

Selective Binding of NH_4^+ by Redox-Active Crown Ethers: Application to a NH_4^+ Sensor

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Two redox-active crown ethers, (1,1'-bi-2-naphthyl)-23-crown-6 incorporating 9,10-anthraquinone (BNAQ) and 1,4-benzoquinone (BNBQ), were synthesized and employed in the selective binding of NH_4^+ over K^+ . Their applications to NH_4^+ detection were studied by cyclic voltammetry and amperometry in aqueous media. The results showed that the magnitude of the quinone redox peak decreased linearly as the concentration of NH_4^+ increased, indicating the formation of BNAQ-NH_4^+ and BNBQ-NH_4^+ complexes. Formation constants of BNAQ-NH_4^+ and BNBQ-NH_4^+ complexes were determined to be 4.3×10^3 and $4.0 \times 10^3 \text{ M}^{-1}$, respectively, which were 2 orders of the magnitude greater than those of BNAQ-K^+ and BNBQ-K^+ complexes. The ^1H NMR titration method carried out in $\text{DMSO}-d_6$ showed that both complexes possessed 1:1 stoichiometry, and association constants were determined to be 648 ± 35 and $600 \pm 47 \text{ M}^{-1}$ for BNAQ-NH_4^+ and BNBQ-NH_4^+ , respectively. Interference effects from other alkali and alkaline earth metal ions in the analysis of NH_4^+ were also investigated. The BNAQ-modified sensor showed a linear response from $1.0 \mu\text{M}$ to 1.0 mM for NH_4^+ , and the detection limit was determined to be $0.9 \pm 0.03 \mu\text{M}$.

Selective binding of NH_4^+ by a synthetic ionophore has fundamental and practical interest in molecular recognition. There has been much attention to developing NH_4^+ sensors based on ionophores for clinical and environmental analyses. For example, the concentration of urea and creatinine in biological samples can be determined indirectly by measuring the amount of NH_4^+ released upon enzymatic reactions involving these substrates.¹ These NH_4^+ sensors are also very useful to determine NH_4^+ or ammonia concentrations in drinking water,² in the air,³ and in the investigation of wastewater.⁴

A neutral antibiotic agent, nonactin, is mostly used in an ion-selective electrode for detecting NH_4^+ down to micromolar

levels.^{5–7} However, nonactin binds only ~ 10 times more selectively to NH_4^+ than to K^+ . To enhance the stability, artificial receptors,^{8,9} cryptand,¹⁰ and crown ether¹¹ were also used in the study of NH_4^+ binding. However, they showed little or no selectivity for binding NH_4^+ over K^+ .

Thus, selective NH_4^+ binding over K^+ with ionophores seemed to be very challenging and difficult. The main reason it has been difficult to obtain selective NH_4^+ binding over K^+ is that the sizes of the two monocations are closely matched. However, NH_4^+ and K^+ are clearly distinct in terms of their symmetry. K^+ has a spherical symmetry and prefers ionic bonds, whereas NH_4^+ has a tetrahedral symmetry and allows for four specifically positioned hydrogen bonds in addition to ionic interactions. The importance of hydrogen bonding and symmetry in the design of NH_4^+ recognition sites has been recognized.^{8,9,12–14}

Crown ethers bearing a redox-active group, such as quinone,^{15–17} have also gathered considerable attention in the study of alkali metal and ammonium ion binding.^{18–21} However, while only the potentiometric NH_4^+ sensors based on an ionophore^{8,9,14,22,23} were

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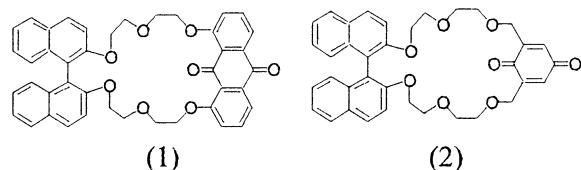


Figure 1. Chemical structures of BNAQ (1) and BNBQ (2).

introduced, NH_4^+ binding and its amperometric sensor application with a redox-active crown ether has not yet been reported. Thus, it is very interesting to use a redox-active crown ether for the fabrication of an amperometric NH_4^+ sensor in this study.

