Interaction between various alkylammonium ions and quinone-derivatized calix[4]arenes in aprotic media [1]

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Abstract

The complexation and electrochemical behavior of redox-dependent ionophores in the presence of various alkylammonium ions were examined with calix[4]arenediquinone compounds. In spite of the small ligating pore, semi-empirical calculation and ^{1}H NMR spectra showed that calix[4]arenediquinones were able to form complexes with protonated amine-type guests by virtue of three or four hydrogen bonds between the guest and carbonyl oxygen atoms in the host molecules. As a result of encapsulation, the structure of the calixarenes underwent a large conformational change, especially in the lower rim, which was rearranged to provide a symmetrically tetragonal binding environment. In addition, the reduction potential of the quinone moiety shifted to the positive direction. The magnitude of the potential shift depended on the strength of the hydrogen bond with the quinone. Therefore, the acidity and capability of forming multiple hydrogen bonds were predominant factors among other properties of the guest. The cooperative shortening effect of neighboring hydrogen bonds between the ammonium ion and carbonyl oxygen atoms produced an extra enhancement by making the redox center easily reducible and fast proton transfer possible. © 1997 Elsevier Science S.A.

Keywords: Calix[4]arenediquinone; Alkylammonium ions; Hydrogen bonding; Encapsulation; Proton transfer; Redox-dependent receptor

1. Introduction

Ionophoric macrocyclic compounds with electrochemically active functionalities have received much attention recently, concerning the development of selective ion-sensing and molecular switching devices. These artificial compounds are redox-dependent receptors which undergo a redox process that changes the binding properties of the receptor [1]. In single receptor molecules, they are capable of both recognizing cationic species and causing a change in electrochemical response as a consequence of complexation. Thus, the potential application of these molecules can cover a wide range such as selective electrochemical detectors [2,3], molecular redox switching [4–6], and a model

study of electron transfer in biological systems [5] to name a few.

On the other hand, quinone is well known as an important functional moiety in biological systems, for example as an electron–proton carrier in respiratory assemblies and in photosynthetic electron flow systems [7]. Numerous reports are devoted to the electron transfer mechanism and its equilibria with protons [8,9]. As a result, the basic concept and mechanism have been well established but its role and application in biological systems remain yet to be solved. Quinone derivatives with diverse substituents and various forms with different oxidation states constitute a vast topic to study. In addition, the application of quinone derivatives, such as polymeric quinone compounds and quinone-modified macrocycles, is provoking a new interest in the development of molecular electronics [10,11] and potentiometric sensors [12–14].

As one of the promising candidates for redox-dependent receptors, extensive work on the synthesis and fundamental electrochemical behavior of quinone-derivatized

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calix[4]arene, in which one or more phenolic ring members are replaced by quinones, has been reported [15–20]. The quinone moiety in calixarene serves simultaneously not only as a redox center, but also as a ligating site. These authors also showed that electron transfer to quinones spatially constrained in the calixarene framework was analogous to that of a sequential p-benzoquinone series separated by methylene linkages [21]. Based on these results, the coulostatic repulsion energy between two reduced quinones was also determined [22,23].

In addition, appropriate substitution in the lower rim of calix[4]arenediquinone was attempted in order to improve selectivity in recognizing cationic guests [24–26]. Because of the limited pore size of the compound, Na^+ formed a complex preferentially and also gave rise to a remarkable enhancement in the electrochemical reduction of quinone [25,27]. When metal ions were added to calix[4]arenediquinone solution, the magnitude of the peak potential shift to the positive direction depended on the charge and size of the cations. Successive addition of an ion capable of encapsulation, such as Na^+, resulted in a quantitative increase in the peak current without changing the peak potential, whereas cations incapable of encapsulation did not show any such effect [28].

In addition to metal ions with a similar size to Na^+, NH_4^+ and $BuNH_3^+$ were reported to form complexes and showed electrochemical enhancement as well, although NH_4^+ showed a somewhat large enhancement considering the pore size of the host. Beer and coworkers suggested that these phenomena probably resulted from NH_4^+ and four tetragonally located oxygen atoms [24,26]. We have shown that the mechanism involving electron transfer followed by proton transfer to quinone is responsible for the relatively large peak shift [28]. So, hydrogen bondings between various alkylammomium ions and quinone are considered to be very closely related to the reduction potential of quinone.

