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Sodium ion sensors based on dibenzo-16-crown-5 compounds with amide side arms

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Lipophilic dibenzo-16-crown-5 compounds with amide-containing side arms attached to the central carbon atom of the three-carbon bridge in the polyether ring have been applied as neutral carriers for sodium ion-selective field-effect transistors (Na^+-ISFET's). ISFET's based on these lariat ether amides exhibit excellent Na^+/K^+ selectivities ($K_{Na,K}^{Pot} = 7 \times 10^{-3}$) and Na^+/H^+ selectivities ($K_{Na,H}^{Pot} = 3 \times 10^{-3}$) with good selectivities for Na^+ over other alkali metal cations and alkaline-earth metal cations. High sensor durability was obtained for these ISFET's.

INTRODUCTION

Considerable attention has focused upon developing ion-selective field effect transistors (ISFET's), which have several advantages compared with conventional ion-selective electrodes (ISE's).[1] These include micro-scale, rapid response, easy fabrication using IC technology, and low output impedance. ISFET's, which possess ion-selective membranes instead of the gate of a metal oxide field effect transistor (MOSFET), work on the same principle as that for MOSFET. The ion-selective membranes of ISFET's can be prepared by casting organic membranes containing proper ionophores on the gate surface (silicon nitride) of ISFET's. In the choice of ionophores some limitations are encountered with their lipophilicities and their solubilities in proper membrane matrices for ISFET's.

As Na^+-selective ionophores for ISE's, an acyclic triamide,[2,3] bis(12-crown-4) compounds,[4,5] disubstituted 16-crown-5 compounds,[6] a hemispherand,[7] and calix[4]arene tetraesters and tetraamides,[8-10] have been reported. However, only a few examples have been reported of good Na^+-ISFET's in terms of selectivity and durability because of the limitations mentioned above.[11]

In previous work, we have prepared derivatives of dibenzo-16-crown-5, such as *sym*-(R)dibenzo-16-crown-5-oxyacetic acid **1** (R = H or alkyl), in which an oxyacetic acid group ($-OCH_2CO_2H$) has been attached to the central carbon of the three-carbon bridge in the polyether ring. Such proton-ionizable lariat ethers[12] in their ionized forms are efficient and selective agents for the solvent extraction of alkali and alkaline-earth metal cations.[13,14]

We have also investigated the influence of non-ionizable side arms, such as $-OCH_2CO_2H$ (unionized), $-OCH_2CO_2C_2H_5$, and $-OCH_2C(O)N(C_nH_{2n+1})_2$ with n = 2-6, upon the complexation of alkali and alkaline-earth metal cations by lariat ethers in polymeric membrane ISE's.[15,16] Among these lariat ethers, the lariat ether amide N,N-dipentyl *sym*-(propyl)dibenzo-16-crown-5-oxyacetamide (**2**) was found to exhibit the greatest Na^+/K^+ selectivity.[16]

In the present study we have examined lipophilic lariat ether amides **2-4** (Figure 1) in terms of potentiometric selectivity for Na^+ in solvent polymeric membrane ISE's and have applied them to ISFET's.

RESULTS AND DISCUSSION

Potentiometric selectivities of lariat ether amides 2-4 in ISE's

Lariat ether amides **2-4** were incorporated into polymeric membranes with poly(vinyl chloride) (PVC) as the polymer matrix and *o*-nitrophenyl octyl ether (NPOE) as the membrane solvent. For the ISE's prepared from these membranes, potentiometric selectivities for Na^+ relative to other alkali and alkaline-earth metal cations and protons were determined by the fixed interference method.[17] Nernstian responses (59 mV decade^{-1}) to the change of Na^+ activity were observed for these solvent polymeric membrane electrodes. Selectivity coefficients

