The Potentiometric Studies on the Effects of Various Functional Groups in Disiloxane as an Anion-Selective Ionophore

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Received September 10, 2004

The potentiometric responses for various anions are investigated with membrane electrode (membrane 1) based on 1,3-diethyl-1,3-dihydroxy-1,3-bis(2-dimethylaminomethyl ferrocenyl) disiloxane. The nitrate ion-selective electrode based on compound 1 gave a good Nernstian response of 58.18 mV per decade for nitrate with the detection limit of -5.66 of log $[NO_3^-]$. Compound 1 has all those functional groups and the other two compounds have less functional group of ferrocenyl or ferrocenyl and hydroxide, respectively. Even though, potentiometric response to anions was excellent at pH 5, the selectivity pattern for all three membrane electrode based on series of disiloxane is almost like Hofmeister sequence at pH 5. However, the membrane electrode 1-3 exhibited very different response to anions at pH 7. In this pH, NH_2 is not protonated and ionophore may act as neutral carrier. Hydrogen bond may enhance the responsibility to hydrogen acceptors and intramolecular electro-active site may increase the permeability of analyte to ionophore in membrane.

Key Words : 1,3-Diethyl-1,3-dihydroxy-1,3-bis(2-dimethylaminomethyl ferrocenyl) disiloxane, Anion-selective ionophore, Potentiometric response

Introduction

Solvent polymeric membrane electrodes incorporating neutral ion carriers are known to be very useful tools for chemical, clinical and environmental analyses as well as in process monitoring. The design of anion receptors is far less developed than the field of cation receptors. Classical liquid membrane electrodes for anions are based on quaternary ammonium salts and their anion responses rely on associated ion exchange. Thus the selectivity of membrane electrodes based on aforementioned ionophores exhibit Hofmeister selectivity sequence based on the analyte lipophilicity. Recently, a series of new anion-selective electrodes has been described, which display a selectivity deviating from the Hofmeister sequence as a result of unique interactions between the carriers and the anions. The development of host-guest chemistry has made it possible to achieve useful selectivity for some weakly lipophilic anions.[1]

Whereas most anion ionophores are organometallic compounds that interact with the analyte by formation of coordination bonds, a number of other approaches to analyte recognition have been used. e.g., if the membrane contains the receptor molecules that are able to bind specific anions, the membrane may become selective towards those anions. For instance, the binding energy of the complex that is formed by the association of the anion and the receptor effectively reduces the transfer energy that is required to extract the anion from the aqueous phase to the membrane.[2] Neutral receptor containing a functionality capable of H-bonding, when positioned correctly in the supramolecular matrix, would be able to differentiate between the three-dimensional shapes of anions.[3-6] The anion selectivity would be amplified with the addition of functional groups containing H-bonds capable of forming bi- and trifurcated bonding arrays.[7] Lewis acid metal centers[2,8-10] or electrophilic carbon atoms[11] can be applied for this purpose, too.

No silicon compound has been reported as an ionophore for any type of ion selective membrane electrodes; presumably, because their electrochemical properties are usually not good enough to be applied for sensors. However, the silicon compounds have some possible advantages as the ionophores, such as the possibility of directly applying self-assembled monolayers or forming molecular imprinting polymers to ionophores over carbon compounds.[12,13] Recently, we synthesized a new type of ionophore based on dihydroxysiloxanes with various combinations of functional groups and investigated their potentiometric performances. We found that some of the membrane electrodes based on dihydroxysiloxanes exhibited good potentiometric performance as an anion sensor and that this performance varied according to the contribution of each functional group.

In this work, we studied the potentiometric performances of ion-selective electrodes based on a series of dihydroxysiloxanes. The experimental conditions of the ionophores were optimized and structural characteristics were explored as their effect on performances. We hope that the basic data obtained in this report open the door for silicon compounds to the world of ionophores.

