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Synthesis and Properties of 1,3,5-Tris(phenoxymethyl)-2,4,6-triethylbenzenes as NH_4^+ Ionophores

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Abstract

The synthesis, spectroscopic characterization, and potentiometric measurements of new 1,3,5-trisphenoxy-2,4,6-triethylbenzenes are described. The cation binding abilities of trisphenoxy-2,4,6-triethylbenzenes were strongly dependent on the substituents introduced on the phenoxy units: the receptors with electron-donating alkoxy groups (–OCH_3 and –$OCH_2C_6H_5$) provided similar potentiometric performance to that of nonactin in PVC-based, ion-selective membrane electrodes. The trisphenoxy-2,4,6-triethylbenzene receptors with ether groups on ortho and meta positions of phenoxy units exhibit almost identical cation recognition properties in the PVC membranes. It is postulated that the electron-donating nature of the alkoxy substituents increases the electron density in the phenoxy units, resulting in increased cation–π interactions.

Introduction

Recent advances in molecular recognition chemistry have produced several synthetic ammonium ion-selective neutral carriers whose potentiometric properties are comparable to or better than those of nonactin in a solvent polymeric membranes [1–6]. For example, we showed that thiazole-containing benzo-crown ethers provide enhanced ammonium ion selectivity over sodium and other alkali metal ions. ^{1}H-NMR spectra, X-ray crystallography and theoretical studies suggested that the thiazole-containing benzo-crown ethers form 2 : 1 complex with ammonium ion through hydrogen bonding [1]. Suzuki *et al*. introduced a novel 19-membered crown compound with three decalino subunits in the macrocyclic system [2]. They proposed that a block-wall effect of the bulky decalino groups is responsible for the increased ammonium ion selectivity over potassium and sodium ions by factors of 10 and 3000 times, respectively. Other notable contributions have been made by Kim's group who showed that the tripodal ammonium ion receptor based on tris(pyrazol-1-ylmethyl)benzene forms ideal ammonium ion complexes through hydrogen bonding interactions [3]. However, the solvent polymeric membrane based on this compound exhibited low sensitivity and high pH dependence. In their subsequent work, a cage type tripodal ammonium ion receptor with two benzene rings rigidly held together by three dialkoxybenzene units was synthesized [4]; it was shown that its potentiometric properties were similar to those of nonactin. These examples clearly demonstrated that synthetic alternatives to nonactin are now available for the preparation of ammonium ion-selective membranes.

Having strong interest in the design of highly ammonium ion-selective neutral carriers, we also have been synthesizing tripodal ammonium ion receptors based on a 1,3,5-tris(phenoxymethyl)-2,4,6-triethylbenzene structure. Figure 1 shows some examples of the tripodal ammonium ion receptors that we have synthesized. We had two objectives in preparing these compounds: development of ammonium ion-selective neutral carriers that surpass nonactin in their potentiometric performance, and improved insight into molecular interactions between tripodal receptors and ammonium ion.

Previous theoretical and X-ray structural studies showed that the central benzene ring of the tripodal receptor plays a significant role in binding ammonium ion through cation – π interaction [4, 5]. However, the cation–π interaction between the substrate and central benzene ring is rather a long range effect compared to interaction with the tripodal phenoxy units. We, thus, postulated that modification of the phenoxy units might influence the ammonium ion binding ability by changing adjacent cation–π interactions as well as the direct hydrogen bonding interaction. In order to see the effect of various substituents on the ammonium ion binding ability of the tripodal receptors, various functional groups, such as –OCH_3, –$OCH_2C_6H_5$, –F, and –NO_2, were introduced on the ortho and meta positions of the phenoxy units, as shown in Figure 1. We then examined their potentiometric characteristics with standard PVC-based solvent polymeric membranes, and attempted to understand the