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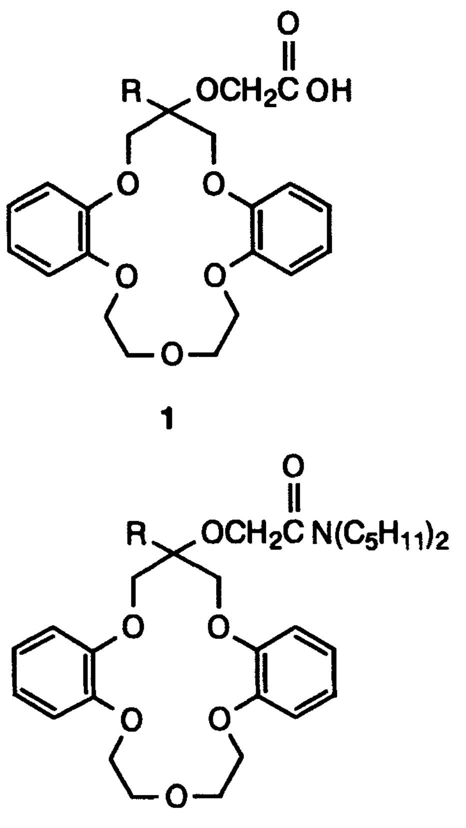

	R
2	$-C_3H_7$
3	$-C_8H_{17}$
4	$-C_{12}H_{25}$

Figure 1 Structures of lariat ether derivatives based upon dibenzo-16-crown-5.

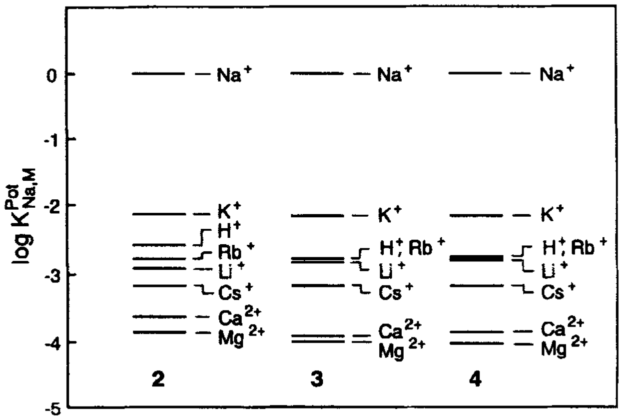

Figure 2 Selectivity coefficients (log $K_{Na,M}^{Pot}$) for ISE's based on lariat ether amides **2-4** for Na^+ over other alkali and alkaline-earth metal cations and H^+.

expressed as log $K_{Na,M}^{Pot}$ values for Na^+ are presented in Figure 2.

Lariat ether amides **2-4** possess a *geminal*-alkyl group at the central carbon of the three carbon bridge in dibenzo-16-crown-5 ring as well as an amide-containing side arm. The alkyl group variation includes propyl, octyl, and dodecyl groups. This structural variation produced no significant change in the Na^+ selectivities over other alkali metal cations (Li^+, K^+, Rb^+, and Cs^+). It is reported that the attachment of long alkyl group to disubstituted 16-crown-5 compounds produces marked diminution for the Na^+ selectivities.[6] However, in the present case enhanced lipophilicity does not diminish the Na^+ selectivity. For Na^+ selectivities relative to Ca^{2+}, Mg^{2+} and H^+, elongation of the *geminal*-alkyl group from propyl to octyl gives an increase in the Na^+ selectivities by 0.16-0.28 unit in the log $K_{Na,M}^{Pot}$ value. Further elongation from octyl to dodecyl produces no significant change in the Na^+ selectivities.

Potentiometric selectivities of lariat ether amides 2-4 in ISFET

Lariat ether amides **2-4** were incorporated into polymeric membranes which were placed on the gate surface of an ISFET. The gate surface was pre-coated by poly(vinyl butyral) (PVB) which is anticipated to serve as an adhesive between the gate surface and the PVC polymeric membranes. PVC polymeric membranes themselves have poor adhesion to the gate surface of ISFET's. It is reported that pre-coating of PVB on the gate surface improves adhesion properties of some bio-related materials, such as enzymes, to the gate surface.[18] PVB was found to also improve the adhesion between PVC membranes and the gate surface.