Experiments

Reagents: Poly(vinyl chloride), *o*-nitrophenyl octyl ether (NPOE), tridodecylmethylammonium chloride (TDMACl) and potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB) were purchased from Fluka (Ronkonkoma, NY). All other chemicals include sodium salts of examined anions were
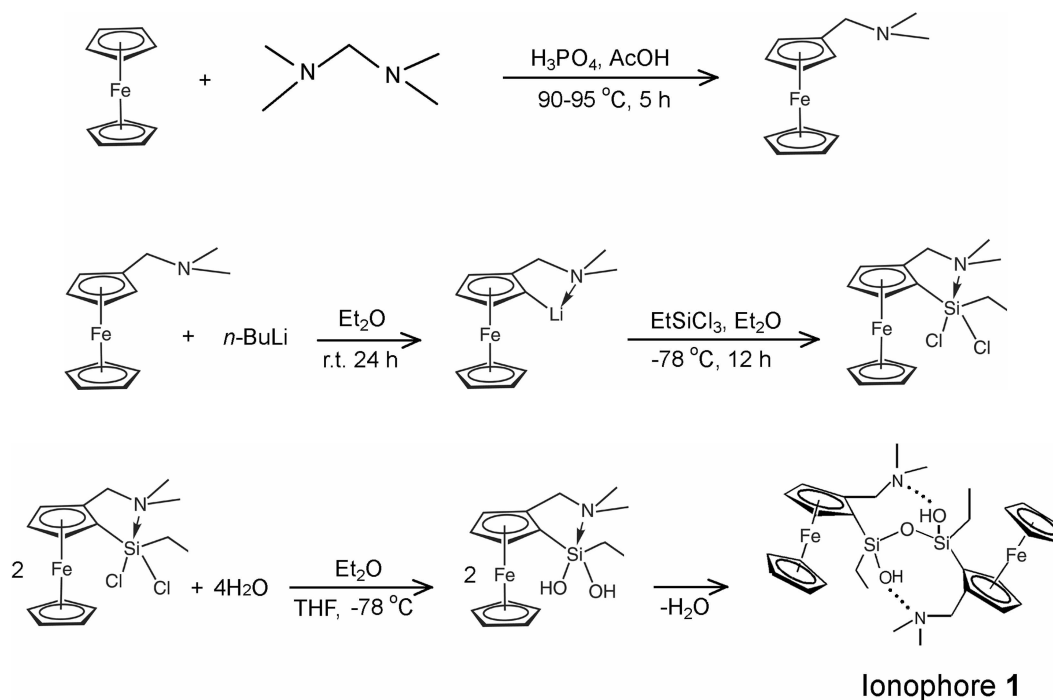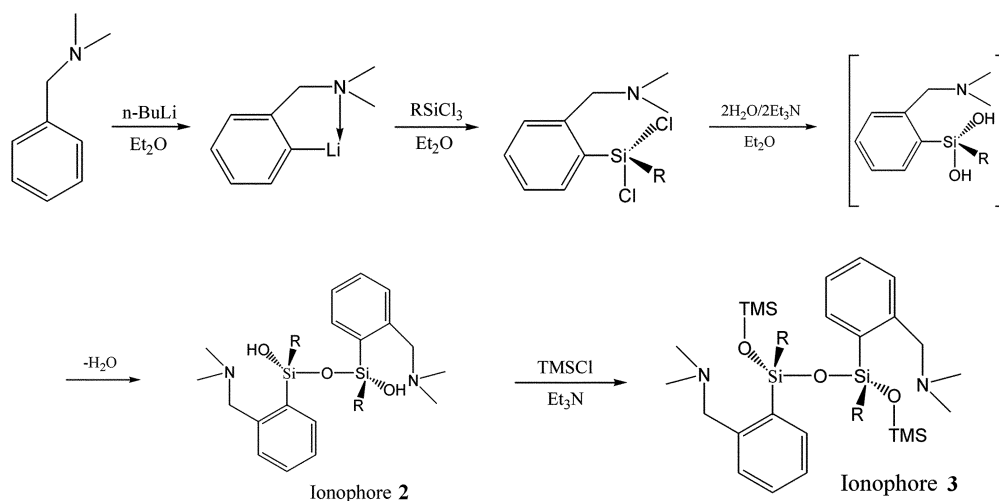
Scheme 1. Synthesis of 1,3-diethyl-1,3-dihydroxy-1,3-bis(2-dimethylaminomethyl ferrocenyl) disiloxane.

analytical reagent grade and used without further purification. Standard solutions and buffers were prepared with the use of deionized water.

