Electrochemical behavior of calix[4]arenediquinones and their cation binding properties [1]

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Abstract

The redox and cation-binding properties of three quinone-functionalized calix[4]arenes have been studied in acetonitrile. Cation-bound calix[4]arenediquinone produces a new set of redox peaks at positively shifted potentials. Thus, the association constant between cation and calix[4]arenediquinone is found to be enhanced by the electrochemical reduction of the receptor molecule. The enhancement is dependent on the charge and size of cations. The magnitude of the potential shift can be explained on the basis of stabilization due to the transition of binding characteristics from ion–dipole to ion–ion interaction by an electron transfer reaction. Substituents in the lower rim exert considerable influence on the redox behavior of the complex. NH_4^+ produces extraordinary voltammetric behavior due to the fact that only NH_4^+ can form hydrogen bondings with calix[4]arenes, in contrast to other metal ions.

1. Introduction

Calix[4]arene derivatives, in which a high degree of preorganization of donor groups is achieved in the cone conformation, are ideally suited for pursuing new cation-binding ligands. Ungaro and Pochini [1] have synthesized an ester-functionalized calixarene. Its structure has both the hydrophobic cone, into which neutral molecules may be bound, and the hydrophilic region, which shows ionophoric properties and is capable of binding alkali and alkaline earth metal cations [2,3].

The basic idea behind a switching process involves the presence of at least two distinct molecular states with widely different cation-binding properties. These molecular states must be easily and rapidly interchangeable via an externally controlled stimulus, e.g. addition or removal of electrons. The electrochemically active groups used in the design of electrochemically switchable crown ethers or calixarenes are quinones, nitro groups, azo groups, ferrocenes, etc. [4].

This electrochemical switching was first reported, with a series of lariat ethers, anthraquinone podands, and bicyclic cryptand derivatives, by Echegoyen, Gokel and coworkers [5–7]. In recent years, electrochemically active calixarenes have been synthesized by the conversion of phenolic rings into quinone and nitroaromatic moieties [8,9]. It is important to identify the effects of electron transfer, derived from electrochemical switching ability in spatially constrained systems. Gutsche, Echegoyen et al. [10] have studied the redox and cation-binding properties of a series of quinone-functionalized calix[4]arenes in acetonitrile. The important principle in the switching redox step involves the reduction of ligand–cation complexes rather than their oxidation. Therefore, the switching involves the development of an additional negative charge and leads to a consequent sizable increase in the binding constant, in some cases as high as 10^6 [11].

Convenient techniques to measure the cation-binding enhancement, cyclic voltammetry and differential pulse voltammetry are employed in this study. On addition of metal ions a new set of peaks is observed at a more

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[1] Dedicated to Professors Kenichi Honda, Hiroaki Matsuda and Reita Tamamushi on the occasion of their 70th birthdays.
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positive potential than the original free ligand wave. This reflects the stabilization of the reduced form, radical anion or dianion in the case of diquinone, and the stabilization of the complex as a result of the intramolecular interaction with the ring-bound cation. These phenomena imply quinone-functionalized calix[4]arene may be applicable to the fabrication of a molecular device to selectively recognize a specfic cation [12,13].

The present paper reports on the electrochemical properties of a series of calix[4]arenediquinones and their complexes with various cations in order to understand the redox mechanism. In addition, factors influencing the enhancement of complexation are described.

2. Experimental

2.1. Apparatus

Electrochemical experiments were performed with a Windows-driven BAS100B/W electrochemical analyzer (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 cm^2), was polished with 0.3 μm alumina (Buehler, Lake Bluff, MN), rinsed with deionized water and then washed carefully with purified acetonitrile. A Pt wire counter electrode and a home-made Ag|Ag$^+$ reference electrode ($+0.270$ V/SCE) were used for voltammetric experiments in nitrogen atmosphere. For potentiostatic bulk electrolysis, a Pt plate (area 3.2 cm^2) working electrode and a Pt gauze counter electrode were used. The counter electrode was kept in a separate compartment containing deoxygenated 0.1 M tetraethylammonium perchlorate (TEAP) in acetonitrile. All experiments were performed at room temperature.

2.2. Reagents

TEAP was prepared by mixing ammonium perchlorate (Aldrich) and tetraethylammonium bromide (Aldrich) in deionized water, then recrystallizing three times from water and drying for 48 h under reduced pressure at 60°C. Acetonitrile (Merck or Fisher, HPLC grade) was boiled with calcium hydride for 48 h and distilled just before use. Supporting electrolyte solutions were deoxygenated with purified nitrogen. Perchlorate forms of Li$^+$, Na$^+$, K$^+$, NH$_4^+$, Mg^{2+} (Aldrich, ACS reagent grade) were carefully protected from moisture throughout the experiment. CaO and La$_2$O$_3$ (Aldrich) were dissolved in 70% perchloric acid (Merck, HPLC grade) and after several evaporation steps, perchlorate salts of Ca^{2+} and La^{3+} were dried under vacuum at 60°C for more than 48 h.

The compounds 5,17-di-tert-butyl-26,28-bis-[(ethoxy-carbonyl)methoxy]-calix[4]-25,27-diquinone (2) and 5,17-di-tert-butyl-26,28-bis[(methoxycarbonyl)methoxy]calix-

[4]-25,27-diquinone (3) were prepared according to the procedure described previously [12]. 5,17-Di-tert-butyl-26,28-bis[(butylcarbamoyl)methoxy]calix[4]-25,27-diquinone (1) was synthesized by a method similar to that of 2 and 3; the results of its analysis were as follows.