A typical response of the **4**-based ISFET to the change of Na^+ activity is shown in Figure 3. A Nernstian response or near Nernstian response was observed for the ISFET up to 3×10^{-5} M. A very rapid response time (within 2 seconds) was obtained for a 10-fold increase in Na^+ activity. For the **2**- and **3**-based ISFET's similar results were obtained.

For the ISFET's based on **2-4**, potentiometric selectivities for Na^+ relative to other alkali and alkaline-earth metal cations and H^+ were determined by the fixed interference method.[17] Selectivity coefficients expressed as log $K_{Na,M}^{Pot}$ values for Na^+ are presented in Figure 4. The Na^+ selectivities relative to other alkali and alkaline-earth metal cations for the ISFET's are almost equivalent to those for the ISE's shown in Figure 2. Excellent selectivity coefficients for Na^+ over K^+ ($K_{Na,M}^{Pot}$ = ca. 7×10^{-3}) were also obtained for these ISFET's. The Na^+/K^+ selectivity approaches the best values reported

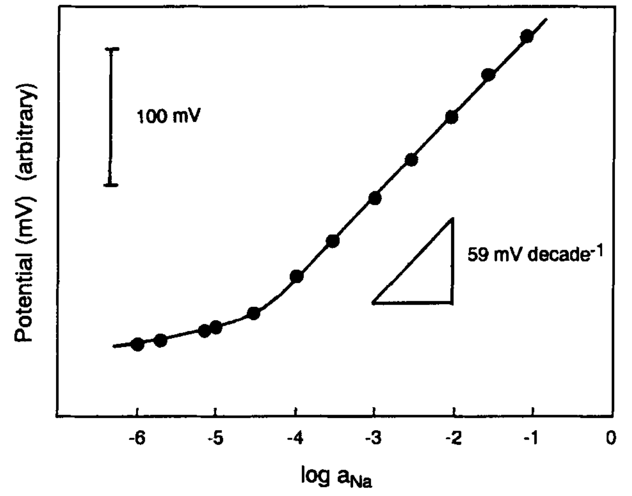

Figure 3 Response of the 4-based ISFET to the change of Na^+ activity.

for ISFET's which employ other neutral-carrier type ionophores.[11]

In analogy with the case of ISE's, ISFET's based on 3 and 4 are superior to the 2-based ISFET for the Na^+ selectivities over Mg^{2+}, Ca^{2+}, and H^+. ISFET's based on a calix[4]arene compound possess relatively poor Na^+/H^+ selectivities ($K_{Na,H}^{Pot} > 10^{-2}$) although they have excellent Na^+/K^+ selectivities. However, ISFET's based on lariat ether amides 3 and 4 have good Na^+/H^+ selectivities ($K_{Na,H}^{Pot}$ = ca. 3×10^{-3}) as well as good Na^+/K^+ selectivities.

As shown in Figure 4, when room temperature vulcanizing type (RTV) silicon rubber membranes were utilized, the Na^+/K^+ selectivities were somewhat decreased compared with the PVC-PVB membrane systems. ISFET's based on 3 with silicon rubber membranes show only slight diminution of their initial responses (slope and selectivity) after 100 days with measurement every six or seven days. In case of the 3-based ISFET with PVC-PVB membrane, some decrease in the Na^+/K^+ selectivity (0.1-0.2 unit in log $K_{Na,K}^{Pot}$ value) was observed after 50 days with measurement every six days.