Even though 1 and 2 are structurally very similar, their electrochemical behavior is not the same. The association constants of $2-NH_4^+$, $2-BuNH_3^+$ and complexes with a few metal ions have already been published [24]. However, a systematic electrochemical study of calix[4]arenediquinone in the presence of a variety of protonated alkylamines, to the best of our knowledge, has not been reported yet. 1 gives a larger electrochemical enhancement than 2 and it clearly shows two separated peaks due to the complex and the free host [28]. Therefore, 1 seems to be a better compound with which to study the correlation between complexation behavior and coupled electrochemistry, so 1 is the subject of electrochemical investigation in this paper.

The purpose of the present paper is to demonstrate the complexation behavior of calix[4]arenediquinone with various types of alkylammonium ions and to show a relationship between the properties of the guests and the electrochemical enhancement of the host.

2. Experimental

2.1. Electrochemistry and ^1H NMR spectroscopy

Electrochemical experiments were performed with a Windows-driven electrochemical analyzer (BAS100B/W) (Bioanalytical Systems, West Lafayette, IN) in acetonitrile (AN) using positive feedback routines to compensate for resistance. The surface of the working electrode, a platinum BAS minielectrode (area $0.030\,cm^2$) was polished with $0.3\,\mu m$ alumina (Buehler, Lake Bluff, MN) and then rinsed with deionized water and washed carefully with purified AN. A Pt wire counter electrode and a home-made $Ag|(0.01\,M)Ag^+$ reference electrode were used for voltammetric experiments. All experiments were carried out in a nitrogen atmosphere at room temperature. ^1H NMR spectra were obtained with a Bruker AMX-500 (500 MHz).

2.2. Reagents and synthesis

Tetrabutylammonium perchlorate (TBAP) was prepared by mixing perchloric acid (70%, Merck) and tetrabutylammonium bromide (Aldrich), then recrystallized three times from ethyl acetate and n-pentane mixed solvent and dried for 48 h under reduced pressure at 60°C [29]. AN (Merck or Fisher, HPLC grade) was distilled with calcium hydride for 24 h just before use.

5,17-Di-$tert$- butyl-26,28-bis[(methoxycarbonyl)methoxy]calix[4]-25,27-diquinone (1) and 5,17-di-$tert$-butyl-26,28-bis[(ethoxycarbonyl)methoxy]–calix[4]-25,27-diquinone (2) were synthesized and identified according to the literature [24]. All ammonium guests used throughout the experiments were perchlorate forms prepared from the corresponding amines and perchloric acid. They were recrystallized from proper solvents, i.e. water for quaternary and primary alkylammonium salts, methylene chloride and diethyl ether for secondary alkylammonium, trimethyl- and triethylammonium salts and methylene chloride and n-hexane for tributylammonium salt. Ammonium perchlorate (Aldrich, A.C.S.reagent grade) and other alkylammonium perchlorates were carefully protected from moisture throughout the experiments.

2.3. Semi-empirical calculation

Geometries of 2 and its complexes with $Bu_nNH_{4-n}^+$ ($n = 0,1,2,3$) were optimized by employing the energy minimization scheme with DISCOVER version 2.8.0 (Biosym Technologies, San Diego, CA) and an IBM RS6000 53H workstation. The initial structure was taken from its X-ray crystallographic structure [26]. $Bu_nNH_{4-n}^+$ is initially positioned so that the nitrogen atom is located at the center of mass of four oxygen atoms from quinones and ester groups. The conjugate gradient scheme was used until an r.m.s. error of $0.4\,J\,mol^{-1}\,A^{-1}$ was reached in the energy mini-

mization. The dielectric constant was set to 1.0 throughout the entire geometry optimization.

3. Results and discussion

3.1. Complexation behavior

Both 1 and 2, as shown in Fig. 1, have two quinones as ring members instead of corresponding p-tert-butyl-phenolic moieties, to which methylester and ethylester groups are tethered respectively. The open structure in the lower rim is supposed to create a more flexible or less preorganized structure. Moreover, if a guest, such as an alkali metal ion requiring eight coordination sites of cubic type, is added to the host solution, the host is deficient by two sites because calix[4]arenediquinones can provide only six oxygen atoms of hard binding sites. As a consequence, 1 and 2 are thought to form less stable complexes with alkali metals and give low selectivity compared to 3 reported previously [27]. The association constants of 2–metal ion complexes have been determined [24,26].

