrochemical response as a consequence of complexation. It is also possible that the electrochemical reaction results in the change of binding ability. As the potential application of these molecules can cover a wide range, they have received much attention recently. For example, they are primary components in electrochemical sensors by acting not only as a receptor for recognition but also as an electrochemical signal generator [3, 4]. RDIs can also be utilized in membrane separation systems that employ a potential gradient [1]. In addition, it is possible to extend toward the development of molecular switching devices [5, 6] and model studies on electron flow mechanism in various biological environments [7].

Studies on calixarenes were initially intended to use them as enzyme mimics, such as hem and aldolase mimics [8]. However, their excellent ion-binding properties were revealed by their capability of transporting metal cations across an organic membrane [9]. Thus, various calixarenes had been synthesized with phenolic groups, to which ion-binding groups such as pendant ester, ketone, amide and thioamide were incorporated [10]. The thermodynamic characteristics of calixarenes such as the structural flexibility are similar to those of crown ethers and other metacyclophanes [11, 12]. The framework of calixarenes is intrinsically flexible so that it needs only small extra energy to undergo structural changes for encapsulating guests. And also the structure of calixarene can be very preorganized to capture guests in the lower rim by replacing *para*-alkyl groups (usually *tert*-butyl) at the upper rim [10]. In these respects, calixarenes have advantages over other class of macrocyclic compounds as ionophores for analytical use. The appearance of diversely modified calixarenes has promoted analytical applications such as ionophores for polyvinyl chloride (PVC)-based ion-selective electrodes (ISEs) and ion-sensitive field effect transistors (ISFETs). This in turn has made calixarenes to be attractive as new candidates of RDI for potentiometric applications.

The goal of this article is to review the electrochemical property of redox-active calixarenes and also to probe the feasibility of their applications. It is in two parts dealing with the electrochemistry of redox-active calixarenes and their applications. With respect to the electrochemistry of calixarenes, descriptions about electrochemical reduction/oxidation of calixarenes with various redox-active groups are followed by explanations of the drastic changes in the presence of ionic species. Subsequent sections discuss the application of functionalized calixarenes for analytical use based on both voltammetric and potentiometric principles.

2. Electrochemistry of Calixarene

The basic strategy to create an electrochemically controllable artificial receptor is simply introducing a redox-active group to an ionophoric compound. In this case, the integrity of RDI lies on the change of structure or charge state as a

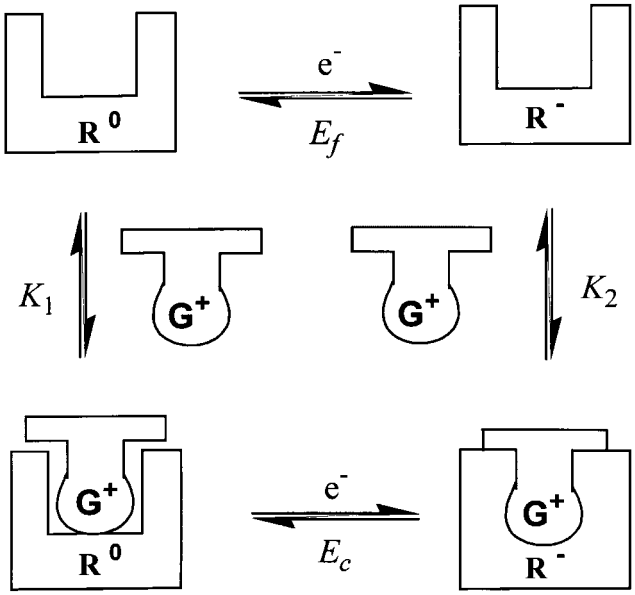


Figure 1. Schematic diagram of electrochemical recognition. $\Delta E_p = E_c - E_f$ = RT/nF ln K_2/K_1. R and G^+ stand for RDI and cationic guest, respectively. The presence of Na^+ can make electrochemical enhancement, K_2/K_1, of even 10^{10} order in acetonitrile when a suitably designed calix[4]arenediquinone is used as a RDI [13]. Molecular switching is possible if $K_1 < 1$ and $K_2 > 1$.

result of electrochemical reduction or oxidation. Figure 1 illustrates the principle of electrochemical recognition. Besides artificial RDIs, the idea can be also applied to redox-active biological receptors such as hormone receptors, enzymes [14], ubiquinone derivatives receptors [15], etc. To achieve relevant RDIs based on the calixarene framework, two different ways have been tried to introduce redox-active groups as shown in Figure 2. One is just the attachment of redox groups to the pendant alkyl chain and the other is conversion of one or more ring members, phenolic moieties to quinone.