Ionophore design and synthesis: The structures of and synthetic procedures for the dihydroxysiloxanes studied are displayed in Scheme 1 and 2. The ionophore based on dihydroxysiloxanes was designed for applying as an ionophore. We introduced the ferrocenyl moiety to the compound to enhance electrochemical properties, such as electro-conductivity. Then we also introduced the hydrogen bonding site of -OH groups and possible cationic site of NH_2 for enhancing sensing performance and selectivity toward anions. That is compound **1**. Compound **2** and **3** were

synthesized, in order to investigate the effect of these aforementioned functional groups on potent performance. Compound **1** has all of the functional groups; compound **2** has all of the functional groups except ferrocenyl and compound **3** is ferrocenyl an −OH less functionality. The dihydroxysiloxanes were synthesized by the method shown in previous reports from our lab and detailed procedures of synthesis will be published elsewhere.[14,15] The synthesis of 1,3-diethyl-1,3-dihydroxy-1,3-bis(2-dimethylamino methyl ferrocenyl) disiloxane is summarized in Scheme 1, and that of 1,3-dihydroxy-1,3-bis(2-aminomethylphenyl)-1,3-divinyldisiloxane and 1,3-bistrimethylsiloxy-1,3-bis(2-aminomethyl phenyl)-1,3-divinyldisiloxane in Scheme 2.

Scheme 2. Synthesis of 1,3-Dihydroxy-1,3-bis(2-aminomethylphenyl)-1,3-divinyldisiloxane and 1,3-bistrimethylsiloxy-1,3-bis(2-aminomethyl phenyl)-1,3-divinyldisiloxane.

**Table 1.** The composition of membrane electrode based on dihydrosiloxanes

Membrane no.	Matrix (33 wt%)	Ionophore (1 wt%)	Plasticizer (66 wt%)	Lipophilic additive (mol% vs ionophore)
1	PVC	Ionophore 1	o-NPOE	–
2	PVC	Ionophore 2	o-NPOE	–
3	PVC	Ionophore 3	o-NPOE	–
4	PVC	Ionophore 1	o-NPOE	TDMACl (50)

Preparation and evaluation of polymer membranes and electrodes: PVC matrix membranes were prepared according to the method as follows: The composition of PVC-based anion-selective membrane was 1 wt % ionophore, 33 wt % PVC and 66 wt % plasticizer with total weight of 200 mg. The membranes were prepared by dissolving the mixture in 5 mL, THF. In each case, after curing, small disks (5.5 mm) were punched from the cast films and mounted in Philips electrode bodies (IS-561; Glasblaserei, Möller, Zürich, Switzerland). The membrane compositions are summarized in Table 1.

The potentiometric behavior of the membrane electrodes was evaluated with conventional ISE configuration. For all electrodes, 0.1 M NaNO₃ was employed as the internal filling solution. The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02). Electrodes were connected through a high impedance amplifier to a computer equipped with an analog-to-digital converter. The cell potentials were measured at ambient temperature (22 °C) by immersing ISEs and a reference electrode in a beaker containing appropriate buffer. The pH test was performed at the universal buffer (11.4 mM boric acid; 6.7 mM citric acid; 10.0 mM sodium dihydrogen phosphate, pH 5.5) with addition of conc-NaOH. The calibration data were obtained from additions of standard solutions. The solutions were magnetically stirred throughout and equilibrium potentials were recorded. Selectivity coefficients were estimated according to the separated solution-matched potential method at an interfering anion concentration of 0.1 M.[15] The detection limits of the membrane electrodes were obtained from the calibration plots following the recommended procedure.[16] The membrane resistance was measured with 4-probe, 2000 multimeter (Model 224 of Keithley, Cleveland, OH).