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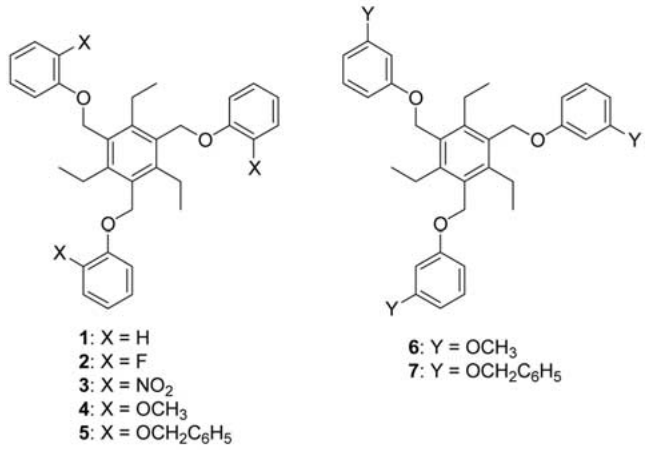

Figure 1. The 1,3,5-trisphenoxy-2,4,6-triethylbenzene derivatives used in this work.

nature of molecular recognition interactions between the tripodal receptors and cations.

Experimental

Reagents

Poly(vinylchloride) (PVC), potassium tetrakis(4-chlorophenyl)borate (KT*p*ClPB), 2-nitrophenyloctyl ether (NPOE), and nonactin were purchased from Fluka Chemie AG (Buch, Switzerland). The 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene was prepared by a known literature procedure [7]. Reagents used for the synthesis of compounds **1–7** were purchased from Aldrich Chemical Co and used as received. All other chemicals used were analytical reagent grade. Standard solutions and buffers were prepared with freshly deionized water (18 MΩ cm).

Synthesis

1,3,5-Tris(phenoxymethyl)-2,4,6-triethylbenzene (**1**). Under argon, a mixture of phenol (469 mg, 4.98 mmol) and K_2CO_3 (1.38 g, 9.98 mmol) in acetone (20 ml) was refluxed at 70 °C for 1 h and then 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (224 mg, 0.51 mmol) was added. The mixture was heated for 4 h. After the solvent was removed, the residue was extracted with CH_2Cl_2, dried and evaporated to dryness. The residue was purified by flash chromatography on silica gel (ethyl acetate-hexane 1 : 4) to give **1** (217 mg, 89%) as a white solid. R_f 0.82 (EtOAc : hexane = 1 : 2); mp 154 °C (CH_2Cl_2-hexane); IR (KBr) 2964, 1598, 1494, 1456, 1236, 1008, 850, 753, 692 cm^{-1}; ^1H NMR δ 6.97–7.37 (m, 5H, $ArCH_2OC_6\mathit{H_5}$), 5.09 (s, 2H, $ArC\mathit{H_2}OC_6H_5$), 2.85 (q, J = 7.5 Hz, 2H, $ArC\mathit{H_2}CH_3$), 1.25 (t, J = 7.5 Hz, 3H, $ArCH_2C\mathit{H_3}$); ^{13}C NMR (75.5 MHz) δ 158.9, 146.2, 131.1, 129.5, 120.9, 114.5, 64.0, 23.0, 16.4; Anal. Calcd for $C_{33}H_{36}O_3$: C, 82.46; H, 7.55. Found: C, 82.60; H, 7.65.

1,3,5-Tris(2′-fluorophenoxymethyl)-2,4,6-triethylbenzene (**2**). The procedure used to synthesize **2** was the same as for the synthesis of **1** starting with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (329 mg, 0.75 mmol), 2-fluorophenol (419 mg, 3.74 mmol) and K_2CO_3 (2.07 g, 14.96 mmol). Compound **2** was obtained as a white solid in 87% yield. R_f 0.58 (EtOAc : hexane = 1 : 2); mp 144 °C (CH_2Cl_2-hexane); IR (KBr) 2965, 1615, 1590, 1457, 1280, 1111, 996, 753 cm^{-1}; ^1H NMR δ 6.91–7.24 (m, 4H, $PhCH_2OC_6\mathit{H_4}F$), 5.16 (s, 2H, $PhC\mathit{H_2}OC_6H_4F$), 2.90 (q, J = 7.5 Hz, 2H, $PhC\mathit{H_2}CH_3$), 1.28 (t, J = 7.5 Hz, 3H, $PhCH_2C\mathit{H_3}$); ^{13}C NMR (75.5 MHz) δ 146.7, 130.6, 124.3, 121.5, 116.5, 116.3, 115.6, 65.8, 23.1, 16.5; Anal. Calcd for $C_{33}H_{33}F_3O_3$: C, 74.14; H, 6.22. Found: C, 73.54; H, 6.36.