As one of the promising candidates for RDI, the synthesis and the study of the fundamental electrochemical behavior of quinone-derivatized calix[4]arene in which one or more phenolic ring members are replaced by quinones have been reported [16–18]. The quinone moiety as a ring member of calixarene plays two roles simultaneously; as a redox center and as a ligating site. This novel structure offers an opportunity to see the effect of successive substitutions of redox units in the constrained annular framework. A quinone-derivatized calixarene enhances the cation binding ability when it is reduced to anionic states as has been described for redox-active crown ethers [19].

Calixarenemonoquinones show very similar redox behavior to that of 1,4-benzoquinone [12, 18]. Also calix[4]arenediquinone shows almost the same electrochemical behavior as calixarenemonoquinone except a shoulder-like peak, as

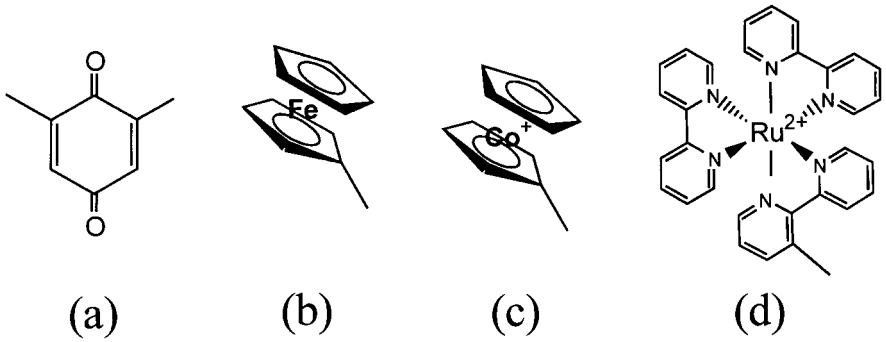


Figure 2. Redox active groups which have been incorporated to the calixarene framework as RDI. (a) quinone [13,16–26], (b) ferrocene [27–31], (c) cobaltocenium [32–34] and (d) ruthenium bipyridine [35, 36].

indicated by Figure 3. These results can be explained by the mechanism suggested in the study on spatially constrained quinones [16]. A systematic study on the effect of the number of the quinone moiety has been reported by Gómez-Kaifer et al. and the redox scheme of quinone-derivatized calix[4]arenes has been proposed as illustrated in Figure 4 [18]. First two cathodic peaks, which are contiguous to each other, are due to the two one-electron reductions of quinone (Q) to its anion radical ($Q^{-\cdot}$). The small difference in the reduction potential of two equivalent redox couples, $Q/Q^{-\cdot}$, stems from a little extra overpotential due to the coulombic repulsion. The coulombic repulsion energy between two reduced quinones was determined from voltammetry [16, 17]. On the other hand, the successive reduction of $Q^{-\cdot}$ to Q^{2-} (dianion) shows only one peak and it appears to be less reversible than that of $Q/Q^{-\cdot}$.

Since an appropriate substitution can allow the quinone-derivatized calix[4]arenes to exhibit high affinity as well as selectivity to cationic species [20–22], the presence of metal ions causes drastic and systematic changes in the electrochemical responses of the compounds as shown in Figure 5. Because Na^+ can fit into such a cavity formed by oxygen donor atoms in calix[4]arenes with little distortion, Na^+ complexes are the most favorable and thereby give rise to a considerable enhancement in the electrochemical reduction of the quinone-substituent [23]. The formation of stable complexes allows the successive addition of Na^+ to make quantitative increases in peak current without any changes in the peak potential. Whereas the reduction potential varies when different cations with different degrees of encapsulation are added [23, 24]. Figure 5 shows that substantially large enhancements in the presence of Ca^{2+} and La^{3+} come from the charge of the encapsulated cation in spite of the similar ionic radii compared to Na^+ [24]. It shows that the electrochemically reduced quinone can be stabilized by the formation of complexes or ion-pairs with cationic guests and the magnitude of stabilization depends on the strength of electrostatic interaction between quinone and guest ions [24]. Effects of metal ions towards various calixarenes are