IR(NaCl): 3369 cm^{-1} (N–H stretching); 1656 cm^{-1} (C=O stretching).

^{1}H-NMR (200 MHz, CDCl$_3$): 0.9–1.14 (m, 6H, CH$_2$CH$_3$), 1.07 (s, 18H, C(CH$_3$)$_3$); 1.34–1.64 (m, 8H, NCH$_2$CH$_2$), 3.15, 4.04 (d each, 4H each, ArCH$_2$Ar); 4.26 (s, 4H, OCH$_2$); 6.70 (s, 4H, C=CH); 6.82 (s, 4H, ArH), 8.27 (br, 2H, NH).

Melting point 280–282°C.

3. Results and discussion

3.1. Voltammetric study of calix[4]arenediquinones

The redox centers in compounds 1, 2 and 3 are two quinone groups facing each other as ring members (Fig. 1). Gomez-Kaifer et al. [10] have studied the electrochemical behavior of four different quinone functionalized calix[4]arenes and reported that the electronic charge in anionic calixarene is localized only on the quinone moiety. Thus, a number of studies on organic compounds, including 1,4-benzoquinone, are considered as useful references to describe and interpret voltammetric results. Based on the general behavior of quinone in an aprotic solvent [14], compounds 1-3 are expected to follow a similar redox mechanism to that suggested by Gomez-Kaifer et al. [10]. (See Scheme 1).

The cyclic voltammogram and differential pulse voltammogram of compound 1 in CH$_3$CN are presented in Figs. 2(a) and 2(b) respectively. Compound 1 exhibits the first wave on a shoulder of the second wave. The third wave, well separated from the second wave, appears at a much more negative potential. Compounds 2 and 3 exhibit a similar trend to that of compound 1. Controlled potential coulometry gives $n = 2.05$ at -1300 mV and $n = 4.23$ at -2200 mV. The number of electrons involved in each peak is therefore determined to be 1, 1 and 2 respectively.
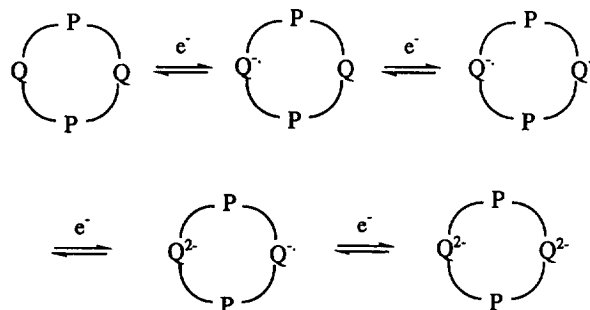
Scheme 1. Redox mechanism of calix[4]arenediquinone. P and Q represent p-tert-butyl phenyl and quinone moieties respectively.

The first and second waves are each found to be quasi-reversible with a single electron transfer. The first and second redox waves are symmetric, but the third wave is less symmetric and the corresponding oxidative wave has a slightly skewed shape. The third wave of a two-electron process corresponds to a combined wave of the third and fourth electron transfer reactions; it also falls into a quasi-reversible regime but seems more sluggish than the first two peaks. Reports on the electron transfer kinetics of the $Q^{-\cdot}/Q^{2-}$ couple show that the transfer rate for the second step is much slower and needs a larger activation energy than that for the first step [15]. A subsequent scan gives exactly the same voltammogram as that of the initial scan, and the peak current of all the peaks is linearly dependent on the square root of the scan rates in the range from 25 to 400 mV s^{-1}. A linear relationship between concentration and peak current is also observed from 0.2 to 1 mM. As a result, there is no adsorption process involved and only the diffusion controlled process exists in our experimental conditions.

All information about compounds 1-3, obtained from various electrochemical experiments, is consistent with the previous studies on quinone-containing compounds in an aprotic solvent such as CH$_3$CN [10,12,14].

3.2. Electrochemical behavior of ammonium complex

Unlike metal ions NH$_4^+$ contains hydrogen as well as one positive charge. Since compounds 1-3 have four carbonyl oxygens, one each from two quinones and two esters, which are geometrically suitable for accommodating tetragonal hydrogen bondings as recently suggested by Beer et al. [12], NH$_4^+$ is expected to form complexes with them, and ammonium complexes are expected to show different electrochemical behavior [13].