Results and Discussions

The potentiometric responses for various anions are investigated with a membrane electrode (1) based on 1,3-diethyl-1,3-dihydroxy-1,3-bis(2-dimethylaminomethyl ferrocenyl) disiloxane. The electrode based on this compound exhibits excellent performance as an anion sensor for I⁻ and NO₃⁻ ions with a Nernstian response to aforementioned anions' activity in the range of 1 × 10⁻⁶-1 × 10⁻¹ M. Thus, we optimized this membrane electrode with a nitrate ion and
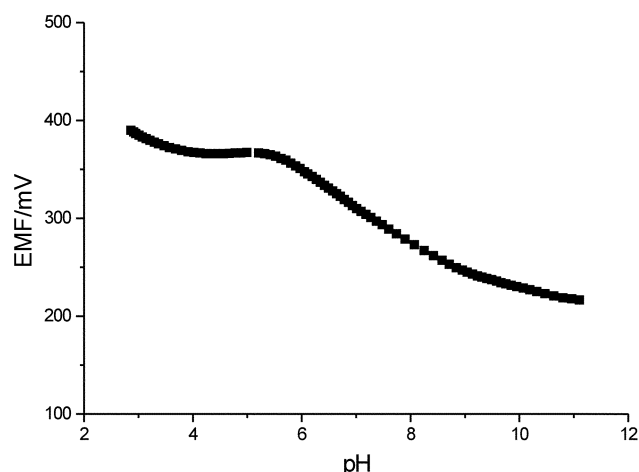
Figure 1. The pH effect on response characteristics of the membrane electrode based on compound 1.

investigated the potentiometric performances and response mechanisms of ion-selective membrane electrode based on a series of dihydroxysiloxanes.

The optimization of membrane sensors based on ionophore compound 1 for the potentiometric response as nitrate ion-selective electrode. It is known that the pH and type of buffer affect on potentiometric performances of electrode based on anion-selective ionophores.[17-20] Especially, the membrane electrode based on 1,3-diethyl-1,3-dihydroxy-1,3-bis(2-dimethylaminomethyl ferrocenyl) disiloxane was expected to exhibit pH response, because of the presence of nitrogen (-NH₂) and oxygen (-OH) atoms in the structure of the ionophore. The response of an electrode toward pH was checked by titrating a universal buffer of pH 2.8 with small aliquots of NaOH while simultaneously monitoring the pH of the sample solution with a combination glass pH electrode. The potential response of the electrode was observed at the buffer solution in the pH range of 2.8 to 12. As seen in Figure 1, the potentiometric response of each membrane electrode is steady at the pH range of 3.0 to 5.5, beyond which the potential changes considerably. This observed drift after pH 5.5 could be due to the partial protonation of the carrier and/or response to OH⁻ ions.

The effects of pH and types of buffers on potentiometric response were also investigated, because it is necessary to optimize and stabilize the analytical performances. The results are listed in Table 2. These results indicate that the potentiometric response (slopes and detection limits) toward nitrate is strongly depends on working pH values and type of buffer solution. The membrane electrodes exhibit the relatively better results at the pH range of 3-5 and the response to nitrate seems to deteriorate to some extent as pH increases. The response to nitrate is decreased 20-30% as the working pH goes to 7-8 and shows super Nernstian behavior at pH 9-10. It was also found that the detection limits decrease one order at the working pH over 7 (response over 10⁻⁵ M) and another order over pH 9 (start response over 10⁻⁴ M) toward nitrate. We think that the response under pH 5 relies on an ion exchange process with intramolecular