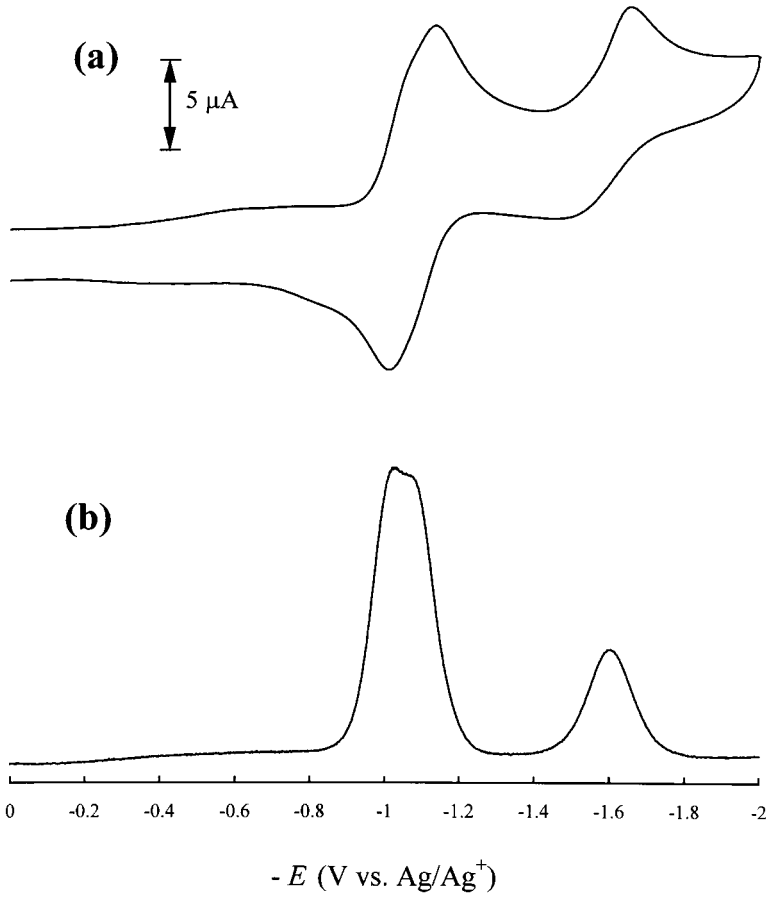


Figure 3. (a) Cyclic voltammogram and (b) differential pulse voltammogram of calix[4]arenediquinone [18, 24]. Calix[4]arenediquinone used in electrochemical test is 5,17-di-*tert*-butyl-26,28-bis[(methoxy-carbonyl)methoxy]calix[4]-25,27-diquinone (**3** in Table I) [13, 24]. Concentration of **3**; 1.0 mM, scan rate; 50 mV/sec, working electrode; glassy carbon (area = 0.071 cm^2), supporting electrolyte; 0.1 M tetrabutylammonium perchlorate in acetonitrile.

summarized in Table I, which shows that the difference between peak potentials due to the reduction of the quinone in the absence and presence of metal ions (ΔE_p) is dependent on the intrinsic ratio of charge to ionic radius of the metal ions. Accordingly, the characteristic ΔE_p can lead to recognition of various alkali, alkaline earth metal and lanthanide ions with different ratio of charge to ionic radius. In addition, the quinone-derivatized calix[4]arenes with suitably modified structure can form stable complexes with Na^+, Ca^{2+} and La^{3+}, while other hard metal ions cause ΔE_p by forming ion-pairs with electrochemically reduced quinone. Thus, a selective and quantitative analysis of these metal ions is possible