Beer et al. [12] have shown that NH$_4^+$ forms a complex with compound 2 and, using UV/Vis spectrophotometry, have determined its association constant to be 1.1×10^4.
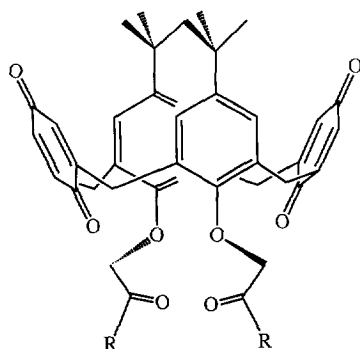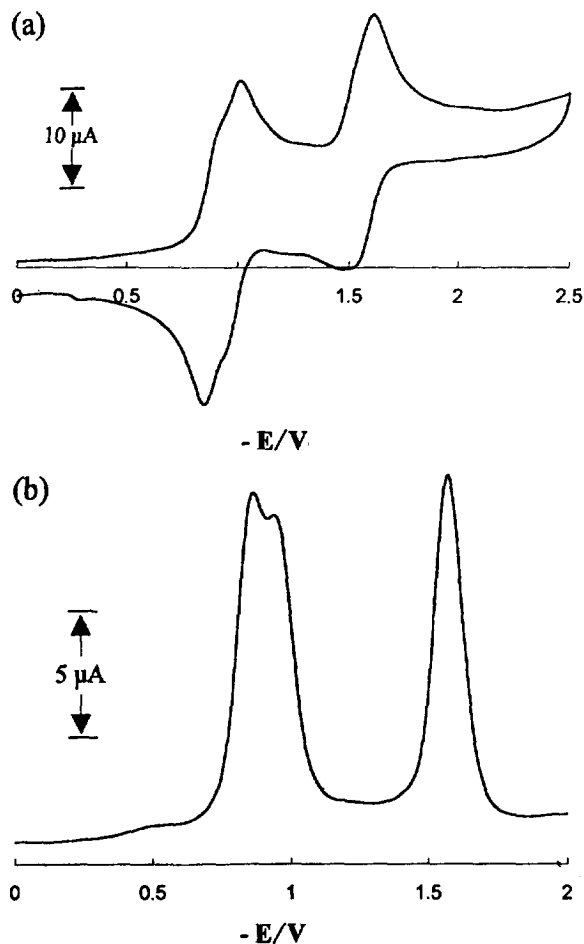
1. R = NHC$_4$H$_9$
2. R = OEt
3. R = OMe

Fig. 2. (a) Cyclic voltammogram and (b) differential pulse voltammogram of 1.0 mM compound 1 in CH$_3$CN under nitrogen atmosphere. Supporting electrolyte, 0.1 M TEAP; scan rate, 50 mV s^{-1}; potentials referenced to Ag/Ag$^+$ electrode.

The X-ray crystallographic structure of compound 2 has been revealed as a cramped cavity, formed by four oxygens from two phenolic rings and two quinone rings [16]. Fig. 3 depicts the ^{1}H-NMR spectra of (a) compound 2 and (b) compound 2 with one equivalent of NH$_4^+$. It proves not only that compound 2 indeed forms a complex with NH$_4^+$, but also that the conformation of quinone moieties is changed by complexation. The split due to coupling of protons in ArCH$_2$Ar clearly becomes large. This result indicates that NH$_4^+$ encapsulated in the lower rim ties up dynamic quinone moieties so tightly with the cone configuration that their inversion processes are inhibited [12,16,17]. Similar NMR data with respect to the interaction between Ba^{2+} [12] and K$^+$ [16] and compound 2 have been observed.

The cyclic voltammogram and differential pulse voltammogram depicted in Fig. 4 show that NH$_4^+$ forms a complex with compound 1. A new peak is observed at a more positive potential than the first peak of the free ligand. In the case of compounds 2 and 3, the potential

the free ligand is enormous, as shown in Table 1. This means that compounds 1-3, especially compounds 2 and 3, are expected to show large enhancement factors of the association constant K_2/K_1, as described in the next section.

The height of the new peak, at around -650 mV, increases with increasing amount of NH_4^+ added. This implies that a new analytical application of this compound is possible. The height of the free ligand wave around

-1000 mV, which is due to the redox process corresponding to $QQ/QQ^{-\cdot}$ and $QQ^{-\cdot}/Q^{-\cdot}Q^{-\cdot}$ couples, decreases but its potential changes to the slightly positive direction when one equivalent of NH_4^+ is added. It vanishes, however, with the addition of two equivalents of NH_4^+. The other free ligand wave, at around -1600 mV, involving $Q^{-\cdot}Q^{-\cdot}/Q^{-\cdot}Q^{2-}$ and $Q^{-\cdot}Q^{2-}/Q^{2-}Q^{2-}$ couples shows the same trend as the wave around -1000 mV.