NH_4^+, however, gives contrary results compared to alkali metal ions in that 1 and 2 form relatively stable complexes with NH_4^+ while the formation of $3-NH_4^+$ has not been reported. ^1H NMR data of $ArCH_2Q$ in Table 1 indicate that NH_4^+ and $BuNH_3^+$ form complexes with 1 but $Bu_2NH_2^+$ and Bu_3NH^+ do not. In particular, the $1-NH_4^+$ complex gives a large split of chemical shift of $ArCH_2Q$, which implies that a rigid cone conformation can be expected upon the encapsulation of NH_4^+ into the pore. 2 also forms $2-NH_4^+$ and $2-BuNH_3^+$ complexes, whose association constants have been obtained by UV–vis spectrophotometry [24].

The length of the alkyl chain of primary alkylammonium ions has only a slight influence on the ^1H NMR
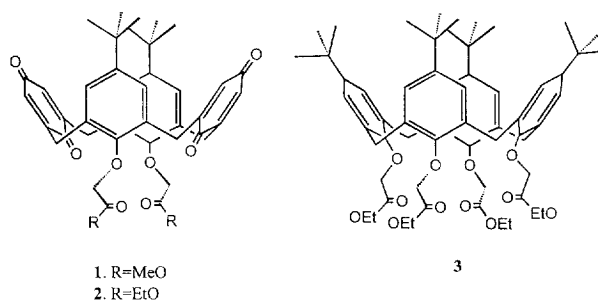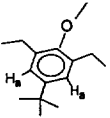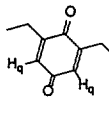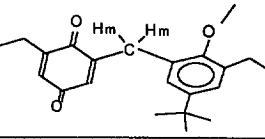

1. R=MeO
2. R=EtO

3

Fig. 1. Structures of model compounds 1–3.

spectra. Also, only negligible complexation is observed for secondary and tertiary alkylammonium ions. A preliminary thermodynamic study provides a good agreement with ^1H NMR in that complexation in the case of NH_4^+, $BuNH_3^-$ and Na^+ is a typical exothermic process, whereas $Bu_2NH_2^+$ and Bu_3NH^+ cause only small heat change comparable to that due to dilution [30].

Calixarenes are usually composed of two parts with mutually opposite characteristics; a hydrophobic site in the upper rim and a hydrophilic site in the lower rim. Cations are likely to be trapped in the hydrophilic side, whereas the hydrophobic upper rim can wrap up neutral organic molecules [27]. For the calix[4]arene in which all ring members are modified with four ethylester groups in the lower rim (3), as seen in Fig. 1, Na^+ fits best into the pore so that very high selectivity over other metal ions, as well as formation of a remarkably stable complex, has been discovered [31]. According to the report concerning thermodynamic phenomena upon complexation between calixarenes and alkali metal ions, ionophoric calixarenes show similar behavior to that of cyclodextrin derivatives rather than to that of porphyrins or cryptands [32]. These results mean that the structure of calix[4]arene is quite flexible

Table 1

Chemical shift of 1 in ^1H NMR spectra in the presence of various alkylammonium ions and metal ions. '−' and '+' signs mean up-field and down-field shift compared to free 1 respectively

Guest			
NH_4^+	-0.061	+0.090	0.351[a]
$BuNH_3^+$	-0.066	+0.048	0.243
$Bu_2NH_2^+$	-0.031	+0.029	0.018
Bu_3NH^+	-0.011	+0.009	0.008
Na^+	+0.090	+0.144	0.281
La^{3+}	+0.105	+0.219	0.064

[a] Two sets of doublets are observed which indicate cone conformation. The magnitude of the split is recorded as the difference between average values of each doublet.

and can be rearranged according to the characteristics of guests.

Unlike **3**, which has too small a cavity and too rigid a structure to entrap a large ion like NH_4^+, **1** and **2** can not only allow large conformational changes but also the formation of hydrogen bonds. Therefore, it is possible for NH_4^+ to form complexes with **1** and **2**, which suppress the freedom of intramolecular structure, although NH_4^+ is too large to be encapsulated into the pore. Primary alkylammonium ions are also expected to form complexes by making three hydrogen bonds. Secondary and tertiary alkylammonium ions such as $Bu_2NH_2^+$ and Bu_3NH^+ have bulky alkyl branches as well as two and one hydrogen atoms respectively which are available for hydrogen bonding.