Table 2. Detection limits and Slopes of Membrane 1 for NO_3^- at various Buffers

Buffers	Detection Limits*	Slope (mV/dec)	note
0.01 M Mg (acetate) pH 7.43	−5.29	49.65	Small response under 10^{-5} M
0.1 M Mg (acetate) pH 8.31	−5.01	43.59	Small response under 10^{-5} M
0.01 M MES^a pH 3.82	−5.44	52.00	
0.1 M MES pH 3.41	−5.30	53.41	
0.01 M MOPS^b pH 4.41	−5.69	56.25	Delayed response time
0.1 M MOPS pH 3.82	−5.70	54.54	Delayed response time
0.01 M TRIS^c pH 9.90	−4.91	61.59	
0.1 M TRIS pH 10.47	−4.74	47.44	Response begin at 10^{-4} M
0.01 M HEPES^d pH 5.01	−5.96	58.49	Best response
0.1 M HEPES pH 4.96	−5.32	56.78	Good response

*Detection limits are based on log value. ^{a}2-[N-morpholino]ethanesulfonic acid]. ^{b}3-[N-morpholino]propanesulfonic acid]. ^{c}Tris[hydroxymethyl]-aminomethane. ^{d}N-[2-hydroxyethyl]piperazine-N'-[2-ethanesulfonic acid]

Table 3. Response characteristics for membrane electrodes based on series of dihydrosiloxanes. HEPES buffer solution (0.01 M at pH 5)

Anions	1^a		2		3	
	Detection Limits^b	Slope (mV/dec)	Detection limits	Slope (mV/dec)	Detection limits	Slope (mV/dec)
SO_4^{2-}	−5.95	7.52	−5.753	16.06	−5.706	13.86
Cl^-	−4.67	38.52	−4.757	30.75	−4.747	23.61
Br^-	−5.37	54.23	−5.245	46.79	−4.963	41.38
acetate	−4.44	18.38	−4.953	27.05	−4.636	25.41
I^-	−6.19	57.74	−6.454	63.56	−5.972	61.33
NO_2^-	−5.02	50.13	−5.138	48.44	−4.792	40.76
NO_3^-	−5.67	58.18	−5.666	53.99	−5.293	50.94

^{a}Membrane electrode. ^{b}Detection limits are based on log value

cation sites of protonated $-NH_3^+$. Then around pH 7, some of $-NH_3^+$ become $-NH_2$ and decrease ion exchange process, but then hydrogen bonding is another factor for response to nitrate ion. At alkaline pH, membrane electrode response nitrate and OH^- to together to exhibit super Nerntian response but detection limit is decreased considerably due to the lack of the ion exchange mechanism. The HEPES buffer solution (0.01 M at pH 5) exhibits better overall response to nitrate than other buffer solutions tested in this experiment.[4] Therefore, the aforementioned optimized system was used as an experimental condition in all the remaining experiments. The level of the fabricated membrane electrode with ionophore compound 1 was very stable upto 20 days. After this time, the slope and detection limit for nitrate slightly decreased, but decreased only 10% in terms of the slope even after the two months.

The structural effect on potentiometric response of membrane sensors based on the series of dihydroxysiloxanes. The ionophore based on dihydroxysiloxanes was designed for applying to detection of anions. The designing an ionophore based on organo-silicon compounds is a somewhat challenging task, because the electrochemical properties of silicon-based ionophores are usually not sufficient for sensor applications. Thus, we introduced the ferrocenyl moiety to the compound to enhance electrochemical properties such as electro-conductivity and diffusibility of ions, even though an electro-active functional group is not
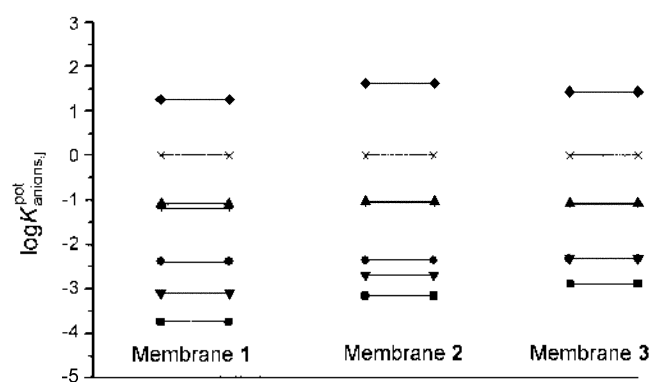
Figure 2. Selectivity coefficients of membrane electrodes based on series of dihydrosiloxanes toward anions: −■− SO_4^{2-} : −▼− acetate; −●− Cl^-: −+− Br^-: −▲− NO_2^-; −×− NO_3^-; −◆− I^-, HEPES buffer solution (0.01 M at pH 5).

recommended for the ionophores.