Single-step chronoamperometry for a $1:1$ complex is
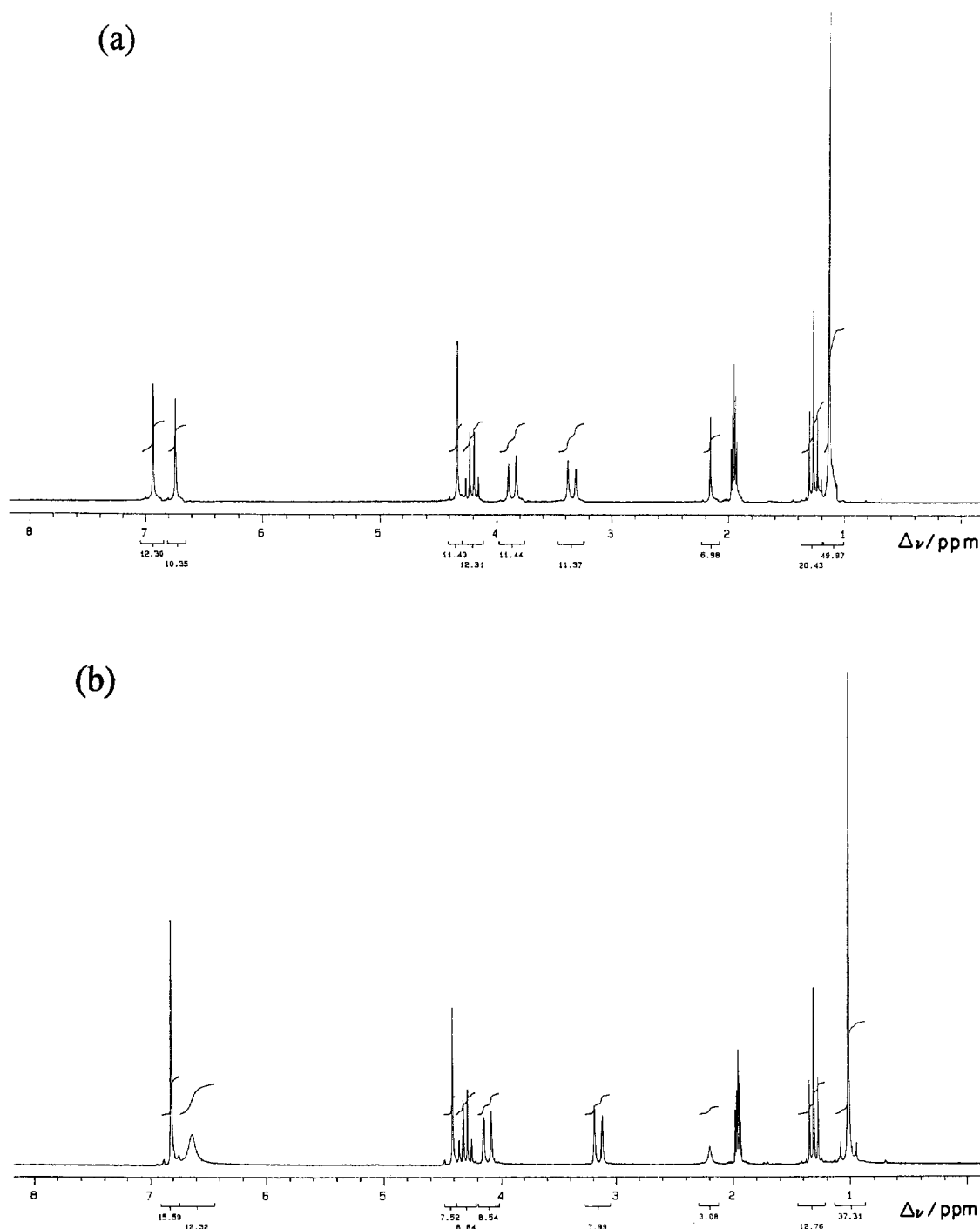

Fig. 3. ^{1}H NMR spectra of compound 2 (a) in the absence and (b) in the presence of one equivalent of NH_4^+ in acetonitrile-d_3 at 25°C.

performed to examine the ratio of the number of electrons involved in the first peak to that in the second peak, where the step potential is adjusted either to -780 mV or -1300 mV. The slope of the I vs. $t^{-1/2}$ plot at -1300 mV is approximately twice that obtained at -780 mV. The same experiment with the solution containing two equivalents of NH_4^+, even at -1500 mV, results in $n = 2.28$. Also, controlled potential coulometry of the solution containing one equivalent of NH_4^+ reveals $n = 1.02$ at -780 mV and $n = 2.16$ at -1300 mV. This implies that there is no redox process of the $Q^- \cdot Q^- \cdot / Q^{2-} Q^{2-}$ couple so that neither $Q^- \cdot Q^{2-}$ nor $Q^{2-} Q^{2-}$ comes into being. In addition, the new peak around -650 mV involves a one-electron and a two-electron process in the case of one and two added equivalents of NH_4^+ respectively. The new peak is a totally irreversible one in the potential window employed in this experiment, as demonstrated by the cyclic voltammogram with various scan rates and switching potential fixed at -780 mV. Another irreversible element

comes from the fact that the peak potentials shift to the negative direction as the scan rate increases.

Fig. 5 is helpful in elucidating the above results. NH_4^+ is able not only to act as a sort of Brønsted acid but also to make hydrogen bondings when it comes to form complexes with suitable ligands [18]. The lower rim of compounds 1–3 is capable of accommodating four hydrogen bondings between four hydrogen atoms of NH_4^+ and four carbonyl oxygen atoms, two each from carbonyl quinones and diesters [12]. According to the model suggested by Kolthoff and Chantooni [19], these hydrogen bondings can be considered along with the concept of heteroconjugation which is known to be observed in solvents lacking hydrogen bonding properties and with dielectric constants of the order of 40 or less, like acetonitrile which is used in this work. After the first electron uptake, the characteristics of the bond between oxygen atoms in quinone moiety and hydrogen must be changed from ordinary hydrogen bonding into a protonated radical anion similar to undissociated

Table 1

Peak potential values and corresponding peak potential shifts for calix[4]diquinones and their cation complexes in cyclic voltammetry