In the present study, we have synthesized two redox-active crown ethers, (1,1'-bi-2-naphthyl)-23-crown-6 incorporating 9,10-anthraquinone (BNAQ) and 1,4-benzoquinone (BNBQ) (Figure 1), in which the crown ether structure was tuned by incorporating a quinone group into the crown cavity. The structures of BNAQ and BNBQ have the correct geometry for binding NH_4^+ by hydrogen bonds and thus showed selective binding of NH_4^+ over K^+ . The quinone functional moiety in crown ethers serves not only as a redox center but also as a ligating site for hydrogen bonding. The interactions between BNAQ and NH_4^+ and between BNBQ and NH_4^+ were studied by the ^1H NMR titration method in $\text{DMSO}-d_6$. The energy-minimized structure of the BNAQ- NH_4^+ complex was evaluated using molecular mechanic simulation. We report here, for the first time, on an amperometric NH_4^+ sensor in which BNAQ was dropped on to a polished glassy carbon electrode followed by Nafion coating to avoid anion interferences. The interactions between crown ether and NH_4^+ or K^+ were electrochemically determined by observing a change in the redox potential or the redox current of a quinone moiety. In this work, cyclic voltammetry and amperometry were used to test the performance of these NH_4^+ sensors based on BNAQ and BNBQ.

EXPERIMENTAL SECTION

Reagents. Tetrahydrofuran, (THF) (99.9%, anhydrous, sealed under N_2 gas), was received from Aldrich Co. Tris(hydroxymethyl)aminomethane salt was obtained from Lancaster Co. The pH of the Tris buffer solution was adjusted with HCl (Junsei Chem. Co. Ltd.). Dimethyl- d_6 sulfoxide ($\text{DMSO}-d_6$) was purchased from Cambridge Isotope Laboratories Inc. Nafion perfluorinated ion-exchange resin was obtained from Aldrich. Ammonium chloride, alkali, and alkaline earth metal chloride salts were from Aldrich.

Standard solutions of 0.01 M were prepared in Tris-HCl buffer and diluted step by step (1.0×10^{-3} – 1.0×10^{-6} M) to an adequate concentration prior to immediate use. Other chemicals were of analytical reagent grade. Distilled water was obtained from a Millipore Milli-Q water purification system (18 $\text{M}\Omega$ cm).

Apparatus. BNAQ- and BNBQ-modified Nafion-coated glassy carbon electrodes (area 0.07 cm^2), an Ag/AgCl (in saturated KCl) electrode, and a Pt wire were used as working, reference, and counter electrodes, respectively. Cyclic voltammograms and chronoamperograms were recorded using a KST-P1 voltammetric analyzer (Kosentech Co.) and a PAR EG&G potentiostat/galvanostat (model 173A). Solutions were degassed for 15 min before any experiments by purging with N_2 gas, which was also flowed over the solution during the experiment. All ^1H NMR spectra were recorded at 300 K on a Varian Unity Plus 300 spectrometer operating at 300 MHz. $\text{DMSO}-d_6$ was used as the solvent. The

titration was done by saturating the host solution with the guest. Molecular modeling was carried out using the PC Spartan Pro.²⁴

Synthesis of BNAQ Crown Ether. A mixture of 2-[2-(1-{2-[2-(2-hydroxyethoxy)ethoxy]-1-naphthyl]-2-naphthyloxy)ethoxy]-1-ethanol (0.49 g, 1.06 mmol) prepared from 1,1'-bi-2-naphthol via the known procedure²⁵ and 1,8-dichloroanthraquinone (Aldrich, 0.25 g, 0.90 mmol) in 25 mL of dry THF was slowly added to a vigorously stirred and refluxing suspension of NaH (60% dispersion in mineral oil, 0.12 g, 3.0 mmol) in 10 mL of dry THF. The reaction mixture was refluxed for 48 h, cooled, and concentrated under reduced pressure. The residue was washed with a brine solution, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 2:1) to afford (1,1'-bi-2-naphthyl)-23-crown-6 incorporating 9,10-anthraquinone (I) (0.26 g, 38% yield) as a yellowish solid material: mp 175–177 $^\circ\text{C}$; ^1H NMR (200 MHz, CDCl_3) δ 3.46–3.56 (m, 2H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.60–3.72 (m, 2H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 3.80 (t, 4H, $\text{CH}_2\text{CH}_2\text{OAr}$), 3.86–3.93 (m, 2H, $\text{ArOCH}_2\text{CH}_2\text{O}$), 4.04–4.30 (m, 6H), 7.11–7.34 (m, 8H, ArH), 7.46 (d, 2H, ArH), 7.59 (t, 2H, ArH), 7.75–7.87 (m, 6H, ArH); ^{13}C NMR (200 MHz, CDCl_3) ppm 67.8, 68.1, 68.7, 68.9, 114.8, 117.5, 117.6, 122.1, 124.0, 124.6, 126.1, 127.6, 127.8, 132.0, 132.4, 152.9, 156.7; ESI-MS m/z ($M + \text{H}^+$) calculated 667.7, found 667.2; IR (KBr pellet) cm^{-1} 3055, 2929, 1672, 1587, 1446, 1242.