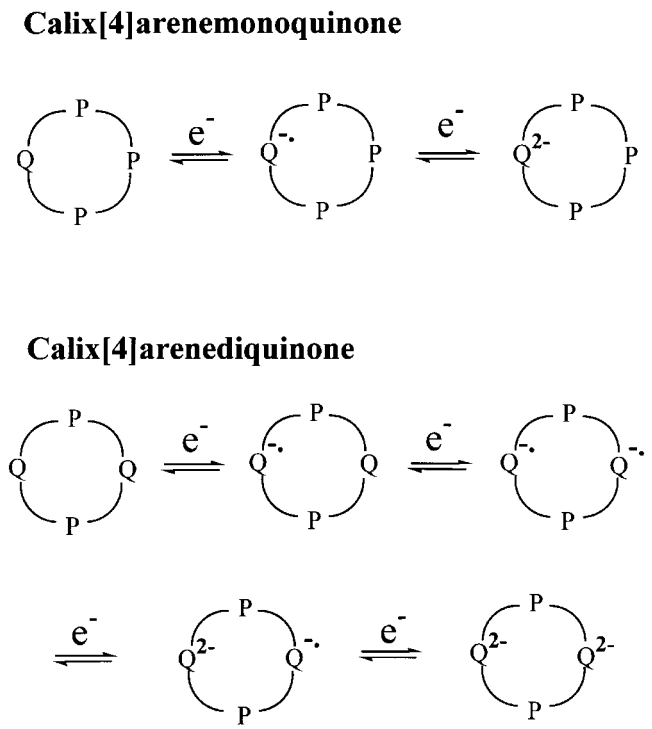


Figure 4. Schematic diagram of redox mechanism in the case of calix[4]arenemonoquinone and calix[4]arenediquinone [18, 24]. P and Q stand for phenolic and quinone moiety, respectively.

in aprotic media by measuring the cathodic current due to the reduction of their complexes which increases quantitatively without any change in peak potential.

Besides metal ions, proton sources with high proton donation power can also affect the reduction of the quinone in calixarenes. NH_4^+ and $BuNH_3^+$ are reported to form complexes and to show electrochemical enhancement as well, although they are both larger compared to the pore size of calixarene [20, 22, 25]. Ammonium ion and primary alkylammonium ions can be distinguished from each other as well as from secondary and tertiary alkylammonium ions based on the degree of enhancement measured by the positive potential shift, as summarized in Table II [25]. Beer et al. have proposed the formation of hydrogen bonds between NH_4^+ and four tetragonally located oxygen atoms [20, 22]. Besides the formation of hydrogen bonds, Kim et al. have explained that the mechanism involving electron transfer followed by proton transfer to quinone is also responsible for a relatively large potential shift [25]. Since the reduction potential of the quinone depends on the strength of hydrogen bonds between the quinone and proton sources, both the acidity of proton source and the formation of extra hydrogen bonds proximal to the redox center affect the electrochemical enhancement [25]. Furthermore, the peak potential shift varies with the structure of calixarenes and is influenced by the

