

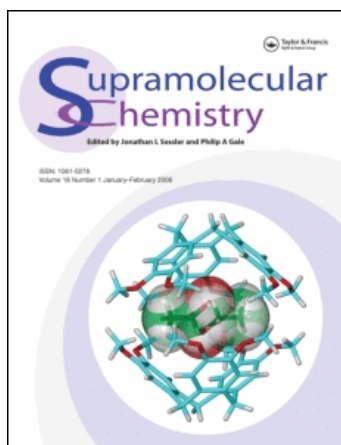
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Anomalous potential response of sodium ion-sensing membrane containing a proton-dissociable calix[4]arene ionophore

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Ion-selective electrodes of plasticized-poly(vinyl chloride) membranes containing a proton-dissociable calix[4]arene ionophore, which carries three ethyl-ester groups and a carboxylic group at the lower rim, show super-Nernstian response to Na^+ activity changes in the high activity ranges under weakly-acidic and neutral-pH conditions. It is proposed that the anomalous potential response is due to enhanced cation complexation by the calixarene ionophore, which is in turn induced by intramolecular interaction of the hydroxyl part of the carboxylic group and Na^+ captured by the ionophoric cavity in the calixarene complex.

INTRODUCTION

Calix[4]arene derivatives incorporating carbonyl bonds such as ester and amide linkages are generally Na^+ ionophores, on which considerable attention has been so far focused as neutral carriers for Na^+ -sensing membranes of ion-selective electrodes. (1–10) We have also been engaged in applications of calix[4]arene neutral carriers to Na^+ sensors, especially in designing calixarene neutral carriers to improve their performance, such as selectivity, durability, and applicability, of calixarene-based Na^+ sensors using plasticized poly(vinyl chloride) (PVC) and silicone rubber (11, 12) as the membrane support. In the course of the study, we have got interested in behavior of a proton-dissociable calix[4]arene ionophore, calix[4]arene tris(ethyl ester)-monoacid **1**, as the ionophore for PVC membrane Na^+ -selective electrodes. It is very intriguing to check if such proton-dissociable calixarene ionophore works as “neutral carrier”.

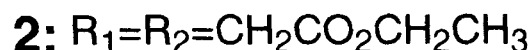
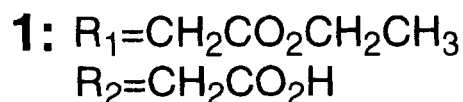
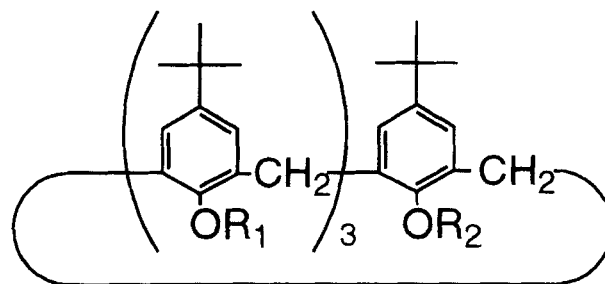
Here we wish to describe anomalous emf response in Na^+ -sensing membranes based on the proton-dissociable calixarene ionophore, **1**, and to compare with that based

on electrically neutral calixarene ionophore **2**, which is a most popular Na^+ neutral carrier.

EXPERIMENTAL

Materials.

The preparation of calix[4]arene tris(ethyl ester)-monoacid **1** (**13**) and calix[4]arene tetraethyl ester **2** (**14**) was made according to a procedure described in the literature. The Na^+ complex of proton-dissociated **1** was prepared by Na^+ extraction from a NaOH aqueous solution to a chloroform solution of **1**. PVC with an average polymerization degree of 1100 was purified by reprecipitation from tetrahydrofuran (THF) in methanol. 2-Ethylhexyl sebacate (DOS) was purified by vacuum distillation. Phenoxyacetic acid was used as received. THF was distilled over Na metal. Alkali and alkaline-earth metal chlorides and ammonium chloride were of



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analytical reagent grade. Water was deionized. The pH values were adjusted with HCl and LiOH aqueous solutions. Any special buffer solution was not used to avoid severe interference by the buffers. The sample solutions for pH 1.3, about pH 5.8, about pH 8.4, and pH 10.3 contained 1×10^{-1} mol dm⁻³ HCl, 1×10^{-5} mol dm⁻³ LiOH, 1×10^{-3} mol dm⁻³ LiOH, and 1×10^{-2} mol dm⁻³ LiOH as the background.