Synthesis of BNBQ Crown Ether. A mixture of 2-[2-(1-{2-[2-(2-hydroxyethoxy)ethoxy]-1-naphthyl]-2-naphthyloxy)ethoxy]-1-ethanol (1.20 g, 2.60 mmol) and 1,3-bis(bromomethyl)-2,5-dimethoxybenzene (0.93 g, 2.86 mmol) prepared from 4-methoxyphenol via the known procedure²⁶ in 200 mL of dry THF was slowly added to a stirred suspension of NaH (60% dispersion in mineral oil, 0.37 g, 7.80 mmol) in 150 mL of dry THF. The reaction mixture was refluxed for 72 h, cooled, and concentrated under reduced pressure. The residue was quenched with 1 N HCl solution and extracted with chloroform. The organic layer was washed with a brine solution, dried over Na_2SO_4 , and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 2:1) to afford (1,1'-bi-2-naphthyl)-23-crown-6 incorporating 1,4-dimethoxybenzene (0.85 g, 52% yield). (1,1'-Bi-2-naphthyl)-23-crown-6 incorporating 1,4-dimethoxybenzene thus prepared (0.60 g, 0.96 mmol) was dissolved in 40 mL of acetonitrile, and a solution of ammonium cerium(IV) nitrate (Aldrich, 2.1 g, 3.84 mmol) in 20 mL of water was added slowly. After checking the completeness of the reaction by TLC, the reaction was finished, and the reaction mixture was extracted with dichloromethane. The organic solution was dried over Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane = 1:1) to afford (1,1'-bi-2-naphthyl)-23-crown-6 incorporating 1,4-benzoquinone 0.46 g, 80% yield) as a reddish solid material: ^1H NMR (200 MHz, CDCl_3) δ 7.93 (d, 2H, Ar), 7.85 (d, 2H, ArH), 7.14–7.42 (m, 8H, ArH), 6.73 (s, 2H, ArH), 4.31 (q, 4H, CH_2), 3.83–4.10 (m, 4H), 2.99–3.51 (m, 12H, CH_2); ^{13}C NMR (200 MHz, CDCl_3) ppm 66.78, 69.98, 70.54, 70.81, 70.92,

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116.65, 120.82, 121.35, 122.96, 123.74, 125.80, 126.12, 127.74, 129.41, 129.49, 132.04, 133.90, 145.67, 154.51; IR (KBr pellet, cm^{-1}) 3055, 2923, 2868, 1651, 1506, 1270.

NMR Titration. A sample containing a known amount of host in a known volume of solvent was taken in an NMR tube, and then the spectrum was recorded. To this sample, a known quantity of guest (NH_4Cl) was added, and the spectrum was recorded again. The process was repeated. Typically 8–10 spectra were recorded for each determination. The concentration of the host was 1.02×10^{-2} M, and the concentration of the guest ranged from 2.55×10^{-3} to 2.85×10^{-2} M. The differences in chemical shift values were calculated by subtracting the chemical shift of the mixture from that of the pure guest.

Electrode Modification. A 10 mM concentration of BNAQ and BNBQ crown ether solutions was prepared in THF, and 4.0 μL of each solution was spun onto the two polished GCEs, separately followed by 4.0 μL of 1.0 wt % Nafion to cover both electrodes by a spin-coating technique at ~ 500 rpm for 3 min. Then, both electrodes were dried over CaCl_2 at room temperature for 2 h and were used in all subsequent experiments.