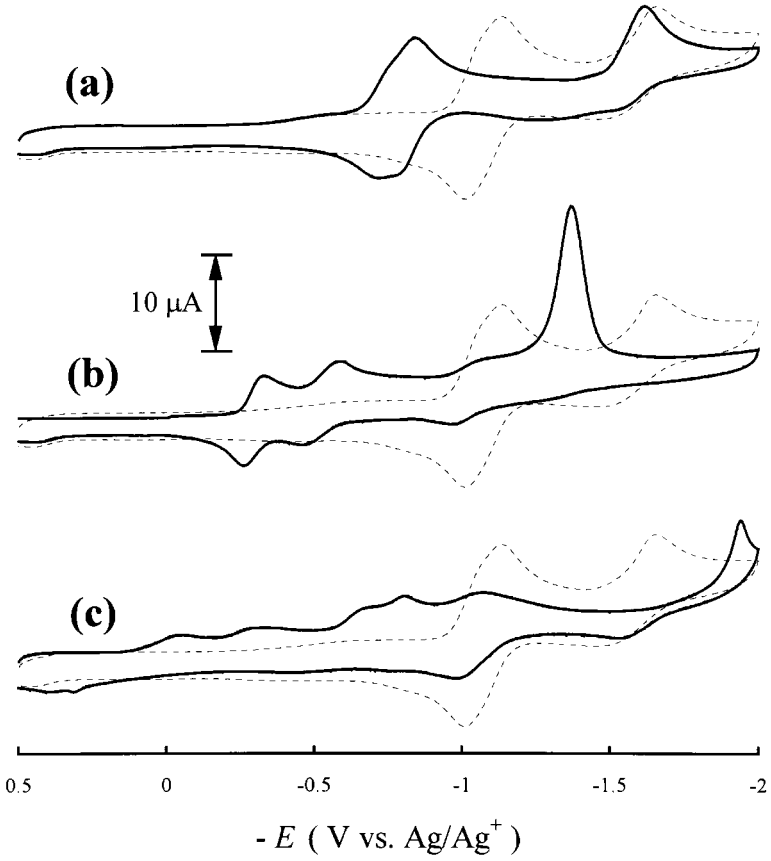


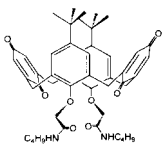
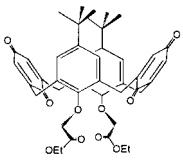
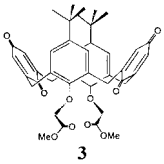
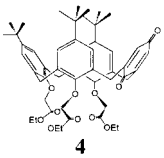
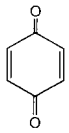
Figure 5. Cyclic voltammograms of calix[4]arenediquinone (**3**) in the presence of various metal ions with similar ionic radius [24]. Solid lines are voltammograms in the presence of Na^{+} (a), Ca^{2+} (b) and La^{3+} (c), respectively and dotted lines are in the absence of any metal ions. Experimental conditions are the same as those in Figure 3.

nature of solvents as well [12, 26]. Consequently, the electrochemical enhancement of calixarene is dependent on various factors such as charge/size of guest, the hydrogen bond between host and guest, and the number of the quinone moiety in the calixarene. Electrochemical properties of various alkylammonium ions are shown in Table II. Studies on calixarenes with more sophisticated structures [37, 38] and an extensive study on conformational conversion of quinone-incorporated calixarenes [39] have been reported.

3. Analytical Applications

Analytical applications of functionalized calixarenes have been concentrated predominantly on electroanalytical techniques such as voltammetry and potentiome-

Table I. Peak potential shifts (ΔE_p) of calixarenes with different structures due to the presence of various cations [13, 24–26]

Host / Guest	 **1** /mV	 **2** /mV	 **3** /mV	 **4** /mV	 /mV
NH_4^+	274	451	526	389	360
Li^+	248	402	430	–	120
Na^+	94	312	318	336	40
K^+	∼0	202	206	250	0
Ca^{2+}	513	735	752	–	280
La^{3+}	791	1021	1035	–	418

Peak potential shift is the difference in peak potentials due to the first reduction of hosts in the presence and absence of a cation ($\Delta E_p = E_{p,\text{presence}} - E_{p,\text{absence}}$). A glassy carbon disk (area = 0.071 cm^2) was used as the working electrode and other experimental conditions are the same as those in Figure 3. All guest ions were perchlorates.

try. Besides electrochemical methods, calixarenes have been used as well for the development of new analytical methods which are beyond the scope of this article.

3.1. VOLTAMMETRY

The voltammetric use of calixarenes can be considered with two classes. One is to utilize the changes in electrochemical responses of redox-active calixarenes as RDI and the other is to observe the change of redox behavior of guests in the presence of redox-inactive calixarenes.

Calixarenes derivatized with quinone can act as an excellent RDI for cationic species whereas ones with other groups such as cobaltocenium and ruthenium bipyridine can recognize anions. Quinone derivatives with ionophoric structures are reported to have an extra advantage over simple quinone compounds because they produce an additional electrochemical enhancement which can be used for further recognition of guests [19]. By virtue of characteristic binding between calixarenediquinone and primary alkylammonium ions, it is possible to analyze primary amines such as neurotransmitters and amino acids selectively by voltammetric techniques [40]. Since the shift of peak potential due to the electrochemical reduction of quinone depends on the acidity of the guest's functional group, various carboxylic acids also can be analyzed quantitatively [12, 25]. The electrochemical response correlates linearly with the concentration of biologically

Table II. ΔE_p of various alkylammonium complexes [25]

Guest ions	$\Delta E_{p(1)}$ /mV	$\Delta E_{p(BQ)}$ [a] /mV	$\Delta E_{p(1)} - \Delta E_{p(BQ)}$ [a]	pK_a [b]
NH_4^+	417	307	110	9.24
$MeNH_3^+$	335			10.64
$Bu\ NH_3^+$	323	197	126	10.64
$Me_2NH_2^+$	274			10.77
$Bu_2NH_2^+$	182	180	2	11.25
Me_3NH^+	215			9.80
Bu_3NH^+	197	211	−14	9.93
Me_4N^+	∼0			–

$\Delta E_{p(1)} = E_{p,\text{presence}} - E_{p,\text{absence}}$ $E_{p,\text{presence}}$ and $E_{p,\text{absence}}$ denote peak potentials, where first electron transfer to **3** occurs, in the presence and absence of a guest, respectively. $\Delta E_{p(BQ)}$ stands for $E_{p,\text{presence}} - E_{p,\text{absence}}$ when 1,4-benzoquinone, which is a host without ionophoric structure, is used instead of **3**. A platinum disk (area = 0.071 cm^2) was used as the working electrode and other experimental conditions are the same as those in Figure 3.