Then we introduced the other functional groups to dihydroxysiloxane back-bone for enhancing response toward anions. The response mechanisms of anionic ionophores are dissociated ion exchange, fit in cavity, ligand binding to central metal site, electrostatic attraction and hydrogen bonding.[5] The dihydroxysiloxane doesn't have a cavity or a central metal site. Thus, we just added the hydrogen bonding site of Si-OH groups and the possible cationic site (-NH_3^-) for enhancing sensing performance and selectivity toward

anions.[4,21,22] That is compound **1**. Our expectation was that the hydrogen bonding would enhance the responsibility to hydrogen acceptors and an intramolecular cation site might increase the permeability of analyte to ionophores in membrane. In addition, this cationic site prevents possible cation responses. Compound **2** and **3** were synthesized in order to investigate the effect on potentiometric performances by the aforementioned functional groups. Compound **1** has all those functional groups and the other two compounds lack the ferrocenyl group (**2**) or ferrocenyl and hydroxide groups (**3**) indicated by numbers in parentheses.

In the Table 3, the potentiometric performances of membrane electrodes based on each ionophore at the optimized conditions (pH 5) are listed respectively. From the comparisons between membrane electrodes **1** and **2**, the detection limits for nitrate are very similar (−5.67 for **1** and −5.66 for **2** of log [NO_3^-]). However, the slope of **1** (58.18 mV/dec) is about 10% improvement from **2** (53.99). From that result, the ferrocenyl group may not be a big factor for anion sensing, but decrease the membrane resistance and thus enhancing ion mobility. The results from the conductivity tests of membrane electrodes **1-3** also support the aforementioned assumption. The conductivity of **1** (3.40 × 10^{-7} S/cm) is much better than that of **2** and **3** (9.12 × 10^{-9} and 3.4 × 10^{-11} S/cm, respectively).

Comparing membrane electrodes **2** and **3**, both the detection limit (−5.29) and the slope (50.94) of **3** are 10% worse than those observed in **2**. We expect the Si-OH group could have big contribution to ion sensing as of Si-O-H - - N-O hydrogen bonding. However, that contribution seems much less important than electrostatic attraction from the protonated NH_2 group.

At pH 5, The selectivity coefficient patterns (Fig. 2) was also obtained with separate solution methods and is very close to the Hofmeister sequence of $ClO_4^- > SCN^- > I^- > NO_3^- > NO_2^- = Br^- > Cl^- > $ acetate $> SO_4^{2-}$ for all three membrane electrodes, even though **1** shows a little better selectivity for nitrate. At lower pH, the ionophores works as a charged carrier, which means that the most dominant force to attract anion to ionophore is an electrostatic attraction force from the NH_3^- cation site. The response differences between membrane electrodes **1** to **3** are relatively small, because the effects of ferrocenyl group and hydrogen bonding are relatively weaker than electrostatic force in this low pH. In addition, this trend is in good agreement with super Nernrtian response to very lipophilic anions (ClO_4^- and SCN^-), while the potentiometric performances of membrane electrodes worsened with the addition of lipophilic additives (membrane electrode **4**, results not shown).[22-24] It is also well known that ion exchange processes are faster than other processes such as chelation, leading to short response time; thus the fast response time (less than 5 sec, Figure 3) of these membrane electrodes supports this assumption.[22]