Electrode Fabrication.

The general procedure for casting ion-sensing membranes is as follows: PVC membranes were prepared by casting from a solution consisting of PVC (50 mg), DOS (100 mg), neutral carrier (10 mg), and tetrahydrofuran (2 cm³) on a flat Petri dish of 20 mm inner diameter. A disk of 7 mm diameter was cut from the membrane with a cork borer and was then incorporated into an electrode body (Philips IS-561 type). The internal filling solution was 1×10^{-3} mol dm⁻³ NaCl aqueous solution. Conditioning of the electrodes thus resulted was made by soaking in the NaCl solution overnight.

Measurements

Potential measurements were made at room temperature using a pH/mV meter (TOKO TP-1000). The reference electrode was a double-junction-type Ag/AgCl electrode with 3 mol dm⁻³ KCl internal solution and 1 mol dm⁻³ CH₃CO₂Li external solution. The electrochemical cell was Ag·AgCl/ 1×10^{-3} mol dm⁻³ NaCl/PVC membrane/sample solution/1 mol dm⁻³ CH₃CO₂Li/3 mol dm⁻³ KCl/AgCl·Ag. The measuring cation concentrations were changed by injection of high-concentration solutions to the testing solutions while stirring with a magnetic stir bar.

The membrane electrical resistivity was measured by ac impedance method, using a U-type cell and a frequency response analyzer and a current amplifier. In the measurement cell, an ion-sensing membrane with 1-cm² area separated two aqueous phases with an identical Na⁺ concentration, in which a pair of spiral Ag-AgCl electrodes of about 1-cm² area were placed. The PVC membranes for ac impedance measurements were prepared in the same way as for the ion-selective electrodes. A disk of 15 mm diameter was cut from the membrane and then conditioned by soaking in a 1×10^{-6} mol dm⁻³ Na⁺ solution overnight before setting in the measurement cell. The frequency range and applied ac voltage were 3000–0.1 Hz and 1 V, respectively. The electrical resistivity was calculated by Cole-Cole plots.

FT-IR spectroscopy was performed by reflection mode. The membranes were conditioned in 1×10^{-1} mol dm⁻³ Na⁺ aqueous solutions of different pH values overnight.

²³Na-NMR spectra were taken in THF-d₆/THF(1/9) at room temperature. The sample was an equimolar mixture

(2×10^{-2} mol dm⁻³ each) of NaClO₄ and **1** (or **2**) and 2×10^{-2} mol dm⁻³ Na⁺ salt of proton-dissociated **1**. The external standard was a 20 mmol dm⁻³ NaClO₄ D₂O solution.

RESULTS AND DISCUSSION

Potential Response Profile

Typical emf response to Na⁺ activity changes for a plasticized-PVC membrane ion-selective electrode based on calixarene monoacid **1** is shown in Figure 1, together with an electrode based on calixarene tetraester **2**. Both of the electrodes exhibit very similar emf response in the lower Na⁺ activity range, the slopes for calibration plots in the activity range of 10^{-5} – 10^{-2} mol dm⁻³ being Nernstian. It should be noted that the electrode based on **1** responds to Na⁺ activity changes with super-Nernstian slope in the Na⁺ activities of higher than 10^{-2} mol dm⁻³. The electrode of **2** still shows a Nernstian response even in such high Na⁺ activities. Only difference in the chemical structure between the active materials for the ion-sensing membranes, **1** and **2**, is the existence of a carboxylic group instead of the ethyl ester in compound **1**. Acid dissociation and/or participation of the carboxylic group in the cation complexation might, therefore, have some relation with the anomalous potential response for calixarene ionophore **1**. Figure 2 demonstrates pH dependence of emf response for the ion electrode based on **1**. At very low pH, where the carboxylic group