1,3,5-Tris(2′-nitrophenoxymethyl)-2,4,6-triethylbenzene (**3**). The procedure used to synthesize **3** was the same as for the synthesis of **1** starting with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (225 mg, 0.51 mmol), 2-nitrophenol (278 mg, 2.00 mmol) and K_2CO_3 (689 mg, 4.99 mmol). Compound **3** was obtained as a white solid in 98% yield. R_f 0.32 (EtOAc : hexane = 1 : 2); mp 177 °C (CH_2Cl_2-hexane); IR (KBr) 2965, 1606, 1585, 1278, 981, 863, 744 cm^{-1}; ^1H NMR δ 7.81 (dd, J = 8.1, 1.5 Hz, 1H, H-3′ of $ArCH_2OC_6\mathit{H_4}NO_2$, 7.57–7.63 (m, 1H, H-5′ of $ArCH_2OC_6\mathit{H_4}NO_2$), 7.26–7.31 (m, 1H, H-4′ of $ArCH_2OC_6\mathit{H_4}O_2$), 7.06–7.11 (m, 1H, H-6′ of $ArCH_2OC_6\mathit{H_4}NO_2$), 5.22 (s, 2H, $ArC\mathit{H_2}OC_6H_4NO_2$), 2.84 (q, J = 4.8 Hz, 2H, $ArC\mathit{H_2}CH_3$), 1.21 (t, J = 7.5 Hz, 3H, $ArCH_2C\mathit{H_3}$); ^{13}C NMR (75.5 MHz) δ 151.9, 147.2, 140.6, 134.0, 129.7, 125.5, 120.8, 114.9, 66.1, 23.1, 16.2; Anal. Calcd for $C_{33}H_{33}N_3O_9$: C, 64.38; H, 5.40; N, 6.83. Found: C, 64.24; H, 5.50: N, 6.64.

1,3,5-Tris(2′-methoxyphenoxymethyl)-2,4,6-triethylbenzene (**4**). Under argon, a mixture of catechol (825 mg, 7.49 mmol) and K_2CO_3 (2.10 g, 15.19 mmol) in acetone (20 ml) was refluxed at 70 °C for 1 h and then 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (338 mg, 0.77 mmol) was added. The mixture was heated for 4 h, and dimethyl sulfate (3.80 g, 30.12 mmol), K_2CO_3 (2.10 g, 15.19 mmol) were added and heated for another 7 h. After the solvent was removed, the residue was extracted with CH_2Cl_2, dried and evaporated to dryness. The residue was purified by flash chromatography on silica gel (ethyl acetate-hexane, 1 : 4) to give **4** (241 mg, 0.42 mmol, 55%) as a white solid. R_f 0.62 (EtOAc : hexane = 1 : 2); mp 139 °C (CH_2Cl_2-hexane); IR (KBr) 2963, 2834, 1599, 1491, 1370, 1285, 1150, 1040, 1015, 759, 686 cm^{-1}; ^1H NMR δ 6.91-7.14 (m, 4H, H of $ArCH_2OC_6\mathit{H_4}OCH_3$, 5.09 (s, 2H, $ArC\mathit{H_2}OC_6OCH_3$), 3.82 (s, 3H, $OC\mathit{H_3}$), 2.92 (q, J = 7.8 Hz, 2H, $ArC\mathit{H_2}CH_3$), 1.27 (t, J = 7.2 Hz, 3H, $ArCH_2C\mathit{H_3}$); ^{13}C NMR (75.5 MHz) δ 150.3, 148.9, 146.6, 130.9, 121.6, 120.8, 114.5, 112.2, 65.7, 55.9, 23.1, 16.5; Anal. Calcd for $C_{36}H_{42}O_6$: C, 75.76; H, 7.42. Found: C, 75.53; H, 7.56.