RESULTS AND DISCUSSION

Host–Guest Interaction Using ^1H NMR Titration. The interaction between BNAQ and NH_4^+ was studied by an ^1H NMR titration in $\text{DMSO}-d_6$. Figure 2A shows the proton NMR spectra (only NH region) for host, guest, and a mixture of host and guest in different mole ratios (host/guest). The spectrum recorded for only crown ether in $\text{DMSO}-d_6$ is shown in Figure 2A-a. A broad peak for NH protons was observed at 7.45 ppm due to nuclear quadrupole broadening (Figure 2A-b), when a spectrum was recorded only for NH_4Cl in $\text{DMSO}-d_6$. Addition of NH_4Cl to the $\text{DMSO}-d_6$ solution of crown ether resulted in a slight upfield shift of protons of the crown ether residues and aromatic rings. The most pronounced changes occurred on the signal of NH protons, and the broad peak of NH protons split into three absorption peaks at 7.41, 7.16, and 6.90 ppm (Figure 2A-c,d). This might be due to the presence of three different spin states of nitrogen in the BNAQ– NH_4^+ complex arising from the spin–spin splitting.²⁸ Addition of an equimolar concentration of NH_4Cl into the BNAQ solution shifted all three peaks of NH protons downfield to 7.44, 7.19, and 6.93 ppm (Figure 2A-e). Addition of an excess of NH_4Cl into the BNAQ solution shifted all three NH protons more downfield to 7.57, 7.31, and 7.06 ppm, indicating strong binding of NH_4^+ with BNAQ (Figure 2A-f–i).

The stoichiometry of the complex was determined by Job's method of continuous variation.^{29,30} Job's plot for the system of BNAQ– NH_4Cl is shown in Figure 2B, where a complexation-induced shift of the center NH proton at 7.16 ppm followed. The total concentrations of BNAQ and NH_4Cl were kept constant. The Job's plot showed a maximum at the mole fraction of BNAQ = 0.5, indicating that the complex possessed 1:1 stoichiometry.

The association constant of the 1:1 complex was determined from the binding curves (Figure 2C). Variation of the chemical

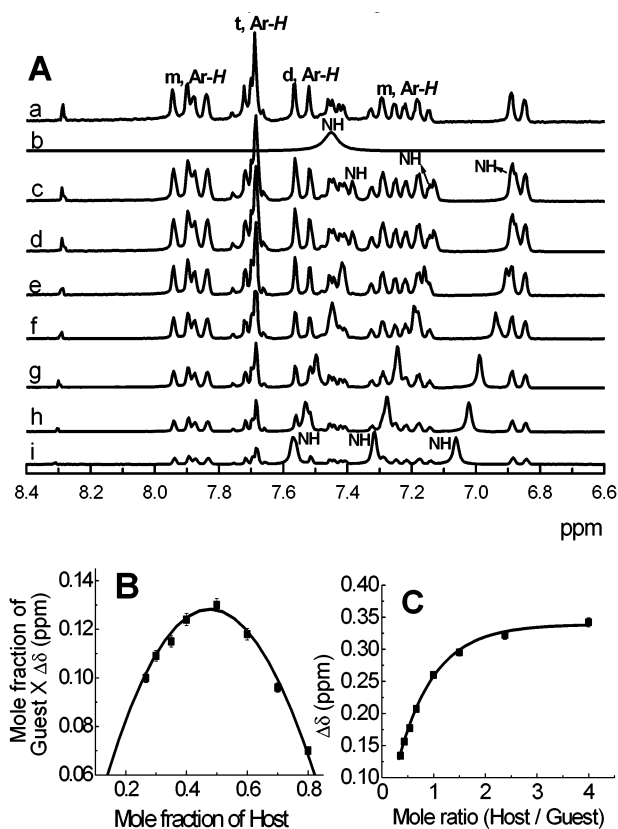


Figure 2. (A) ^1H NMR spectra (NH region) of (a) BANQ (10.2 mM) in $\text{DMSO}-d_6$, (b) NH_4Cl (10.2 mM) in $\text{DMSO}-d_6$, and (c–i) BANQ and NH_4Cl in different mole ratios: (c) 1:0.42, (d) 1: 0.667, (e) 1:1, (f) 1:1.5, (g) 1:1.85, (h) 1:2.30, and (i) 1:2.78. (B) Job's plot for the system containing BANQ (10 mM) and NH_4Cl (10 mM) in $\text{DMSO}-d_6$. The change in the proton chemical shift of the NH proton at 7.16 ppm was followed. (C) ^1H NMR titration curve of NH_4Cl and BANQ.

shift with respect to changes in the host–guest ratio is the basis of the NMR titration technique for the determination of the association constant. The observed chemical shift of the monitored signal, δ_{obsd} is given by³¹

$$\Delta\delta = \Delta\delta_{\text{max}}/2(b - \sqrt{b^2 - 4R}) \quad (1)$$

where $R = H_0/G_0$, $b = (1 + R + 1)/G_0K$, and K is the association constant. Thus, the experimental data were fitted to this nonlinear expression and the value of K was determined as $648 \pm 35 \text{ M}^{-1}$. The association constant of the BNBQ– NH_4^+ complex was also determined as $600 \pm 47 \text{ M}^{-1}$. The stability constants of the 18-crown-6– NH_4^+ complexes in DMSO were reported to be 302 and 73 M^{-1} ,^{32,33} both of which were significantly smaller than our results.