Semi-empirical calculation provides information about the structural rearrangement of calix[4]arenediquinone in the presence of NH_4^+ and $BuNH_3^+$. Even though structures are optimized without considering any solvent effect, the computational work makes it possible to predict the binding sites, the extent of conformational change, and the relative location of the guest, etc. Fig. 2 illustrates the optimized structures of **2**, **2**–NH_4^+ and **2**–$BuNH_3^+$, and Table 2 summarizes the results of simulated geometries before and after complexation. Upon the addition of NH_4^+, two carbonyl oxygen atoms of ethylesters and two of quinones create a symmetrically tetragonal binding environment through an extensive structural rearrangement. The optimal location of the captured NH_4^+ is the center of the pore and the four hydrogen bonds are almost linear ($\angle NHO_{ql}$ is 170° in Table 2) and the estimated distance between the nitrogen and oxygen atom is less than 2.8 Å. As a consequence of widening of the space between two

substituents in the lower rim, the phenolic moieties rise vertically and the quinones become tilted. If the same calculation is performed with $BuNH_3^+$, it indicates that two oxygen atoms of ethylesters and only one of the quinones provide sites for hydrogen bondings. In the cases of $Bu_2NH_2^+$ and Bu_3NH^+, two and one hydrogen bonds respectively are possible, but simulated results show that they move out from the pore, which indicates that no encapsulation is possible in solution.

With respect to interacting sites between calix[4]arenediquinone and guest, the chemical shifts of ArH and QH of ^1H NMR spectra provide other meaningful evidence for judging the extent of hydrogen bonding. Upon the addition of alkylammonium ions and NH_4^+, as shown in Fig. 3 and Table 1, a down-field shift of QH(H$_q$) and an up-field shift of ArH(H$_a$) are observed. The down-field shift of QH has the same trend as the magnitude of the split of chemical shifts due to the methylene group (ArCH_2Q). The chemical shift of ArH shows two contradictory types of behavior: an up-field shift in the presence of NH_4^+ and $BuNH_3^+$, but a down-field shift upon the addition of Na^+ and La^{3+}. The magnitudes of the up-field shift due to NH_4^+ and $BuNH_3^+$ are almost the same, and that of the down-field shift in the case of La^{3+} is much larger than that due to Na^+. Based on the split of chemical shifts of the methylene group (ArCH_2Q) and semi-empirical calculation results, two possible explanations can be made.

One explanation is the conformational fixation effect and the other is the cation field effect. The former is the change of electric field from neighboring phenolic and quinone moieties induced by structural fixation. Complexation prevents quinone moieties from free rotation along the
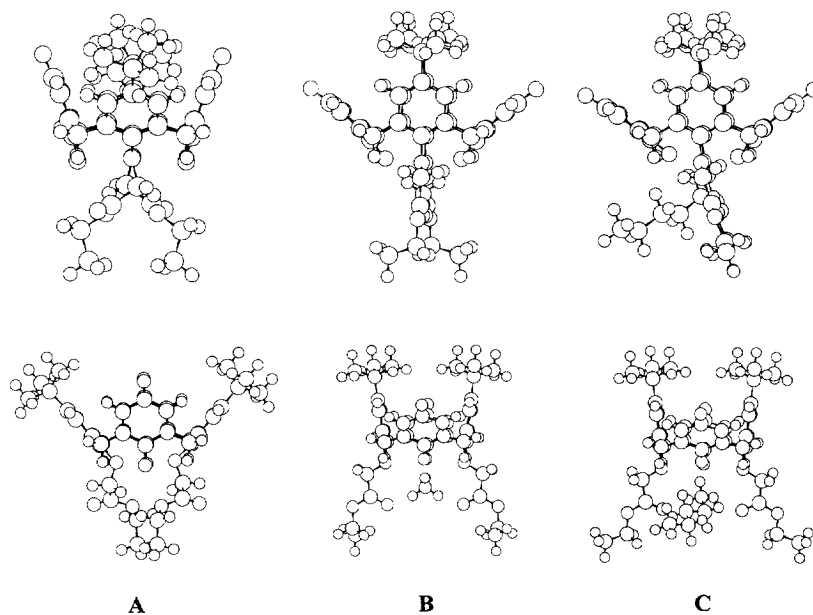

A   **B**   **C**

Fig. 2. Semi-empirically optimized structure of **2** in the absence of any guest (A), in the presence of NH_4^+ (B) and $BuNH_3^+$ (C). Upper figures show phenolic rings, while the lower figures show quinone rings.