1,3,5-Tris(2′-benzyloxyphenoxymethyl)-2,4,6-triethylbenzene (**5**). The procedure for the synthesis of **5** was the same as for the preparation of **4** starting with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (225 mg, 0.51 mmol), catechol (550 mg, 5.00 mmol), K_2CO_3 (1.40 g, 10.13 mmol) and benzyl bromide (1.35 g, 7.89 mmol). Compound **5** was obtained as a white solid in 73% yield. R_f 0.72 (EtOAc : hexane = 1 : 2); mp 97–98 °C (CH_2Cl_2-hexane); IR (KBr) 3032, 2954, 2869, 1591,

1490, 1377, 1286, 1177, 1150, 1028, 830, 760 cm^{-1}; ^1H NMR δ 7.20–7.45 (m, 5H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 6.62–6.67 (m, 4H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 5.05 (s, 2H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 5.05 (s, 2H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 2.82 (q, J = 7.2 Hz, 2H, $ArCH_2CH_3$), 1.22 (t, J = 7.2 Hz, 3H, $ArCH_2CH_3$); ^{13}C NMR (75.5 MHz) δ 149.7, 149.4, 146.5, 137.3, 131.0, 128.4, 127.7, 127.5, 121.9, 121.6, 116.1, 115.1, 71.1, 66.4, 23.1, 16.7; Anal. Calcd for $C_{54}H_{54}O_6$: C, 81.17; H, 6.81. Found: C, 81.02; H, 6.88.

1,3,5-Tris(3′-methoxyphenoxymethyl)-2,4,6-triethylbenzene (**6**). The procedure employed to prepare **6** was the same as for the synthesis of **4** starting with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (331 mg, 0.75 mmol), resorcinol (825 mg, 7.49 mmol), K_2CO_3 (2.10 g, 15.19 mmol) and dimethyl sulfate (3.80 g, 30.12 mmol), K_2CO_3 (2.10 g, 15.19 mmol). Compound **6** was obtained as a white solid in 44% yield. R_f 0.66 (EtOAc : hexane = 1 : 2); mp 123–124 °C (CH_2Cl_2-hexane); IR (KBr) 2963, 2834, 1591, 1491, 1370, 1285, 1150, 1040, 1015, 759, 686 cm^{-1}; ^1H NMR δ 6.56-7.28 (m, 4H, $ArCH_2OC_6H_4OCH_3$), 5.08 (s, 2H, $ArCH_2OC_6H_4OCH_3$), 3.82 (s, 3H, $ArCH_2OC_6H_4OCH_3$), 2.85 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 1.25 (t, J = 7.5 Hz, 3H, $ArCH_2CH_3$); ^{13}C NMR (75.5 MHz) δ 160.9, 160.2, 146.2, 131.0, 130.0, 106.7, 106.4, 101.1, 64.1, 55.3, 22.9, 16.4; Anal. Calcd for $C_{36}H_{42}O_6$: C, 75.76; H, 7.42. Found: C, 75.65; H, 7.51.

1,3,5-Tris(3′-benzyloxyphenoxymethyl)-2,4,6-triethylbenzene (**7**). The procedure used to prepare **7** was the same as for the preparation of **4** starting with 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (331 mg, 0.75 mmol), resorcinol (825 mg, 7.49 mmol), K_2CO_3 (2.10 g, 15.19 mmol) and benzyl bromide (2.03 g, 11.86 mmol), K_2CO_3 (2.1 g, 15.19 mmol). Compound **7** was obtained as a white solid in 34% yield. R_f 0.74 (EtOAc : hexane = 1 : 2); mp 121 °C (CH_2Cl_2-hexane); IR (KBr) 3032, 2958, 2869, 1591, 1490, 1370, 1285, 1150, 1028, 830, 760, 685 cm^{-1}; ^1H NMR δ 7.30–7.46 (m, 5H, H of $ArCH_2OC_6H_4OCH_2C_6H_5$), 6.62–7.26 (m, 4H, H of $ArCH_2OC_6H_4OCH_2C_6H_5$), 5.06 (s, 2H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 5.05 (s, 2H, $ArCH_2OC_6H_4OCH_2C_6H_5$), 2.81 (q, J = 7.5 Hz, 2H, $ArCH_2CH_3$), 1.23 (t, J = 7.2 Hz, 3H, $ArCH_2CH_3$); ^{13}C NMR (75.5 MHz) δ 160.2, 160.1, 146.2, 136.9, 131.0, 130.0, 128.6, 128.0, 127.6, 107.3, 107.1, 102.0, 70.1, 64.1, 23.0, 16.4; Anal. Calcd for $C_{54}H_{54}O_6$: C, 81.17; H, 6.81. Found: C, 81.00; H, 7.01.