Molecular Modeling of the NH_4^+ Binding with BNAQ.

Figure 3 shows the energy-minimized structure of the BNAQ– NH_4^+ complex. The optimum location of captured NH_4^+ was the center of the cavity, which allowed it to form hydrogen bonds with three ether oxygen atoms and one quinone oxygen atom.

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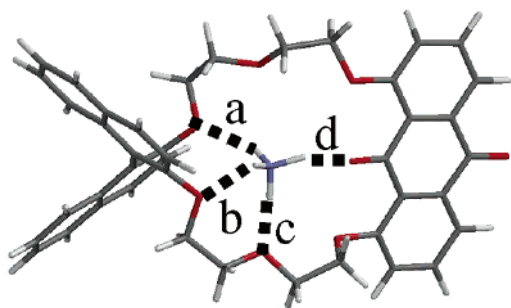


Figure 3. Energy-minimized structure of BNAQ complexed with NH_4^+ .

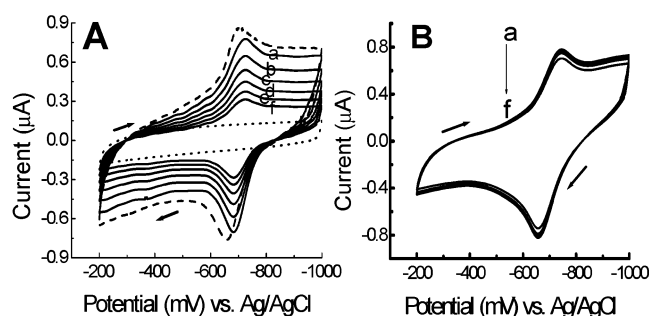


Figure 4. (A) CVs recorded for a Nafion-coated bare GCE (dot line), a Nafion-coated BNAQ-modified GCE without NH_4Cl in a Tris-HCl buffer solution (pH 7.0) (dash line), and a Nafion-coated BNAQ-modified GCE with NH_4Cl (solid line): (a) 10 μM , (b) 25 μM , (c) 50 μM , (d) 0.1 mM, (e) 0.5 mM, and (f) 1.0 mM. (B) a Nafion-coated BNAQ-modified GCE with KCl: (a) 10 μM , (b) 25 μM , (c) 50 μM , (d) 0.1 mM, (e) 0.5 mM, and (f) 1.0 mM. The scan rate was 100 mV/s.

The three anchoring hydrogen bonds between NH_4^+ and oxygen atoms of crown ether have the short $\text{N}-\text{H}\cdots\text{O}$ distances, which are as follows: (a) $\text{N}-\text{H}\cdots\text{O} = 1.9 \text{ \AA}$, (b) $\text{N}-\text{H}\cdots\text{O} = 2.0 \text{ \AA}$, and (c) $\text{N}-\text{H}\cdots\text{O} = 1.8 \text{ \AA}$. The estimated $\text{N}-\text{H}\cdots\text{O}$ (d) distance between NH_4^+ and the oxygen atom of quinone was 1.5 \AA , which was shorter than other $\text{N}-\text{H}\cdots\text{O}$ distances between NH_4^+ and ether oxygen atoms. The shorter distance means stronger hydrogen bonding. In addition, the tetrahedral complexation geometry of BNAQ for NH_4^+ in the energy-minimized structure may give favorable NH_4^+ binding over K^+ through hydrogen bonding. This may offer enhanced NH_4^+/K^+ selectivity over nonactin. It is reported that the crown ether backbone of nonactin is quite flexible and allows for the formation of wrapping-type complexes with both NH_4^+ and K^+ .¹⁰ In such complexes, the ions are enveloped by the nonactin structure, which is essential for binding K^+ , because in this conformation only octahedral binding geometry is provided. On the other hand, BNAQ possesses a rigid backbone structure that cannot easily form a wrapping-type complex. Thus, an octahedral binding site is not provided and K^+ binding seems to be unfavorable.