[a] 1,4-Benzoquinone.

[b] Acid dissociation constant of alkylammonium ion in aqueous media at 25 °C where ionic strength is zero.

important analytes such as ammonium ion, glycine, dopamine, histamine, maleic acid and pyruvic acid in acetonitrile-water mixed solvent [40]. In addition, the electrochemistry of calixarenequinone suggests a convenient method for selective analysis of hard metal ions such as alkali, alkaline earth and lanthanide ions. Calixarenediquinones show an exceptional affinity to Na^+, Ca^{2+}, Ba^{2+} and La^{3+}. The range of peak potential shift is so wide from *ca.* 0.4 V for Na^+ to *ca.* 1.0 V for La^{3+} that very selective analysis is possible [25].

Beer et al. reported variously designed compounds including calixarenes with cobaltocenium for systematic study on selective anion recognition [32–34]. Among cobaltocenium derivatives, calixarenes with a single cobaltocenium moiety in the upper rim recognizes acetate anion in acetonitrile as shown in Table III [34]. Calixarenes with two cobaltocenium moieties are selective to dicarboxylate dianion adipate in acetone [33]. But it seems that the structural advantage of the calixarene framework is not clear and electrochemical selectivity depends seriously on solvent properties. In a similar way to the studies on the cobaltocenium derivatives, calixarenes with one and two ruthenium bipyridines were prepared and the effect of anions was investigated [35]. This study claims that calixarenes with one ruthenium bipyridine exhibits more selective affinity towards $H_2PO_4^-$ than calixarenes with two ruthenium bipyridyl moieties or ruthenium bipyridine derivatives without the

Table III. Complexation and ΔE_p of cobaltocenium calix[4]arene in the presence of various anions [34]

Anions	Stability constant[a] /m^{-1}	ΔE_p [c] /mV
Cl^-	70	60
Br^-	–[b]	–
NO_3^-	125	20
HSO_4^-	40	10
$H_2PO_4^-$	6380	130
$CH_3CO_2^-$	41520	155
$PhCO_2^-$	38400	140
$PhCH_2CO_2^-$	22270	150
$C_{10}H_{17}CO_2^-$	19750	135

[a] Stability constants were determined by ^1H NMR anion titration in $(CD_3)_2SO$, in which errors are estimated to be $\leq$10%.
[b] The stability constant could not be calculated in this solvent because of very weak binding.
[c] Peak potential shifts were obtained in acetonitrile solution containing 0.1 M NBu_4PF_6 as supporting electrolyte. Cathodic shifts of cobaltocenium/cobaltocene redox couple in the presence of anions (up to 5 equivalent) added as their tetrabutylammonium salts.

calixarene structure. In addition to this study, acyclic and macrocyclic derivatives with ruthenium bipyridine are compared with calixarene derivatives in terms of structural effect to anion recognition ability [36].

As shown in the study by Kaifer et al., one would expect that electrochemically active organic amines bound to calixarene could be detected voltammetrically [41, 42]. However, no notable report has yet been published on the practical application of calixarenes for electrochemically active organic analytes.

3.2. POTENTIOMETRY

The first calixarene-based ISE was reported by Diamond et al. in 1986 [43]. Since then, calixarenes have been widely employed as a new class of macrocyclic ionophores in a potentiometric application. O'Connor et al., who reviewed electroanalytical applications of calixarenes, described that the targets of ISEs based on calixarenes are mostly concentrated on five species; Na^+, K^+, Cs^+, heavy metal ions and organic amines [44]. In particular, Na^+ and Cs^+-selective ISEs have been

Table IV. The change of reduction potential of ruthenium bipyridyl calix[4]arene due to various inorganic anions [35]