Table 2
Results obtained by semi-empirical calculation of 2 and its complexes

		2	2–NH$_4^+$	2–BuNH$_3^+$	2–Bu$_2$NH$_2^+$
Distances/Å	O$_{ql}$–O$_{ql}$/O$_{qu}$–O$_{qu}$	5.17/8.52	3.99/11.84	3.64/12.05	4.68/9.57
	O$_p$–O$_p$/C$_p$–C$_p$	3.55/9.27	5.29/6.28	5.35/6.27	4.10/8.56
	O$_e$–O$_e$	7.11	5.12	5.21	6.75
	N–O$_e$		2.79	2.85 (2.91)[a]	2.82 (6.80)[a]
	N–O$_{ql}$		2.75	2.81 (2.91)[b]	2.83 (6.45)[b]
	H–O$_e$		1.72	1.84 (2.07)[a]	1.82 (6.78)[a]
	HO$_{ql}$		1.79	1.87 (2.57)[b]	1.81 (5.74)[b]
Angles/deg	N–H–O$_{ql}$		170.08	150.37	166.02
	H–O$_{ql}$=C		175.84	170.38	140.96

O$_{ql}$, oxygen atom of quinone in the lower rim; O$_{qu}$, oxygen atom of quinone in the upper rim; O$_e$, carbonyl oxygen atom of ester groups; O$_p$, ethereal oxygen atom of phenolic moieties; C$_p$, carbon atom of phenolic ring connected to t-butyl group in the upper rim side.
[a] Relevant distance with the other ester group.
[b] Relevant distance with the other quinone moiety.

axis of methylene groups in both sides and causes the structure to be frozen in a rigid cone conformation, as shown in Fig. 2. As a result, a mutual ring current effect, the phenolic ring to QH and quinone moieties to ArH, becomes significant. Considering only the structural as-

Fig. 3. ^{1}H NMR spectra corresponding to ArH and QH of 1 in the absence of any cationic guest (A), in the presence of an equimolar amount of Bu$_2$NH$_2^+$ (B), BuNH$_3^+$ (C), NH$_4^+$ (D) and Na$^+$ (E). All alkylammonium salts added as guests are perchlorate form and solvent is AN-d_3.

pects of 1 and 2, ArH becomes shielded, while QH is deshielded because of the different geometrical location of each nuclei and the direction of electric field from two different ring members. Therefore, if the guest has a small ionic field and does not interact directly with the phenolic moiety, chemical shifts due to ArH must be toward up-field; however, it is down-field for QH. On the other hand, the cationic field of the guest can influence the chemical shift in a different fashion. When a positive charge is located in the lower rim and contacts closely all ring members, both ArH and QH are supposed to undergo a deshielding effect whose magnitude depends on the ionic field of the cationic charge.

Na$^+$ gives rise to down-field shifts of both ArH and QH, and La^{3+}, similar size with a high ionic field, causes a larger down-field shift than Na$^+$. Although NH$_4^+$ also has a positive charge, its estimated ionic radius is much bigger than Na$^+$ or La^{3+}. Moreover, the positive charge density of NH$_4^+$ is thought to be concentrated at the four hydrogen atoms that take part in hydrogen bonding while that of the metal ions is spherically delocalized.