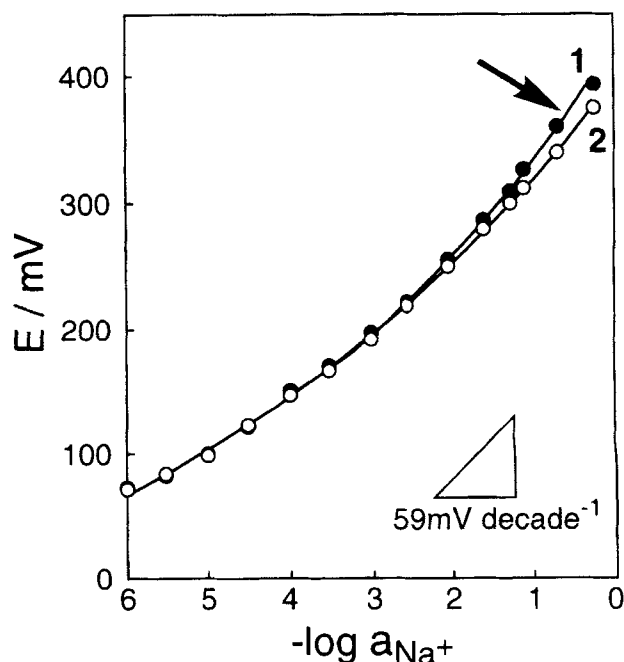


Figure 1 Typical potential response profiles for PVC membrane electrodes based on calixarene monoacid **1** (●) and calixarene tetraester **2** (○) under neutral pH conditions.

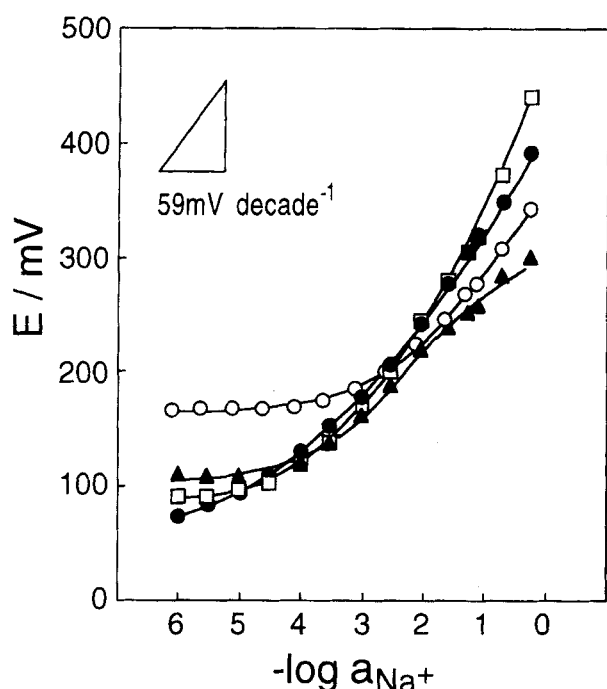


Figure 2 pH dependence of potential response for PVC membrane electrodes based on calixarene monoacid **1** (○) pH 1.3; (●) pH 5.8; (□) pH 8.4; (▲) pH 10.3.

hardly proton-dissociate, Nernstian response was observed even in the high Na^+ activity ranges ($>10^{-2} \text{ mol dm}^{-3}$), although H^+ interferes with Na^+ response severely. On raising the pH to 5.8 and then to 8.4, super-Nernstian response was found in the high Na^+ activity. The super-Nernstian response was more remarkable at pH 8.4 than at pH 5.8. At pH 10.3, on the other hand, the electrode response turned out to be significantly sub-Nernstian. This suggests that calixarene monoacid, **1**, works as a neutral carrier of Na^+ in a similar way to the calixarene tetraester **2**, when it is very hard to dissociate a proton under acidic conditions like pH 1.3. On the contrary, the calixarene monoacid proton-dissociates to a great extent at pH 10.3, taking into account the pK_a values (10.0 in methanol (13)). FT-IR spectroscopy of the PVC membranes based on calixarene monoacid **1** after treatment by Na^+ solution of various pH shows the degree of the proton dissociation of **1** in membrane (Figure 3). Weak and strong absorptions (around 1600 and 1400 cm^{-1}) assigned to COO^- vibration were observed at pH 9.3 and >12 , respectively, indicating that the proton dissociation occurs abruptly at the higher pH than 9 even in the membranes. The resulted anion formation cancels out the charge separation induced by Na^+ complexation of the calixarene ionophoric cavity, thus suppressing the Nernstian response to Na^+ activity changes.