	ΔE_p/mV		
Anions/Receptors	calix[4]arene-Ru(bpy)$_3$	calix[4]arene-[Ru(bpy)$_3$]$_2$	open chain-Ru(bpy)$_3$
$H_2PO_4^-$ [a]	175	30	130
HSO_4^-	15	<5	15
Cl^-	70	30	65
Br^-	60	15	60
I^-	40	–	10

ΔE_p values mean the cathodic shift of reduction potential in the presence of anions (up to 10 equivalent) added as their tetrabutylammonium salts and were obtained in acetonitrile containing 0.1 M NBu_4PF_6 as supporting electrolyte. Solutions were *ca.* 5×10^{-4} M of compound and potentials were determined with reference to a Ag^+/Ag electrode (330 ± 5 mV vs. SCE) at 21 ± 1 °C at 50 mV/sec.

[a] Dimethylsulfoxide was added (up to 50% v/v) before the addition of $H_2PO_4^-$ to prevent precipitation of complex.

proven to be so successful that *tert*-butylated calix[4]arene ethyl ester is commercialized as an ionophore for Na^+-selective ISE [45–48]. This is based on the fact that calix[4]arenes and calix[6]arenes have an inherently suitable pore for Na^+ and Cs^+, respectively.

Cadogan et al. showed that K^+-ISE, which needs a host molecule with a pore of the intermediate size between those of calix[4]arene and calix[6]arene, can be achieved by inserting an additional ethereal oxygen between two of the four methylene bridges [49]. 1,3-Alternate calix[4]arenecrown-5 conformers were reported to show an excellent K^+/Na^+ selectivity, which is even superior to valinomycin [50]. Moreover, calixarene telomer based on calix[4]arene-crown-5 has been reported as a K^+-selective ionophore [51]. As a new approach, incorporation of quinone into calix[4]arene enlarges the effective pore size so that calix[4]arenediquinones show more selectivity toward K^+ rather than Na^+ [52].

Other than the conventional ISE based on PVC membrane, there has been a move not only toward different electrode configurations such as ISFET [53, 54], optode [55, 56] and coated wire electrode [57] but also to utilize other polymer matrices like silicon rubber [58]. Many valuable applications have been reported to clinical analysis employing miniaturized Na^+-selective ISE [44] and to flow injection analysis using a calixarene-based potentiometric detector [59] including sensor arrays [60, 61] which allow multicomponent determination possible.

The cavity of calix[6]arene or calix[4]arene-crown-6 is suitable for entrapping Cs^+ [62, 63]. Recently, doubly crowned calix[4]arenes in 1,3-alternate conformation can be utilized as Cs^+-selective carriers in supported liquid membrane [64]. Shinkai et al. have synthesized an ionophore with high Ca^{2+}-selectivity determined by extraction experiments [65]. In order to develop calixarene-based ISEs sensitive

to various heavy or transition metal ions, calixarenes with soft donor atoms are necessary. Several papers have been reported on Ag^{+} [66, 67], Cd^{2+} [67], Pb^{2+} [67], Cu^{2+} [67, 68] and Hg^{2+} [68]-selective calix[4]arenes with soft donor atoms such as nitrogen and sulfur. Direct comparison among these ionophores appears to be difficult because each has employed different methods to check the selectivity e.g. conventional ISE [66], extraction [67] and ISFET [68]. In addition, studies have demonstrated that calixarenes can form complexes with organic cations and thus are suitable ionophoric platforms for organic potentiometric analysis [69, 70]. According to these reports, the best response is obtained for primary amines with no substituent adjacent to the amino group, for example, analytes such as 1-octylamine, dopamine and hexylamine.

4. Perspectives of Calixarene Chemistry

Calixarenes are stable and easy to synthesize and modify. Moreover, they can form polymer [71, 72], dendritic network particles [73] and liquid crystalline systems since columnar mesophases are possible [74]. Therefore, the application of calixarenes covers surprisingly diverse ranges and is on the way to spread wider. Fields such as development of new catalysts [75], non-linear optics [76] and removal of heavy metal ions and/or uranyl ion in environmental engineering [67, 77] are employing calixarenes actively even though they are omitted in this review. In the future, molecular electronics, a model study on electron/proton flow in biological systems and other biomimetic approaches using calixarenes, in our minds, are predicted to be prosperous as interdisciplinary subjects involving electrochemistry, organic synthesis and other related sciences.

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