The potentiometric performances toward various anions by membrane electrodes based on disiloxane at higher pH (0.01 M HEPES buffer solution pH 7) were also compared
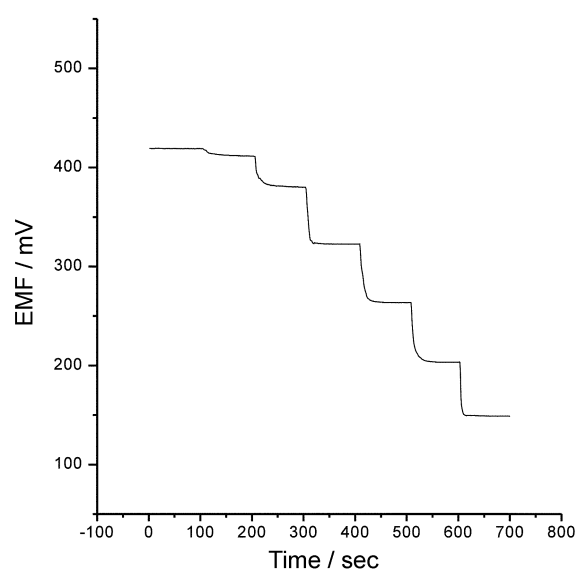
Figure 3. Dynamic response curve of membrane electrodes based on ionophore 1: HEPES buffer solution (0.01 M at pH 5).

for all three membrane electrodes (for ionophores **1-3**). It is probable that the ionophores are not protonated at higher pH and thus act like neutral carrier. It might be that the hydrogen bonding is the major force to response to anions at this higher pH. In contrast to the responses at pH 5, the performances at higher pH changed significantly. The slopes decreased as order of 50.12 mV/dec, 39.34 and 18.04 of membrane electrodes **1, 2** and **3**, respectively. Detection limits also decreased one order each for **1, 2** and **3**. At pH 7, the slope for nitrate decreased to about 15% from pH 5 for membrane electrode **1**. This ~8 mV/dec slope decrease is a bit smaller than expected, because we had earlier concluded that contribution of hydrogen bonding is smaller than electrostatic attraction for response to nitrate based on the results of the slope difference of membrane electrodes **1** and **2** at pH 5.

The change at membrane electrode **2** is much bigger than that of **1**. That slope is smaller than 40 mV/dec and is another 20% decrease from membrane **1** at pH 7 and 30% from pH 5 of membrane electrode **2**. This membrane electrode does not have either an electro-active group (ferrocenyl) or a charged group (protonated NH_2) to enhance ion mobility in the membrane, thus the response is significantly decreased. We could assume that ~40 mV of response comes from hydrogen bonding of -OH group. The result from membrane electrode **3** at pH 7 also follows this pattern. The ionophore compound **3** doesn't have the hydrogen bonding site by that the hydrogen of −OH group is substituted with TMS. As mentioned above, this membrane electrode almost lost its anion response behavior. If hydrogen bonding is the major response mechanism for nitrate as expected at pH 7, the selectivity should be enhanced toward hydrogen bonding anions. Indeed, enhanced selectivity toward hydrogen bond acceptor anions such as Cl^- and Br^-, and oxygen containing acid anions of acetate and nitrate were noticed. As expected, the effect on selectivity changes was bigger at membrane

electrode **2** than **1**, because the response to the most of the anions by membrane electrode **3** is negligible, the selectivity changes for this electrode won't be mentioned.

In conclusion, the selectivity pattern for all three membrane electrode based on series of dihydrosiloxane is almost like the Hofmeister sequence seen at pH 5. We think, this behavior can be explained by the reliance of potenti-ometric response on ion exchange process with intramolec-ular $-NH_3^-$ cation site. If an ionophore acts a charged carrier in the anion-selective sensor membrane, an electro-active group (ferrocenyl group), a hydrogen bonding site, or even an additional cation site shows very little impact on response to anions. However, the membrane electrodes **1-3** exhibited very different response to anions at pH 7. In this pH, NH_2 is not protonated and the ionophore may act as neutral carrier. As stated earlier, hydrogen bonding will enhance the responsiveness to hydrogen acceptors and an intramolecular electro-active site may increase the permeability of analyte to the ionophore in the membrane.

This is the first report that disiloxane containing functional groups such as ferrocenyl moiety, NH_2 group and silicon hydroxyl group exhibited possible usage and response mechanism as an ionophore for an anion sensor. We hope that this work act as a stepping stone for the design of silicon and high resistance compound-based ionophores.

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