What then happens in the Na^+ complexation by calixarene monoacid **1** in the medium pH ranges causing

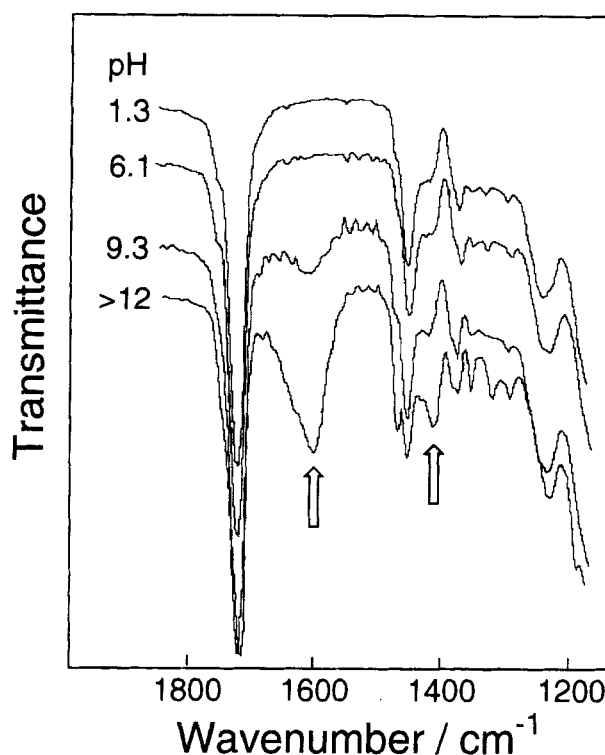


Figure 3 IR spectra for PVC membranes based on calixarene monoacid **1** after treatment by Na^+ aqueous solutions with different pH.

the super-Nernstian electrode response? A possibility is participation of the carboxylic group in Na^+ complexation of the calixarene ionophoric cavity in **1**. If this is the case, mixtures of electrically neutral calixarene **2** and phenoxyacetic acid might behave in a similar way to calixarene monoacid **1**, as active materials of the ion-sensing membranes. Addition of phenoxyacetic acid to calixarene tetraester **2**, however, did not modify the electrode potential response profile for **2** itself, as shown in Figure 4. Also, variation of pH conditions for Na^+ -measuring solutions (from pH 1.3–10.3) hardly brought about any significant difference in the potential response profile. These results clearly deny the intermolecular participation of the free or proton-dissociated carboxylic acid (phenoxyacetic acid) in the cation complexation and ion exchange of **2**.

Intramolecular Interaction of Complexed Na^+ with a Carboxylic Group

The other plausible origin for the super-Nernstian response of the PVC membrane electrode based on calixarene monoacid **1** is intramolecular participation of its carboxylic group in the Na^+ complexation of the calixarene ionophoric cavity.

In order to obtain some information about the cation complexation of calixarene ionophores at the surface of the ion-sensing membranes, electrical resistivity for