Instrumentation

The ^1H and ^{13}C NMR spectra were obtained on Varian UNITY Inova 300WB FT-NMR spectrometer. The chemical shifts in the ^1H NMR spectra are reported in δ units downfield from the internal tetramethylsilane. The IR spectra were measured with a Galaxy FT-IR 7000 spectrophotometer. Mass spectra were recorded on a Shimadzu QP-1000 spectrometer. Elemental analyses were performed on a Calro Erba 1106 elemental analyzer at the Center for Scientific Instruments at Kyungpook National University.

Preparation of electrodes and their potentiometric evaluation

Ion-selective membranes were prepared with eight different ionophores; the seven synthesized compounds **1–7** and one natural compound nonactin. Membrane cocktails were formulated by dissolving 2.0 mg of ionophore, 66 mg of PVC and 132 mg of plasticizer (DOA) in 1.0 ml tetrahydrofuran, poured into glass rings (i.d. = 22 mm) mounted on a glass slide, and dried overnight in a dust-free chamber at room temperature. Membrane disks (d = 5.5 mm) were punched out of the master membranes and mounted in Philips electrode bodies (IS-561; Glasbläserei Möller, Zürich, Switzerland). The inner filling solution for all electrodes was 0.1 M NH_4Cl. An Orion (Cambridge, MA, USA) sleeve-type double-junction Ag/AgCl electrode (Model 90-02) was used as the external reference. The potential differences between the ion-selective electrode and the reference electrode were measured using a PC equipped with a 16-channel high-impedance input voltmeter (Model KST101B, KOSENTECH, Busan, Korea). Dynamic response curves and calibration plots were obtained by adding calculated amounts of standard solutions to 200 ml of stirred background electrolyte (0.05M TRIS-HCl, pH 7.4) at room temperature; concentrations of primary and interfering ionic species were varied from 10^{-6} to 10^{-1} M. The response of the electrode to pH changes was tested by adding aliquots of NaOH solution to a buffer composed of 11.4 mM boric acid-6.7 mM citric acid-10.0 mM NaH_2PO_4 at room temperature. The solutions were magnetically stirred during all e.m.f. measurements. Selectivity coefficients were determined by using the matched potential method at an interfering ion concentration of 0.10 M [8]. Other response characteristics, e.g., detection limits, response slopes, and response times, were determined according to the IUPAC recommendation [9].

Results and discussion

Simple semi-empirical modeling of the compound **1**-ammonium ion complex (PM3 level calculation with Chem3D program) suggests that the ammonium is nested on the center of tripodal phenoxy units through hydrogen bonding. The three phenyl rings are oriented outward with respect to the nested ammonium ion, suggesting that direct interaction with the tripodal phenyl rings may not be a significant factor for ammonium ion complexation in the theoretical model. Previous *ab-initio* studies for the receptors with tripodal azole and azoline subunits (e.g., pyrazole, pyrazoline, oxazole, oxazoline, imidazole and inidazoline) showed that a subtle interplay of charged H-bonds and cation–π interaction with the central benzene are responsible for enhanced ammonium ion selectivity [5]. If the hydrogen bonding interactions with the tripodal phenoxy units and the cation–π interaction are strong enough to hold ammonium ion within the receptor, we expect that the compound **1**-based, ion-selective membrane will exhibit appreciable cationic responses. However, as shown in Figure 2, the compound