On the basis of this consideration, up-field shifts of ArH indicate that NH$_4^+$ makes only a slight contribution to the chemical shift of ArH except through conformational fixation of the whole structure. Ammonium ion has no direct interaction with the phenolic moieties but only with the quinones. Regarding NH$_4^+$ as a hydrogen bond donor, this phenomenon also gives evidence supporting the proposal that the association of calix[4]arenediquinone and NH$_4^+$ is based on hydrogen bonding between NH$_4^+$ and carbonyl oxygen atoms from ester groups and quinones. If complexation of primary alkylammonium ions such as BuNH$_3^+$ is treated in the same manner, it is reasonable to assume that two oxygen atoms from ester groups and one from quinone play the role of hydrogen bond acceptors. Secondary and tertiary alkylammonium ions capable of taking part in up to two hydrogen bonds, however, do not form complexes which are stable enough to produce a noticeable change of the chemical shift in the ^{1}H NMR
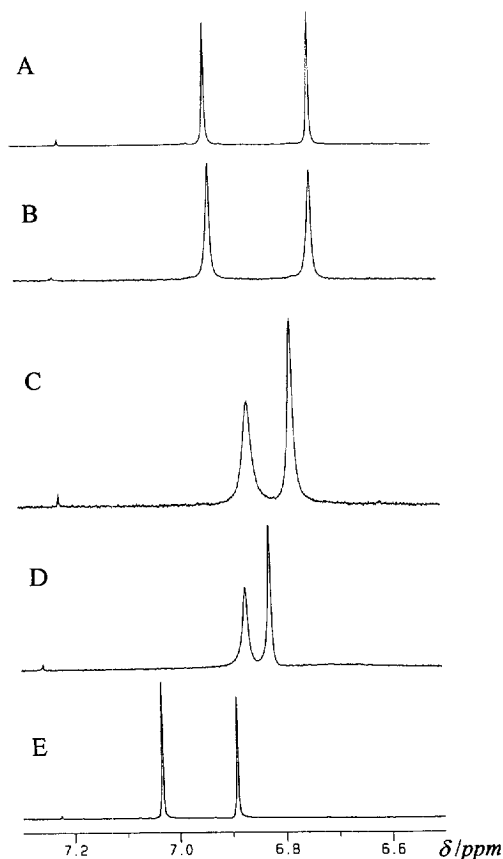
spectrum or a change of temperature in a calorimetric titration.

3.2. Electrochemical response in the presence of protogenic guests

NH_4^+ and $BuNH_3^+$ have been reported to form complexes with calix[4]arenediquinones bearing ethylester substituents or polyethers interconnecting two phenyl moieties in the lower rim [24,26,33]. They give rise to positive potential shifts of electrochemical reduction of the quinone moieties in the calixarene framework. In the reduction process of quinone, NH_4^+ acts as a proton donor, namely a Brønsted acid, as well as a cationic species [28]. When metal ions are added as guests, the shift in reduction potential ΔE_p depends on the charge and the size of the ions [28]. However, ΔE_p due to protogenic species such as NH_4^+ and $BuNH_3^+$ is larger than that due to Na^+ although they are much bigger. Referring to the report that the electrochemical behavior of calix[4]arenediquinones upon the addition of NH_4^+ or $BuNH_3^+$ is quite different from the case of metal ions, this result implies that there might be a relationship between ΔE_p and the characteristics of protogenic guests in addition to the charge and size [28,34].

Fig. 4 illustrates the cyclic voltammograms of 1 in the presence of two different butylammonium ions. ΔE_p upon the addition of Bu_3NH^+ is smaller than that of $BuNH_3^+$,
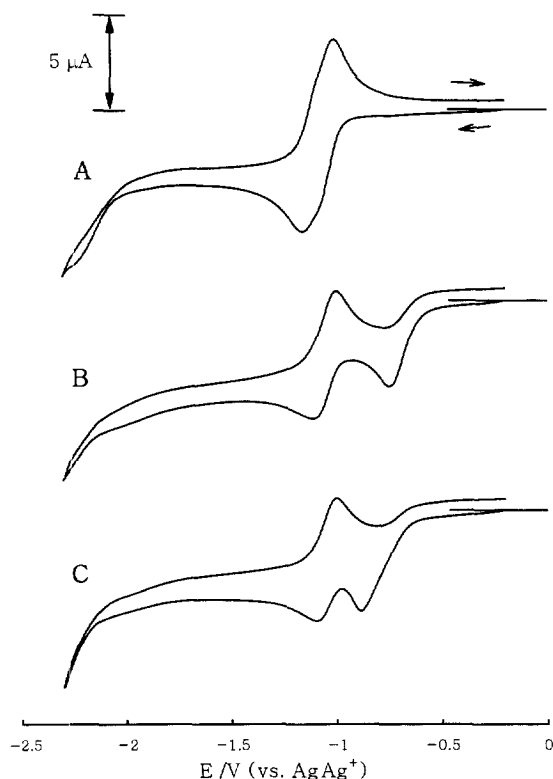

Fig. 4. Cyclic voltammograms of 1 in AN in the absence (A), and presence of 1.0 equiv. of n-butylammonium ion (B) and tributylammonium ion (C). Supporting electrolyte: 0.1 M TBAP. Scan rate: 50 mV s⁻¹. Working electrode: platinum disk.