Host–Guest Interaction Using the Electrochemical Method.

Cyclic voltammograms (CVs) were recorded for the BNAQ- and BNBQ-modified electrodes. CV exhibited no peak when a Nafion film-coated bare GCE was used in the blank solution (0.01 M Tris-HCl buffer, pH 7.0) (Figure 4A, dotted line). A redox peak was observed at $-0.69/-0.66 \text{ V}$ versus Ag/AgCl when CV was recorded in a blank solution with a Nafion-coated BNAQ (Figure 4A, dash line) or BNBQ-modified electrodes. The peak separation

of this redox peak was 33 mV. This redox peak is related to quinone reduction as a two-electron-transfer process, which is present in the crown ether moiety. The peak current of the redox peak was proportional to the scan rate, indicating that the current flow is due to the surface-confined process of quinone groups in the adsorbed crown ether. The redox peaks were not symmetric due to the kinetic limitation of the electron-transfer reaction of BNAQ.³⁴

The pH dependence³⁵ of this quinone reduction peak was also studied between pH 2.0–11.0. The peak potential of the redox peak did not shift significantly toward a negative potential in the pH ranges between 2 and 4.5 and 8.0 and 11.0. However, the peak potential shifted toward the negative potential as the pH of the medium was increased from 4.5 to 8.0. The slope of the half-wave potential versus pH plot between pH 4.5 and 8.0 was found to be -56.5 mV/pH , indicating that a proton was involved for each electron transfer of the quinone group in this pH range. When CV was recorded (Figure 4A, solid line) for the BNAQ-modified electrode in a Tris-HCl buffer solution (pH 7.0) of 1.0 μM NH_4Cl , the redox peak shifted ($-0.72/-0.68 \text{ V}$) slightly toward the negative potential. The peak currents decreased below that recorded in a blank solution. The other crown ether, BNBQ, also showed a similar trend with NH_4^+ . This might be related to an interaction between the quinone groups of BNAQ and BNBQ crown ethers and NH_4^+ . The peak current decreased linearly as the NH_4^+ concentration increased up to 1.0 mM, indicating the formation of $\text{BNAQ}-\text{NH}_4^+$ and $\text{BNBQ}-\text{NH}_4^+$ complexes, which decreased the quinone peak current as the concentration of NH_4^+ ion increased. Further increase in the NH_4^+ concentration did not decrease the peak currents due to the saturation of $\text{BNAQ}-\text{NH}_4^+$ and $\text{BNBQ}-\text{NH}_4^+$ complexes on the electrode surfaces. CVs were also recorded for K^+ with BNAQ- (Figure 4B) and BNBQ-modified electrodes at pH 7.0 in concentration ranges between 1.0 μM and 1.0 mM. The peak current decrease was much smaller than that observed in the case of NH_4^+ . It means that the formations of $\text{BNAQ}-$ and $\text{BNBQ}-\text{K}^+$ complexes were due less to the poor complex ability of BNAQ and BNBQ and more to the K^+ .

The formation constants of $\text{BNAQ}-\text{NH}_4^+$, $\text{BNBQ}-\text{NH}_4^+$, $\text{BNAQ}-\text{K}^+$, and $\text{BNBQ}-\text{K}^+$ complexes can be determined from the following equation^{36–38} derived from the Langmuir isotherm:

$$[\text{guest}]/I_p = 1/K_f C + [\text{guest}]/C \quad (2)$$

However, in the present study, when the concentrations of NH_4^+ or K^+ were increased, the current of the quinone redox peak decreased due to the complexation ability of BNAQ and BNBQ adsorbed onto the electrode surface. This is opposite from the above equation, which was derived from the case when the peak current was increased with increasing concentration of a redox-active molecule. The current of the quinone redox peak decreasing with increasing NH_4^+ and K^+ concentrations in the present work

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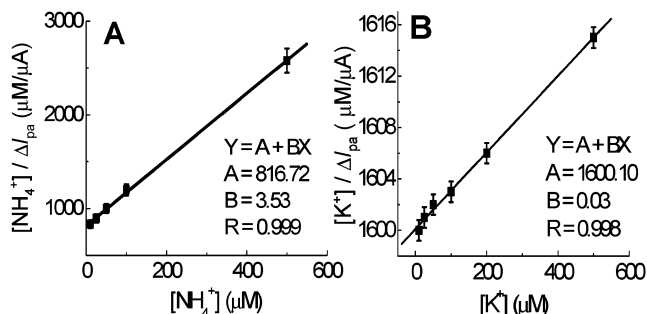