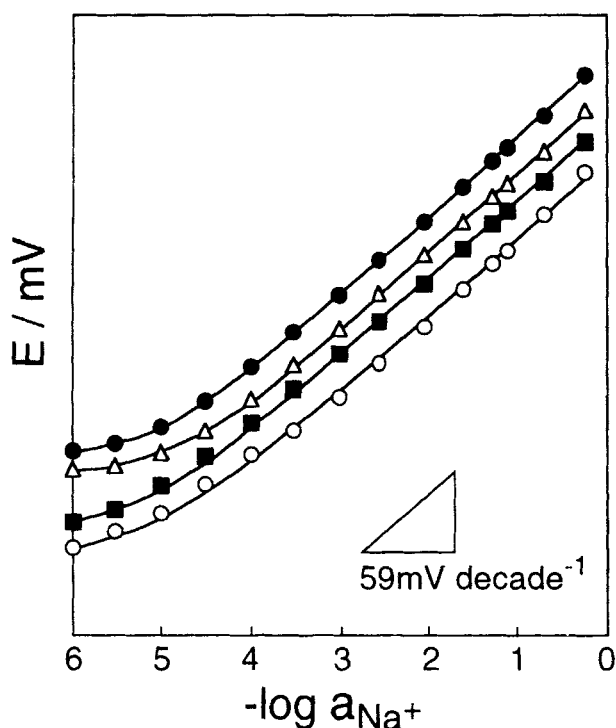


Figure 4 Effect of addition of phenoxyacetic acid (PA) to PVC membranes based on calixarene tetraester **2**. Ratio in weight of PA and **2** (constant weight): (O) without PA; (■) 1/1; (Δ) 3/1; (●) 7/1.

plasticized-PVC membranes based on calixarene ionophores **1** and **2** was measured in Na^+ aqueous solutions with various concentrations under neutral pH conditions, by using ac impedance method (Figure 5). In general, the electrical resistivity is higher in the membrane of calixarene monoacid **1** than in that of calixarene tetraester **2**. This implies the lower Na^+ -exchanging ability for **1** than for **2**. It is worth noting that the membrane resistivity for the **1** system depends considerably on the Na^+ concentrations, while that for the **2** system does not very much. Specifically in high Na^+ concentration ranges, the **1** membrane exhibited a steep decrease in the electrical resistivity. This anomalous decrease in the electrical resistivity means effective Na^+ -exchange by calixarene monoacid **1** at the interface between the membrane and aqueous phases. The effective Na^+ complexation of **1** at the high Na^+ concentration ranges, in turn, may be related to the super-Nernstian response of the **1**-containing membrane. ^{23}Na -NMR spectroscopy may give good information about Na^+ complexes. Figure 6 shows a comparison of ^{23}Na -NMR spectra for Na^+ complexes of **1**, **2**, and Na^+ salts of proton-dissociated **1**. The **1** system is quite similar in the NMR spectrum to the **2** system, which suggests that Na^+ can be accommodated in the calixarene ionophoric cavity in both the systems of **1** and **2**. The significant peak shift to the higher frequency for Na^+ salts of proton-dissociated **1** is probably attributed to intramolecular ion-pair formation of the

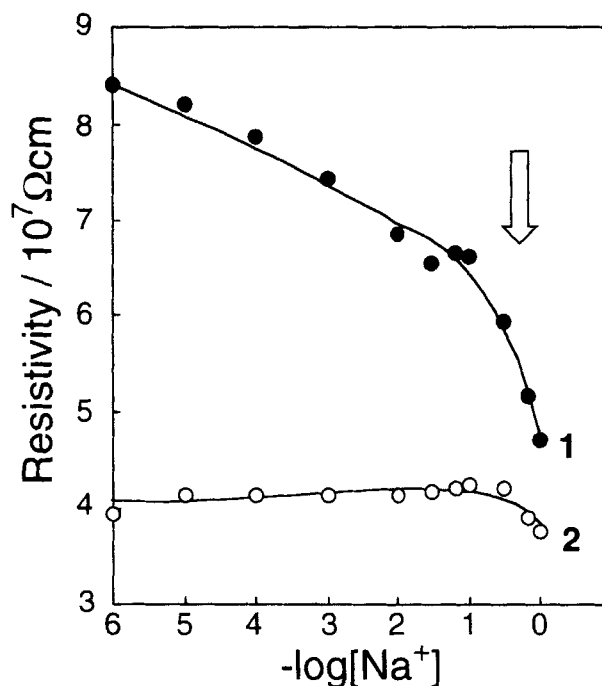


Figure 5 Electrical resistivity for PVC membranes based on calixarene monoacid **1** (●) and calixarene tetraester **2** (○) in Na^+ aqueous solutions.

resulted carboxylic anion and Na^+ complexed by the calixarene ionophoric cavity. Definitely, two different types of Na^+ complexes of calix[4]arene monoacid **1** are