Table 3

Peak potential shifts of 1 in the presence of various protogenic guests by cyclic voltammetry. $\Delta E_p = E_{p,complex} - E_{p,free\ host}$ with respect to first electron transfer

Guest ions	$\Delta E_{p(1)}$ /mV	$\Delta E_{p(BQ)}$ [a] /mV	pK_a [b]
NH_4^+	417	307	9.24
$MeNH_3^+$	335		10.64
$EtNH_3^+$	313		10.64
$BuNH_3^+$	323	197	10.64
$PhCH_2NH_3^+$	401		9.35
$Me_2NH_2^+$	274		10.77
$Et_2NH_2^+$	232		10.93
$Bu_2NH_2^+$	182	180	11.25
Me_3NH^+	215		9.80
Et_3NH^+	158		10.72
Bu_3NH^+	197	211	9.93
Me_4N^+	~ 0		—

[a] 1,4-Benzoquinone.
[b] Acid dissociation constant of alkylammonium ion in aqueous media at 25°C at zero ionic strength.

but its electrochemical behavior appears to be same. Voltammetric data with various alkylammonium series shown in Table 3 indicate that the ΔE_p obtained with primary alkylammonium ions (RNH_3^+) seems to be almost independent of the length of alkyl chain (R) from methyl (C1) to hexyl (C6) and fairly distinguishable from those due to NH_4^+ and $R_2NH_2^+$ as well as R_3NH^+. As for $R_2NH_2^+$ and R_3NH^+, ΔE_p decreases with an increase of pK_a. The acidity effect indicated by pK_a is highest when benzylammonium ion is used as a guest. It produces a larger shift than the other primary aliphatic ammonium ions mentioned above. Even though the pK_a values were obtained in aqueous media and they may be different in AN, we are able to make a qualitative indication. The quaternary ammonium ion, Me_4N^+, which has no proton to release, gives no enhancement as expected.

Even if $R_2NH_2^+$ and R_3NH^+ do not form stable complexes, noticeable electrochemical enhancements are still observed. It is not surprising that the reduction of p-benzoquinone is also enhanced in the presence of protogenic species which are acting as hydrogen bond donors, and that ΔE_p depends only on the acidity of these donors. Table 3 shows that there is little difference in the ΔE_p between p-benzoquinone and 1 where the same guest is employed. NH_4^+ and RNH_3^+ still produce a considerable enhancement of 1 compared to that of p-benzoquinone. Benzoquinone derivatives, such as 2,6-dimethyl-1,4-benzoquinone, show diverse reduction potentials depending on the number as well as on the kind of substituent, and the observed E_p also varies with the kind of added cation. Nevertheless, only the absolute values of the potential differ, while the whole trend is the same as that of p-benzoquinone [9,10,35,36]. Table 3 indicates that stable complexation with more than three hydrogen bonds causes an extra shift in E_p. This additional enhancement is found when the electrochemically active host molecule bears a macrocyclic cavity-like structure which can encapsulate

guest ions through strong hydrogen bonds. Therefore, it can be concluded that there are two factors affecting ΔE_p in the electrochemical enhancement from various types of alkylammonium ions: the acidity of the guest and the stability of the encapsulated complex which is closely related to the number of hydrogen bonds.

On the other hand, there seems to be no trend in the second electron transfer with respect to either the acidity or the number of alkyl chains of the guest molecule. This is because amines, after they release a proton to the radical anion of the initially reduced quinone moiety, neither act as a proton source nor stabilize the other reduced quinone moiety on the opposite side [28,37].

3.3. Mechanistic considerations and cooperative effect of neighboring hydrogen bonding

The fundamental mechanism involving electron transfer and proton transfer was reported on the $1-NH_4^+$ complex [28]. According to that report, an unusually large ΔE_p due to the addition of NH_4^+ is observed because electron transfer followed by proton transfer produces a semiquinone instead of the less stable radical anion. In order to elucidate the effect of the acidity of the guest and the complexation on ΔE_p it is necessary to examine the relationship between the strength of the hydrogen bond and electron transfer.

Fig. 5 illustrates a simplified mechanism of a typical electrochemical electron transfer followed by proton transfer (EC mechanism). Firstly, electron transfer into the quinone yields the radical anion, which transforms the interaction between oxygen and hydrogen atoms from a weak hydrogen bond to a strong electrostatic interaction. As a result of subsequent proton transfer, the stable semiquinone is produced because the O–H bond comes close to having a predominantly covalent character [9].