Figure 5. (A) $[\text{NH}_4^+]/\Delta I_p$ vs $[\text{NH}_4^+]$ and (B) $[\text{K}^+]/\Delta I_p$ vs $[\text{K}^+]$ plots. The currents were obtained from the CV in Figure 4 with a BNAQ-modified electrode in a Tris-HCl buffer solution containing various NH_4^+ and K^+ concentrations at the scan rate of 100 mV/s.

can be explained by the following equation:

$$[\text{M}^+]/\Delta I_p = 1/K_f C + [\text{M}^+]/C \quad (3)$$

where M^+ is NH_4^+ or K^+ , ΔI_p is the difference between the peak currents of the redox reaction of quinone in the presence and absence of NH_4^+ or K^+ , K_f is the formation constant of the complex, and C is a constant. The K_f values of BNAQ- NH_4^+ , BNBQ- NH_4^+ , BNAQ- K^+ , and BNBQ- K^+ complexes were determined from the slope and intercept of the plot of $[\text{M}^+]/\Delta I_p$ versus $[\text{M}^+]$. Figure 5 shows the plot of $[\text{M}^+]/\Delta I_p$ versus $[\text{M}^+]$ for the BNAQ- NH_4^+ and BNAQ- K^+ complexes. The K_f values were determined to be 4300 ± 120 , 4000 ± 77 , 19.0 ± 0.5 , and $18.0 \pm 0.8 \text{ M}^{-1}$ for BNAQ- NH_4^+ , BNBQ- NH_4^+ , BNAQ- K^+ , and BNBQ- K^+ complexes, respectively. The K_f values in water obtained from electrochemical methods for BNAQ- NH_4^+ and BNBQ- NH_4^+ complexes were larger than K values in DMSO obtained from NMR titrations. This might be due to the solvent effect. Since in the process of complex formation, the ligand should compete with solvent molecules for the cation. Thus, the stability of the resulting complex must be influenced by the solvating ability of the solvent as measured by the Gutmann donor number (DN).³⁹ The DN value of DMSO (29.8) is higher than the DN value of water (18).⁴⁰ Therefore, the solvating ability of DMSO toward NH_4^+ might be stronger than that of water. Thus, the association constant of the BNAQ- NH_4^+ and BNBQ- NH_4^+ complexes in DMSO was found to be smaller than the formation constant values in water. The similar binding of BNAQ and BNBQ with NH_4^+ might be due to the similar structure of these two crown ethers. The formation constants of the BNAQ- NH_4^+ and BNBQ- NH_4^+ complexes were over 2 orders of magnitude greater than that of BNAQ- K^+ and BNBQ- K^+ complexes. These results for the selectivity of NH_4^+ to K^+ (ratio of the two formation constants, $K_{f,\text{NH}_4^+}/K_{f,\text{K}^+}$) are comparable with the reported ratio of two equilibrium constants for the binding of NH_4^+ ($4.0 \times 10^6 \text{ M}^{-1}$) and K^+ ($8.8 \times 10^3 \text{ M}^{-1}$) with an artificial receptor, which is until now most selective for the binding of NH_4^+ over K^+ .⁴ The value of the equilibrium constant for the binding of NH_4^+ , as determined by the extraction method, was 2 orders of magnitude (1.59×10^2)

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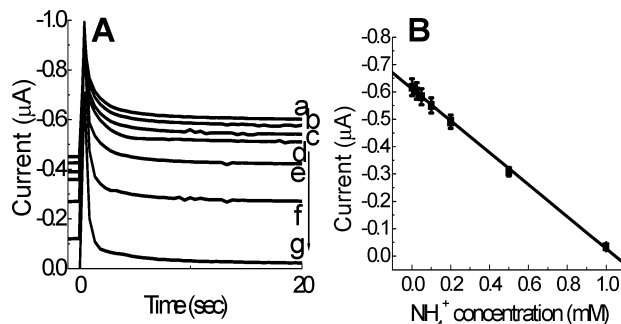


Figure 6. (A) Chronoamperograms recorded with a BNAQ-modified electrodes for (a) 1.0 μM , (b) 25.0 μM , (c) 50.0 μM , (d) 0.1 mM, (e) 0.2 mM, (f) 0.5 mM, and (g) 1.0 mM NH_4^+ in a Tris-HCl buffer solution of pH 7.0. (B) A calibration plot obtained from the chronoamperometric experiments.

greater than that for the binding of K^+ and was smaller than our $K_{f,\text{NH}_4^+}/K_{f,\text{K}^+}$ value (2.3×10^2).