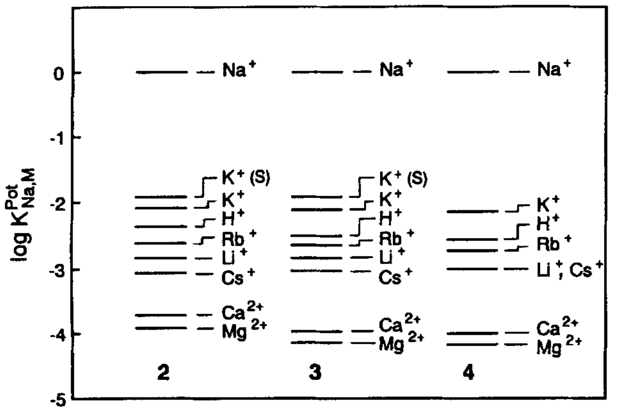

Figure 4 Selectivity coefficients (log $K_{Na,M}^{Pot}$) for ISFET's based on lariat ether amides 2-4 with PVC-PVB membranes for Na^+ over other alkali and alkaline-earth metal cations and H^+. K^+(S) means the log $K_{Na,K}^{Pot}$ value for ISFET's with a RTV silicone rubber membrane.

In conclusion, we have shown that dibenzo-16-crown-5 compounds with a N,N-dipentyl oxyacetamide group and a long-chain *geminal*-alkyl group attached to the central carbon of the three-carbon bridge are excellent ionophores for Na^+-ISFET, as well as for Na^+-ISE, in terms of the Na^+/K^+ and Na^+/H^+ selectivities and ISFET durability.

MATERIALS AND METHODS

Materials

PVC and PVB were purchased from Wako Pure Chemical Industries. NPOE and potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) were obtained from Dojindo Laboratories (Kumamoto, Japan). The RTV silicon rubber used was Shin-Etsu Silicon KE47T. Alkali and alkaline-earth metal chlorides and tetrahydrofuran (THF) were reagent-grade chemicals. Lariat ether amides 2-4 are known compounds.[16]

Preparation of ISE membranes and ISE measurements

ISE membranes were prepared from PVC, NPOE, the lariat ether amide, and KTpClPB in a similar manner to that described in our previous paper.[16] Potentiometric measurements with the ISE membranes were carried out at 24-25°C with a voltage meter (Denki Kagaku Keiki (DKK) PHL-40 pH meter), a double junction Ag-AgCl reference electrode (DKK number 4083), and a magnetic stirrer to agitate the sample solution. The electrode cell was Ag-AgCl/0.10 M NaCl/PVC membrane/sample solution/0.10 M NH_4N O_3/3.0 M KCl/Ag-AgCl. Single ion activities were obtained as described in our previous paper.[15]

The selectivity coefficients ($K_{Na,M}^{Pot}$) were determined by the fixed interference method.[17] The background concentrations of interfering ions were $5.0 \leq 10^{-2}$ M for K^+, 1.0×10^{-1} M for other alkali metal ions and H^+, 1.0 M for Mg^{2+}, and 5.0×10^{-1} M for Ca^{2+}. For a given polymeric membrane system, the potentiometric selectivity was determined twice for each of two independently prepared membranes. The average value for the potentiometric selectivity was calculated from the values obtained for the four measurements.

ISFET fabrications

ISFET tips which have a gate size of 10×370 μm were supplied by Shindengen Electric. An aliquot (2 μL) of a dichloromethane solution of PVB (10 mg mL^{-1}) was placed on the gate surface of an ISFET tip and the tip was allowed to stand for 8 hours at room temperature. An aliquot (2 μL) of a THF solution (500 μL) containing PVC (15 mg), NPOE (30 mg), and the lariat ether amide (5 mg) was then placed on the gate surface and the resulting tip was dried at room temperature overnight. The ISFET tip was conditioned by soaking in a 0.10 M NaCl solution of 24 hours before use.

In case of silicone rubber membrane-coated ISFET's, a chloroform solution (500 μL) containing a lariat ether amide (5 mg) and a RTV silicon rubber (45 mg) was used as a coating solution.

ISFET measurements

Measurements with a coated ISFET tip were carried out at 24-25°C with an ISFET pH/mV meter (Shindengen Electric) and a DKK number 4083 reference electrode with 3.0 M KCl internal solution and 0.10 M NH_4NO_3 external solution. The selectivity coefficients ($K_{Na,M}^{Pot}$) were determined in a similar manner to that described in the ISE measurements. For a given ISFET tip system, the selectivity was determined twice for each of two independently prepared tips. The average value for the selectivity was calculated from the values obtained for the four measurements.

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