Ligand	Cation	$-E/$(mV) vs. Ag/Ag$^+$						$\Delta E_{p,1}$ (mV)	$\Delta E_{p,2}$ (mV)	$\Delta E_{p,m}$ (mV)
		$E_{pc,1}$	$E_{pc,2}$	$E_{pc,3}$	$E_{pa,1}$	$E_{pa,2}$	$E_{pa,3}$			
Compound 1	Free	918	1005	1621	838	945	1536 c	–	–	–
	NH$_4^+$	644	1005	1621	– a	838	– a	274	0	137
	Li$^+$	670	– a	–	– a	–	–	248	–	–
	Na$^+$	824 g	860 g	– a	734	805	– a	94	145	120
	K$^+$	943 f	–	1347	831 b	–	–	–25 f	62	18
	Mg^{2+}	278	489	– a	132	366	– a	640	516	578
	Ca^{2+}	405	594	930 e	253 b	504	–	513	411	462
	La^{3+}	127	380	880 e	450 b	–	–	791	625	708
Compound 2	Free	1072	1145	1720	1009	1080	1555 c	–	–	–
	NH$_4^+$	621	1082	1545	320 e	986	– a	451	63	257
	Li$^+$	670	1070 e	–	480 b	–	–	402	75	237
	Na$^+$	760	837	1640	721	775	– a	312	308	310
	K$^+$	870	940	1591	806	882	1450 c	202	205	204
	Mg^{2+}	440	775	1098	18	340	724(948)	632	370	501
	Ca^{2+}	337	595	(1060)1333 d	267	483	1333	735	550	643
	La^{3+}	51	332	1057 e	–243 b,e	935 e	–	1021	813	917
Compound 3	Free	1080	1136	1659	1010	1057	520 c	–	–	–
	NH$_4^+$	554	1082	1561	–67	993	– a	526	54	290
	Li$^+$	650	1060 e	– a	450 b	– a	– a	430	76	253
	Na$^+$	762	832	1615	717	776	– a	318	304	311
	K$^+$	874	937	1572	820	892	1464 c	206	199	203
	Mg^{2+}	443	711	(1080)2073	– a	1010	1457 c	637	425	531
	Ca^{2+}	328	586	(1060)1373 d	261	464	978	752	550	651
	La^{3+}	45	307	(1070 e)1940	– a	987 e	1543 c	1035	829	932

All data were obtained by cyclic voltammetry with one equivalent of cation added to 0.5 mM free ligand in acetonitrile. Scan rate, 50 mV s^{-1}; electrolyte, 0.1 M TEAP; error range, ± 5 mV.

$\Delta E_{p,1} = E_{pc,1,complex} - E_{pc,1,free\ ligand}$.

$\Delta E_{p,2} = E_{pc,2,complex} - E_{pc,2,free\ ligand}$.

$\Delta E_{p,m} = \frac{1}{2}(E_{pc,1,complex} + E_{pc,2,complex}) - \frac{1}{2}(E_{pc,1,free\ ligand} + E_{pc,2,free\ ligand})$.

a Ill-defined or broad wave such that it is difficult to measure the potential.

b Anodic wave with a spike shape.

c Skewed wave.

d Sharp and large reduction wave supposed to be due to the subsequent reduction of adsorbed complex.

e Broad wave in which several waves seem to be overlapped.

f Single wave with the merged first and second waves.

g Potentials of two waves so close that measured data become less accurate. Error range, ± 10 mV.

phenolic acid. Potential shifts due to the complexation of calix[4]arenediquinone with various alkylamines confirm the fact that influences due to the presence of hydrogen bonding and acidity of proton source are significant [20].

The presence of protons in an aprotic solvent is known to influence the reversibility of quinone couples [21]. Reports exist which provide evidence that prior protonation gives rise to a new reduction peak involving the reduction of QH$^+$ at a positively shifted potential [22,23]. In the case of 1 : 1 complex, NH$_4^+$ appears to behave like a proton source in the first electron transfer process. Hence a proton of NH$_4^+$, which is directed to reducible quinone, is supposed to be attracted to a radical anionic oxygen atom and the whole complex becomes neutralized. Then, NH$_4^+$ is relatively basic compared with before the one electron uptake. Accordingly, NH$_4^+$ does not have a strong influence on the second electron transfer to the opposite quinone moiety and the redox process corresponding to the second electron uptake both remains and maintains its reversibility in the 1 : 1 complex at approximately the same potential. On the basis of this argument, the first electron transfer
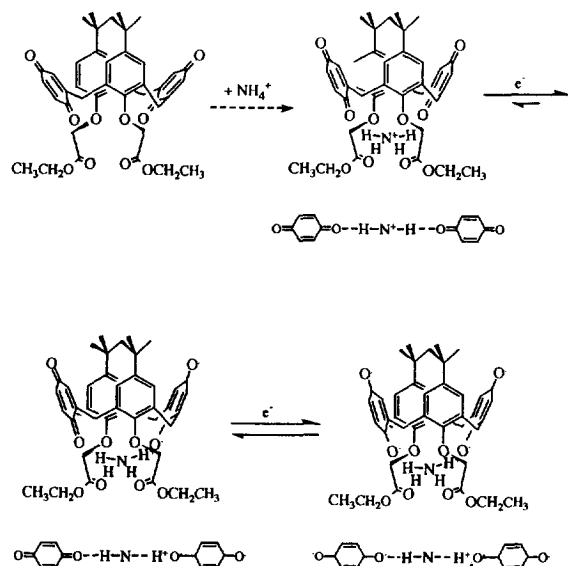

Fig. 5. Electron transfer mechanism of the 1 : 1 complex of compound 1 with NH$_4^+$.

process is enhanced considerably both by the prior protonation which stabilizes semiquinone, and the electrostatic interaction. However, the second reduction becomes scarcely more facile than that of a free ligand, and further reduction is observed almost at the same potential.