The interaction of BNAQ and BNBQ with other alkali and alkaline earth metal cations, such as Li^+ , Na^+ , Rb^+ , Cs^+ , Ca^{2+} , Mg^{2+} , Sr^{2+} , and Ba^{2+} , were also studied by cyclic voltammetry. The redox current did not decrease as the concentration of the above metal ions increased, indicating noncomplexing ability of BNAQ and BNBQ to these metal ions with the exception of Rb^{2+} . For Rb^{2+} , the redox current scarcely decreased as the concentration increased, indicating very poor complex ability of BNAQ and BNBQ to Rb^{2+} . The noncomplexing ability of these two crown ethers to the other metal ions might be due to two effects, a size fit and low coordination geometry, as also found for another ammonium ionophore.¹⁰ Neither BNAQ nor BNBQ can form wrapping-type complexes; thus, the binding of these crown ethers to the smaller cations are unfavorable. Similarly, the binding of bigger cations was also unfavorable because these crown ethers cannot hold the bigger cations in their cavity. Moreover, all these metal cations have spherical symmetry and prefer ionic interactions.

Analytical Performance. The analytical performance of the modified electrode to the detection of 50.0 μM NH_4^+ was tested in the presence of 10.0 mM alkali and alkaline earth metal ions, such as Li^+ , Na^+ , K^+ , Cs^+ , Rb^{2+} , Ca^{2+} , Mg^{2+} , Sr^{2+} , and Ba^{2+} employing cyclic voltammetry and chronoamperometry. In this case, the peak current to NH_4^+ only decreased about 4–6%, indicating that the modified electrode exhibited anti-interfering selectivity for NH_4^+ detection.

The effect of BNAQ amount on the reduction of peak current in the presence of 0.1 mM NH_4^+ was also studied by changing the molar concentration of BNAQ from 1.0 to 20.0 mM in THF. The maximum reduction in the peak current for 0.1 mM NH_4^+ was obtained when the modified electrode was prepared from a 10.0 mM BNAQ solution. The observed difference in the peak current did not change significantly at over 10.0 mM BNAQ concentration.

Figure 6A shows the chronoamperograms recorded with BNAQ-modified electrodes for NH_4^+ determination at -680 mV between 1.0 μM and 1.0 mM in a Tris-HCl buffer solution (pH 7.0). The steady-state current decreased linearly with increasing concentration of NH_4^+ from 1.0 μM to 1.0 mM. Figure 6B shows the calibration plot obtained from the chronoamperometric experiments. The calibration plot was linear. The reproducibility,

expressed in terms of relative standard deviation, was found to be 5.5% at a concentration of 0.1 mM NH_4^+ . The linear dependence of the chronoamperometric current with increasing concentration of NH_4^+ gave the regression equation of $I (\mu\text{A}) = -(0.61 \pm 0.004) + (0.58 \pm 0.008)[\text{NH}_4^+]$ with a correlation coefficient of 0.999. The detection limit was determined as $0.9 \pm 0.03 \mu\text{M}$ based on three times the standard deviation of the blank (without NH_4^+).

CONCLUSIONS

We have reported here the synthesis of two redox-active crown ethers in which anthraquinone and benzoquinone groups were incorporated into the crown cavity. Due to the incorporation of a quinone group in the crown cavity, tetrahedral complexation geometry was achieved and both crown ethers showed selective binding of NH_4^+ over K^+ through hydrogen bonding. An amperometric NH_4^+ sensor developed with BNAQ crown ether showed selective NH_4^+ detection without any interference from other alkali and alkaline earth metal ions. The other crown ether, BNBQ, can

also be used in the fabrication of NH_4^+ sensors. The BNAQ sensor can detect lower concentration of NH_4^+ than that by nonactin and artificial receptors⁹ based on potentiometric sensors.

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SUPPORTING INFORMATION AVAILABLE

Detailed derivation of the nonlinear equation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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