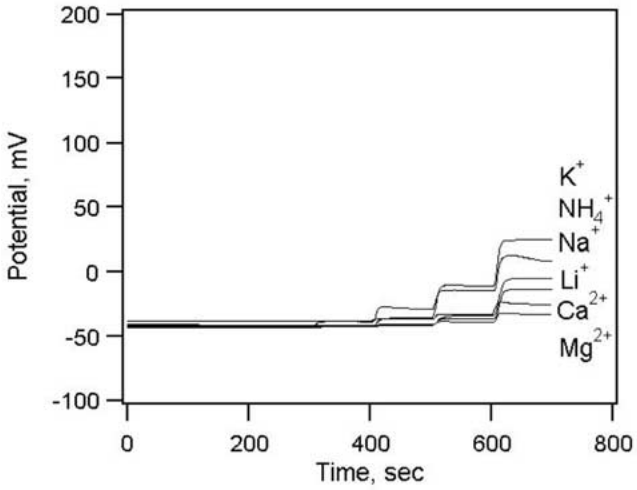

Figure 2. Potentiometric response of the compound **1**-based PVC membrane.

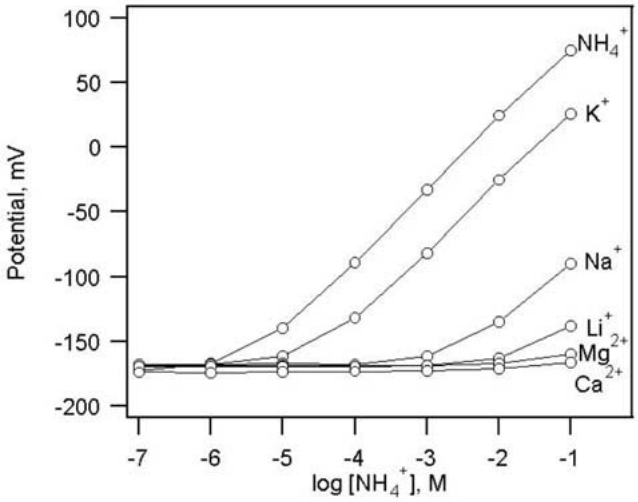

Figure 3. Calibration plot for the ion-selective membrane based on compound **5**.

1-based membrane exhibits little response to alkali and alkaline earth metal cations, as well as to ammonium ion, indicating that the H-bonding interactions with the tripodal phenoxy units and the cation – π interaction are insufficient for cation binding. Introduction of both weakly and strongly electron-withdrawing groups (–F and $–NO_2$) on the ortho positions of phenoxy units did not improve the binding ability of the receptors. Thus the potentiometric responses of compound **2**- and **3**-based membranes were virtually the same as those of the plasticized PVC-membranes with no ionophore.

In order to increase the hydrogen bonding interaction between the phenoxy groups and ammonium ion, we introduced two different electron-donating ether groups ($–OCH_3$ and $–OCH_2C_6H_5$) on the ortho positions to yield compounds **4** and **5**. It was anticipated that the six ether oxygens in the substituents enhance cation complexation resulting in improved ammonium ion selectivity. However, semi-empirically calculated models indicate that the ether-containing substituents tend to orient outward in a way minimizing the steric repulsion among them. We did not carefully consider the detailed energetics of complexation process in this simple modeling study. Instead, we compared their experimental potentiometric properties. Figure 3 shows the calibration plot of the compound **5**-based ion-selective membrane to various cations. The responses of the compound **4**-based membrane were almost identical. As summarized in Table 1, the potentiometric performance of the membranes based on compounds **4** and **5** is very close to that for nonactin based membranes, especially in terms of their ammonium ion selectivity over sodium and potassium ions. This reveals that the enhancing the membranes of ether oxygens in the substituent greatly increases the binding ability of tripodal phenoxy receptors. However, it is still not clear whether all three ortho dialkoxybenzene units participate in binding the complexed cations.

To probe the role of ether substituents in the tripodal phenoxy receptors, we changed the substitution sites of the $–OCH_3$ and $–CH_2OC_6H_5$ groups from ortho to meta positions in compounds **6** and **7**. The distances between the new ether oxygens and the nested cation are farther separated in **6** and **7** than in **4** and **5**. Therefore hydrogen bonding interactions between the new ether oxygen and ammonium ion should be substantially reduced in compounds **6** and **7**. However, the potentiometric responses of the ISE membranes based on **6** and **7** are nearly almost identical to those observed with membranes based on **4** and **5**. Although the response slope of the compound **6**-based membrane, 50 mV/dec., was slightly reduced, other potentiometric properties were virtually the same for all ether group substituted tripodal phenoxy receptors as shown in Table 1.