When two equivalents of NH$_4^+$ are added, however, the second NH$_4^+$ anchored in the upper rim appears to play the role of a proton source for the reduction of the other quinone, opposite to the previously reduced one. The enhancement of the first electron transfer is not considered to be different from that of the 1 : 1 complex. The second reduction step, however, is noticeably enhanced because of the presence of the second NH$_4^+$. The third and fourth electron transfer steps are not observed in the potential range employed in the experiment in the presence of two equivalents of NH$_4^+$, as shown in Fig. 6. Two reasons can be suggested why the reduction of semiquinone to dianion is not observed. First, the complexation with NH$_4^+$ may stabilize semiquinone intermediately so as to raise the activation energy of the reduction process from Q$^-$Q$^-$ to Q$^-$Q^{2-}. Second, any chemical reaction may be coupled, for example disproportionation of the radical anion itself, water catalyzed disproportionation, production of an adsorptive ion pair composed of a cation and radical anion, etc. Subsequent scans in cyclic voltammetry show almost the same voltammograms as that of the initial scan. While the switching potential and scan rate are varied, there is no significant change in peak shape, $-I_a/I_c$ and E_p. This implies that no chemical reaction is coupled, or if it is then it is very sluggish. Therefore, hydrogen bondings seem to stabilize the semiquinone radical anion and shift the reduction potential to the far negative direction. The oxidation of calix[4]arenetetrahydroquinone in DMF observed at +0.77 V vs. SCE could also support the stabilization by
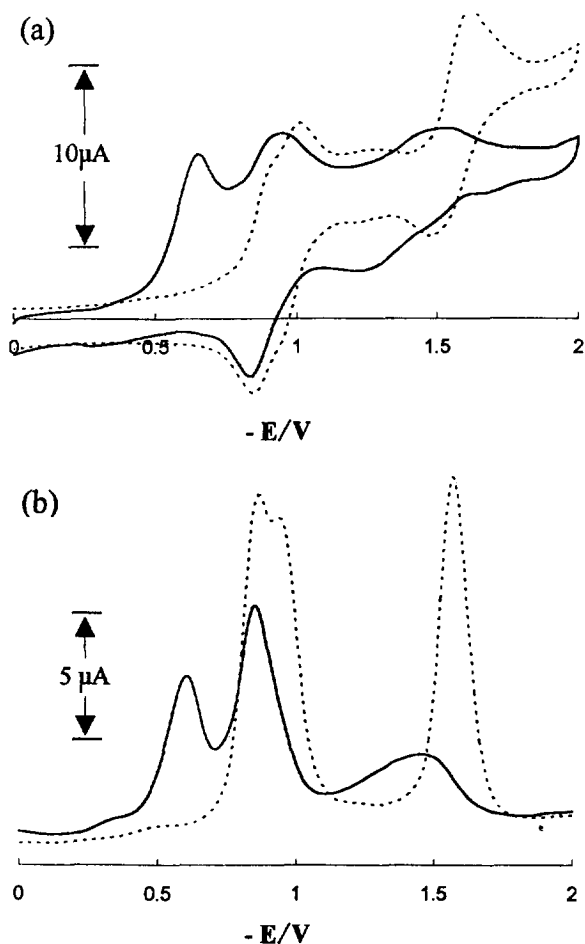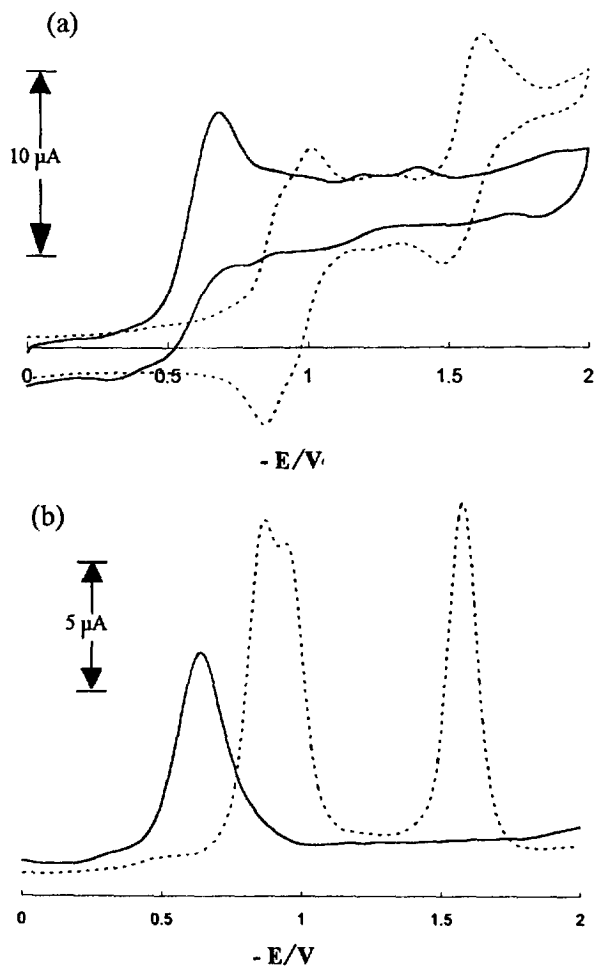

Fig. 4. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 1.0 mM of compound 1 in the absence (-----) and presence (———) of one equivalent of NH$_4^+$. Other experimental conditions are the same as in Fig. 2.