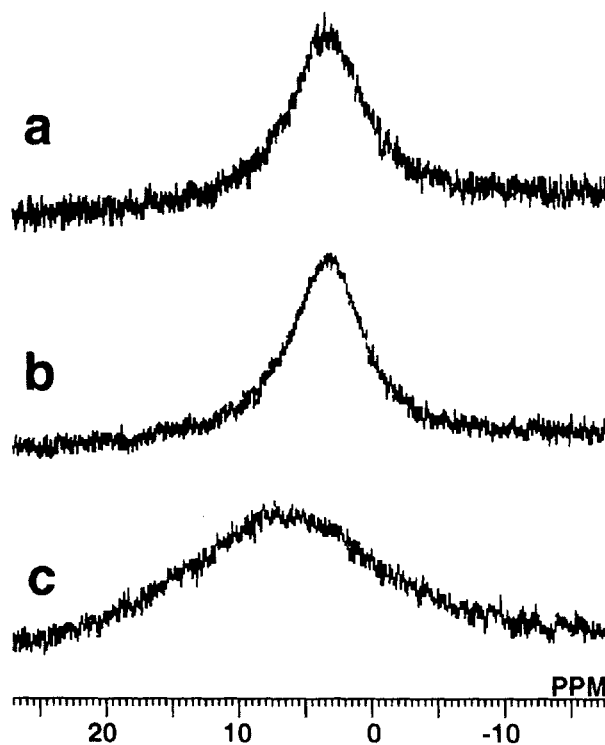
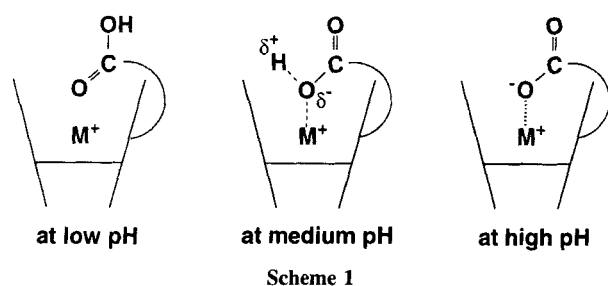


Figure 6 ^{23}Na -NMR spectra for $\text{Na}^+/\mathbf{1}$ (1/1) (a), $\text{Na}^+/\mathbf{2}$ (1/1) (b), and Na^+ salt of proton-dissociated **1** (c) in THF.



formed in the membrane phase under the low and high pH conditions of Na^+ aqueous phases, as schematically illustrated in Scheme I. Under low pH conditions (like pH 1.3), the hydroxyl part of the carboxylic group in **1** that remains proton-undissociated hardly takes part in Na^+ complexation, although the carbonyl probably contributes to the Na^+ complexation. In that case, calixarene monoacid **1** works as a neutral carrier, as is the case with calixarene tetraester **2**, the Na^+ -sensing membrane of **1**, therefore, exhibiting Nernstian response to Na^+ activity changes. Under high pH conditions (like pH 10.3), the carboxylic anion ion-pairs with Na^+ in the calixarene ionophoric cavity, depressing the emf response to Na^+ . What type of **1**– Na^+ complexes is then formed under medium pH conditions? Although the carboxylic group of **1** is still not easy to dissociate a proton under medium pH conditions, the OH moiety of carboxylic group may be polarized more than under low pH conditions. A plausible **1**– Na^+ complex formed under medium pH conditions is in the middle of Scheme I. The negatively polarized oxygen atom interacts intramolecularly with Na^+ complexed by the calixarene ionophoric cavity, thus promoting the Na^+ -complexing ability of **1**. Possibly, the polarization of the OH moiety and thereby Na^+ -complexation enhancement are stressed in the high Na^+ activity ranges, that is, under the more polar circumstance, which thus affords the super-Nernstian response to Na^+ activity changes of the **1**–containing membranes.

In conclusion, plasticized-PVC membrane electrodes based on calix[4]arene monoacid **1** respond to Na^+ activity changes in a super-Nernstian way in the high

activity ranges, unlike the electrodes based on calix[4]arene tetraester **2**. We propose that the anomaly in the potential response by the electrodes of **1** is ascribable to the intramolecular participation of polarized OH moiety of the carboxylic group in the Na^+ complexation, especially in the high Na^+ activity range.

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