However, the radical anion from the electrochemical reduction of quinone is not the final product. It is only an ephemeral intermediate because the semiquinone is so stable that it is formed by fast proton transfer. Hence, the influence of subsequent proton transfer on ΔE_p should be
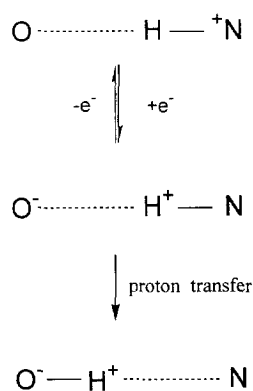
Fig. 5. Electrochemical reduction followed by proton transfer mechanism.

examined for a further understanding. The hydrogen bonding between quinone and ammonium ion is classified as a heteroconjugated type that corresponds to a weak bond [38,39]. A weak or medium hydrogen bond in which the length between the carbonyl oxygen and the nitrogen atom is longer than 2.6 Å is reported to show a good correlation of strength with the length [39,40]. In AN, single hydrogen bonding between p-benzoquinone and the ammonium ion is thought to be so weak that its length exceeds at least 3.0 Å, as long as there is no concomitant interaction like that between the enzyme and substrate. Assuming that NH_4^+ is encapsulated into the pore in the lower rim, whereby four hydrogen bonds are produced between the oxygen atoms and the nitrogen atom, a semi-empirical calculation shows that its length can be estimated to be less than 2.8 Å, as shown in Table 2 [26,41]. If primary alkylammonium ions are employed as guests, three hydrogen bonds are possible. In this case, two neighboring hydrogen bonds would assist the shortening of the remaining one connected with the redox center by making a tripodal rigid linkage. The length between the nitrogen of the amine and the oxygen of the quinone is a little longer than in the case of NH_4^+, but it is still short compared to a single hydrogen bond between p-benzoquinone and amine and falls around 2.85 Å, as shown in Table 2. Although secondary alkylammonium ions are also calculated to make a short distance of less than 2.9 Å, the real length in AN is supposed to be much longer because the guest molecules stay outside of the pore according to the computer simulation, so their complexes may not be as stable as $1-NH_4^+$ and $1-RNH_3^+$.

The shorter distance means stronger hydrogen bonding, which allows fast proton transfer by lowering the energy barrier involved in the second step in Fig. 5 [40]. Regarding this mechanism as E_rC_i or E_qC_i, E_p depends on a kinetic variable λ, which is related to a coupled chemical reaction (k_{PT}) [21,42]. According to Savéant's theory, the larger k_{PT} makes λ larger and E_p shifts more positively. Table 3 indicates that ΔE_p apparently depends on the acidity and the capability of making a stable complex, as discussed in Section 3.2. Acidity is known to be the most important factor in determining the strength of hydrogen bonding. Thus, an acidic guest acts as a good hydrogen bond donor and makes the bond length short [38]. Also, the formation of stable complexes through multiple hydrogen bonds results in the same effect. Consequently, shortened hydrogen bonding allows fast proton transfer and induces a positive peak potential shift. Therefore, in addition to energetic considerations, the nature of hydrogen bonding can also explain a large electrochemical enhancement due to the presence of NH_4^+ or RNH_3^+.

The essence of the electrochemical enhancement lies in the strength of hydrogen bonding and the net charge of complex along the electron transfer process. Thus, remarkable effects of dielectric constant and hydrogen bond donating or accepting ability of solvent are observed. The

results of the solvent effect will be reported in a separate article.

4. Conclusions

Calix[4]arenediquinone, as one of the suitably modified ionophores and promising redox-dependent receptors, has a more flexible structure than that of **3**, which is a well-known excellent Na^+ ionophore. It gives characteristic electrochemical responses to various alkylammonium ions including ammonium ion in AN. The electrochemical property of quinone-derived calixarene compounds such as **1** is studied and the reduction of quinone moieties occurs at a more positive potential when ammonium or alkylammonium ion is present. The magnitude of potential shift depends strongly on the size and structure of alkylammonium ions as well as solvents used. This can be interpreted on the basis of the nature of hydrogen bonding between the guest and the calix[4]arene molecule. Distinct E_p values make the selective recognition possible of ammonium ion and of biologically important alkylamine-type organic compounds. Furthermore, a model study employing the artificial receptor, which is capable of forming multiple hydrogen bonds, might elucidate the role of the hydrogen bond in biological systems such as, for instance, in the interaction between enzyme and substrate and electron flow in biological membranes. Also, it is expected to provide basic information towards the construction of a molecular switching device.

Acknowledgements

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