(a)

10 μA

- E/V

(b)

5 μA

0   0.5   1   1.5   2

- E/V

Fig. 6. (a) Cyclic voltammograms and (b) differential pulse voltammograms of 1.0 mM of compound **1** in the absence (-----) and presence (————) of two equivalents of NH_4^+. Other experimental conditions are the same as in Fig. 2.

protonated dianion(hydroquinone) in the course of electrochemical oxidation [24].

3.3. Electrochemical behavior of metal ion complexes and the substituent effect

If metal ions are chosen as guest ions, a situation different from the case of an ammonium complex must be considered. Two variables, charge and size, are taken into account in understanding the electrochemical results of metal ion complexes. The ligating sites of compounds **1–3** are assumed to be four carbonyl oxygens, one each from two quinones and two esters as described in the previous section. Many aromatic compounds including 1,4-benzoquinone are known to form ion pairs in the presence of alkali and alkaline earth metal ions as a result of reduction. This causes the positive shift of the reduction potential, whose magnitude depends on the concentration of metal ions and the effective ionic potential ϕ_{eff} (defined as $z/(r + \delta)^{-1}$ where z is the charge, r is the Pauling radius

and δ is the Latimer-type correction factor) [25,26]. ΔE_p in the reduction potential of 1,4-benzoquinone is proportional to the ϕ_{eff} value of metal ions [27]. Metal ion complexes can be considered to undergo a transition of the nature of a host–guest interaction during electrochemical reduction. Ion–dipole interaction is predominant in the neutral ligand complex but ion–ion interaction or electrostatic interaction becomes an overwhelming factor after electrochemical electron donation.

Table 1 shows that the larger the charge and the smaller the size of metal ion, the greater the value of ΔE_p. ΔE_p exhibits a similar trend to that expected due to the ion pair effect between 1,4-benzoquinone and metal ions. This means that the ΔE_p value of the compounds **1–3** after complexation with a series of metal ions exhibits the trend $La^{3+} > Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$, consistent with ϕ_{eff} series of metal ions. Accordingly, the dominant factor influencing the enhancement is how much sequestered cation prefers the ion pair with quinone moiety. This result confirms the potential shift data obtained with compound **2** and alkali and alkaline earth metals [12]. Although the trend of ΔE_p with complexes of compounds **1–3** is akin to that with 1,4-benzoquinone, there are several different points between the two systems. The ΔE_p of the former is much larger than that of the latter and the reduction potential of the former does not change with the concentration of metal ions up to one equivalent of the ligand. In addition, a small quantity of cation can make the complex peak distinct and large by sequestration in the cavity. Even though Li^+ is too small to be captured by the ligating site of compounds **1–3**, a small change in ΔE_p of the Li^+ complex is observed through increasing the Li^+ concentration.

The ion pair effect also has considerable influence on reversibility. Complexes of Li^+ having large ϕ_{eff} value and small size exhibit irreversible redox behavior, as shown in Fig. 7. Based on our previous argument, metal ions such
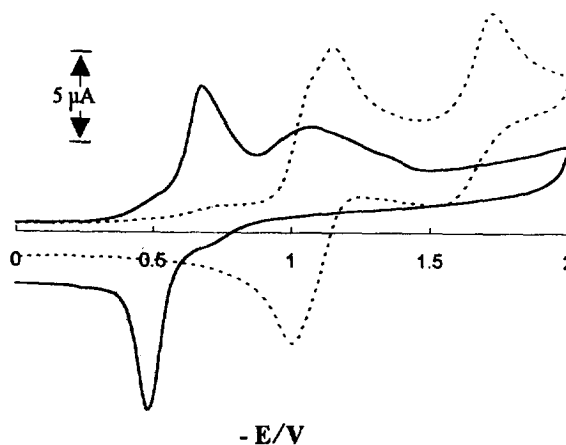

5 μA

0   0.5   1   1.5   2

- E/V

Fig. 7. Cyclic voltammogram of 0.5 mM compound **2** in the absence (-----) and presence (————) of one equivalent of Li^+. Other experimental conditions are the same as in Fig. 2.

as Na$^+$ and K$^+$, with large size but small charge, are expected to form a comparatively weak ion pair so that their ion–dipole interaction energies are comparable with ion–ion interaction. Hence, the oxidation of Na$^+$ and K$^+$ complexes becomes facile compared with other metal complexes. Fig. 8 shows the voltammetric responses of variously charged metal ions with compound 3 [18]; very similar results are observed with compounds 1–2. Pronounced reversibility is preserved in the case of Na$^+$ and enhancement to a two electron uptake is observed [18]. In this case, the scheme for reduction and complexation, as shown in Fig. 9, is valid. Complicated electrochemical behavior, such as the adsorption peak with Ca^{2+} and the irreversible nature of La^{3+}, are observed in Fig. 8. However, the enhancement of the first electron is clearly shown to be dependent on the number of charges. The relationship between the enhancement factor, K_2/K_1 or K_3/K_1, and the shift of the half-wave potential $\Delta E_{1/2}$, is known to be $\exp(nF\Delta E_{1/2}/RT)$ [28]. Assuming $\Delta E_{1/2} \approx \Delta E_p$, K_3/K_1 values for Na$^+$ complexes with compounds 1–3 are evaluated to be in the range $1.4 \times 10^4 \sim 3.3 \times 10^{10}$, and those for K$^+$ complexes in the range $4.0 \sim 8.0 \times 10^6$.