These results demonstrate that the enhancement of ammonium ion-selective binding ability of tripodal phenoxy receptors is markedly dependent on the choice of substituents. Electrostatic interaction between the tripodal phenoxy units and cation–π interaction with the central benzene are insufficient to nest ammonium ion or other cations. Ortho- or meta-substituted ether groups substantially increased the cation binding ability of the tripodal phenoxy receptors. However, the nature of increased cation binding ability is not apparent because they provide virtually the same potentiometric properties with a significant difference in the distance. This indicates interaction between the ether oxygens and the cation. It is also possible that the electron-donating nature of the ether groups increased the π-electron density in the phenoxy units, resulting in the increased cation–π interactions. Simple theoretical models were insufficient to explain the marked change in the cation binding ability of tripodal phenoxy receptors by ether substituents.

As summarized in Table 1, the tripodal phenoxy receptors with alkoxy substituents (i.e., **4**, **5**, **6** and **7**) provide potentiometric performance, especially the ammonium ion selectivities over sodium and potassium ions, similar to that for nonactin. Their pH responses were also very similar to each other (Figure 4) in solvent polymeric membranes. These results may imply that the cation size-selective binding sites formed by oxygen atoms have certain limitation

Table 1. Potentiometric properties of ion-selective membranes based on 1,3,5-trisphenoxy-2,4,6-triethylbenzene derivatives.

Membrane No.[a]	Ionophore	Slope[b] (mV/dec)	Det. Limit[c] $-\log[NH_4^+/M]$	Selectivity coefficient ($-\log k^{pot}_{NH_4^+,J}$)				
				K^+	Na^+	Li^+	Ca^{2+}	Mg^{2+}
4	4	55.3	5.5	1.0	2.8	3.9	5.0	4.7
5	5	54.8	5.6	1.0	2.9	4.0	5.0	4.8
6	6	50.0	5.4	0.9	2.9	3.8	4.4	4.4
7	7	55.1	5.6	1.0	2.8	3.9	5.2	4.7
8	Nonactin	58.1	6.0	1.0	2.9	4.5	5.9	5.0

[a] Membranes containing **1–3** did not exhibit appreciable responses.
[b] Slopes from 10^{-4} to 10^{-1} M (mV/decade).
[c] Logarithmic scale.

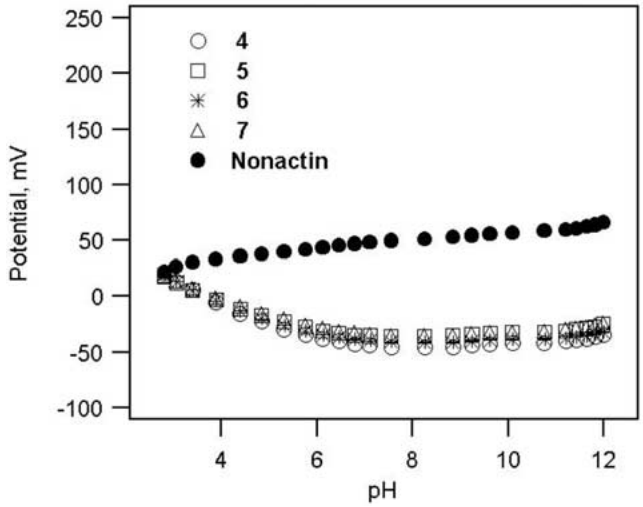

Figure 4. pH-response of the ion-selective membranes based on 1,3,5-trisphenoxy-2,4,6-triethylbenzene derivatives **4–7** and nonactin.

in discriminating alkali metal cations over ammonium ion. Introduction of hetero atoms or functional groups that can promote the formation of hydrogen bonding around the cation binding sites may be necessary to yield neutral carriers with better ammonium ion selectivity than nonactin. Design and synthetic efforts in this direction are in progress.

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