Compound 1 has a secondary amide group bound to carbonyl carbon as a substituent, while compounds 2 and 3 have ethoxy and methoxy groups respectively in corre-
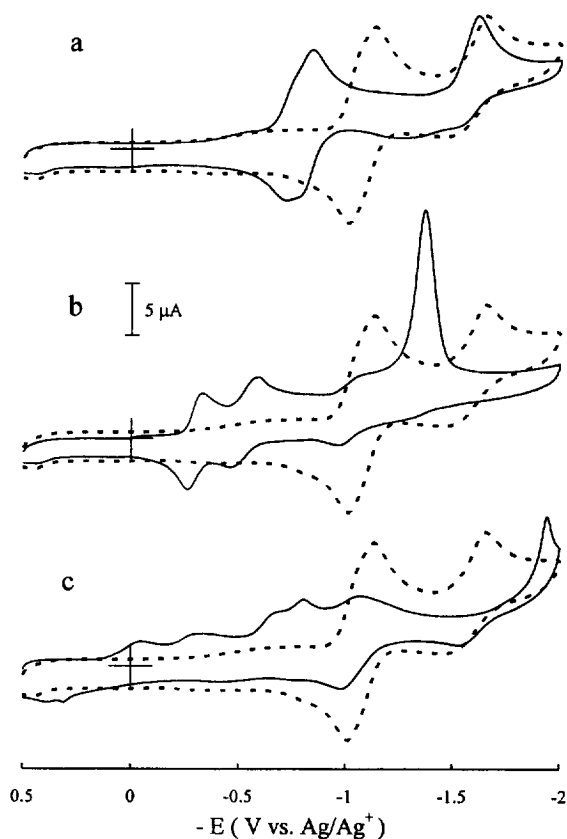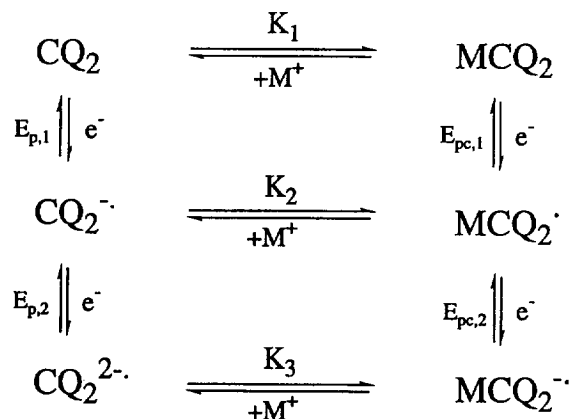
Fig. 9. Square scheme of cation binding redox mechanism of electrochemically-active ligand.

sponding sites. Moreover, the substituent of compound 1 bears a relatively large alkyl group. In Table 1, the ΔE_p values of all metal ion complexes with compound 1 are found to be relatively small compared with those with compound 2 and 3 complexes. Although there is no firm evidence to explain the above results, two possible explanations can be suggested. The first is based on the steric effect, which may be severe in the case of compound 1, so that the reduced complex is hard to stabilize. The second is a hypothesis that the secondary amide group may form hydrogen bondings with carbonyl oxygen atoms of the opposite substituent, so that extra energy is required to break the hydrogen bonding and to capture the cation which is already attached to the ligand, presumably as a perching complex. A further plausible reason may come from the fact that the larger basicity of carbonyl oxygen atoms makes a neutral ligand complex more stable in compound 1 than in compounds 2 or 3. However, extraction experiments reveal that compound 1 is unfavorable for binding cations compared with compounds 2 or 3. Accordingly, the former two possibilities are considered to be reasonable.

4. Conclusions

We have probed the electrochemical behavior of calix[4]arenediquinones and their complexes with various cations. The redox behavior of the free ligand is well understood on the basis of the constraint concept of two 1,4-benzoquinone groups which are independent of each other. Compounds 1–3 have favorable structures for accommodating NH$_4^+$ so that a stable NH$_4^+$ complex can be formed in spite of its large size. The redox behavior of the NH$_4^+$ complex is unique compared with that of metal ion complexes, and can be explained by regarding NH$_4^+$ as a Brønsted acid or proton source to form hydrogen bondings. When metal ions are used as guests, the ion pairing effect is found to be a predominant factor in determining the ΔE_p

Fig. 8. Cyclic voltammogram of 0.5 mM compound 3 in the absence (------) and presence (———) of one equivalent of (a) Na$^+$, (b) Ca^{2+} and (c) La^{3+}. Other experimental conditions are the same as in Fig. 2.

values of complexes. Since Na^+ and K^+ form weak ion pairs while maintaining some reversibility, the enhancement factor can be evaluated from the corresponding relationship with the ΔE_p data. Enormously large potential shifts are observed in the first electron transfer reactions of quinone moiety in calix[4]arenediquinones bearing simple methylester substituents when metal ions, especially trivalent ion, are added. In addition, the substituent effect of calix[4]arenediquinone in which a carbonyl group is contained can be discussed in terms of steric effect and hydrogen bondings between secondary amide and carbonyl oxygen atoms in the other substituent.

Acknowledgments

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