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Tunable chemical sensors: light-switched ion selective electrodes on the basis of a photoresponsive calix[4]arene

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Keywords: Ion Selective Electrode, Host-Guest Interaction, Supramolecule, Calixarene, Anthracene, Photodevice.

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Immobilization of a novel photoresponsive ionophoric calix[4]arene (1) in plasticized poly(vinyl chloride) membranes provided new Switch-functionalized Ion Selective Electrodes (SISEs). In comparison with the conventional ion selective electrodes technique, one significant advantage was obtained that the SISEs method can reversibly regulate the selectivity from one target ion to other ions by external light irradiation. Ion selectivity studies demonstrated that the electrodes using ligand 1 plasticized with tris(2-ethylhexyl) phosphate or di(2-ethylhexyl) phthalate showed affinity for Li^+ ion or Cs^+ ion, respectively, against other alkali and alkaline earth metal ions in the dark whereas the excellent Na^+ ion selectivity appeared upon 365 nm irradiation. This is *a new methodology to assign one electrode to detect two metal ions.*

INTRODUCTION

The determination of different ions by using potentiometric analysis with Ion Selective Electrodes (ISEs) has been well documented and demonstrated over the past 30 years.[1-3] The ISEs technique has become a major and essential analytical method to determine the concentrations of ions such as H^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, etc. in biological fluids such as whole blood, plasma, serum, and urine in clinical laboratories. It has also found extensive applications in food analysis, environmental control, and industry products analysis. More recently, sensors for biomolecules have also been developed on the basis of ISEs.

ISEs are frequently termed as Na^+-selective electrodes, K^+-selective electrodes, or Cs^+-selective electrodes. Namely, such type of electrodes can selectively determine only one specific ion through specific ion binding in a sample solution. It is difficult or almost impossible to determine the concentrations of several target ions simultaneously by using one working electrode system. This seems a inherent drawback of the present ISEs technique. In order to simultaneously determine the concentrations of several target ions, multielectrodes are necessary. For instance, to determine the concentrations of the Na^+ and Cs^+ ions, or Na^+ and Li^+ ions in the same sample solution, at least two working electrodes are necessary: one is a Na^+-selective electrode and another is a Cs^+-selective or Li^+-selective electrode. Consequently, the electrode scale will increase and the measurement system becomes more complicate to fabricate the detector equipment. This is a serious limitation particularly for the development of microelectrode systems.

In an attempt to overcome the shortcoming of the conventional ISEs technique, we here introduce the first approach to the design and construction of the novel tunable ion selective electrodes which allow the selective discrimination of several target ions in one sample solution. Our strategy can be outlined briefly as follows: in essence, the observed ion selectivity of ISEs is based on the specific binding between the target ion and the ligand incorporated within the matrix membrane. Hence in principle, if the chemical composition of the ligand species could be modulated in a reversible nondestructive manner upon certain external disturbance such as light or electrical signals, as a consequence, the resulting ion selectivity should be regulated in a similar way.

It is well known that many chemical species undergo reversible interconversions and the stationary states can be shifted photochemically or electrochemically. Such processes have been extensively investigated and reviewed especially from the viewpoint of supramolecular chemistry.[4-6] Thus, the problem left here would

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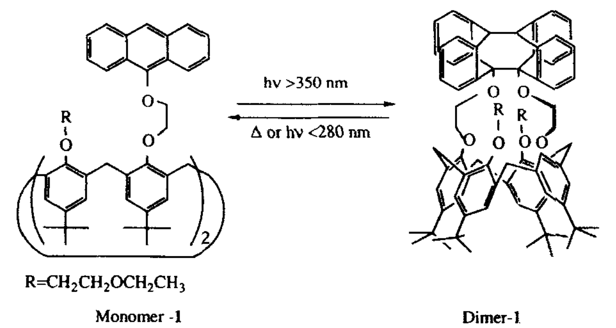


Scheme 1 Structure of bianthracene incorporated in calix[4]arene neutral ligand 1.

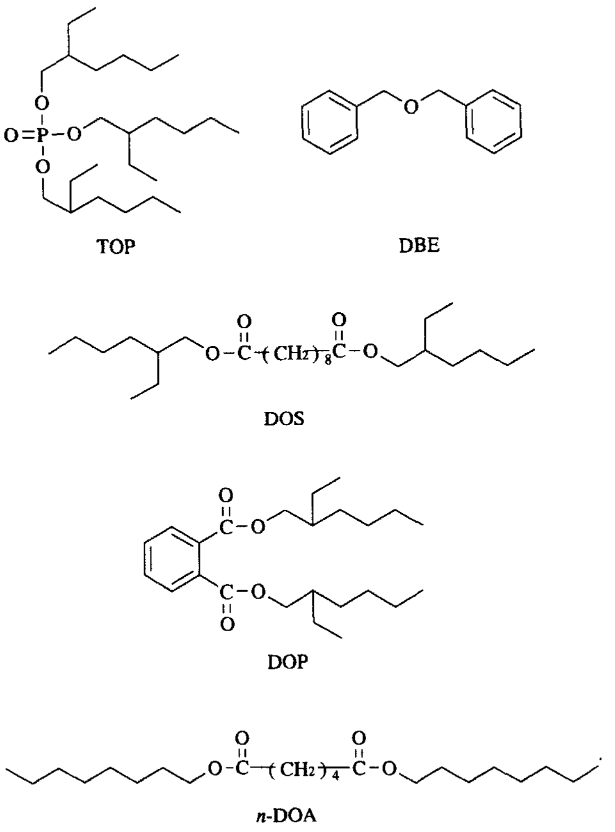
be to search some appropriate method by which outside stimuli are efficiently transduced to the metal-binding site. Fortunately, we have already found that this requirement can be satisfied by a photoresponsive host-guest system derived from bianthracene incorporated into calix[4]arene (Scheme 1).[7,8] Upon 365 nm irradiation monomer-**1** is readily converted to dimer-**1** and the reverse splitting process occurs thermally or photochemically.[9] Two-phases solvent extraction experiments have confirmed that monomer-**1** and dimer-**1** show the different binding ability toward common alkali metal ions.[7] In principle, therefore, the combination of the concepts of electrochemistry and photoresponsive supramolecules might afford the possibility to design and construct the novel light-switched ion selective electrodes for the simultaneous determination of several target ions. As far as we know, no tunable ion selective electrodes have ever been designed according to these concepts.

EXPERIMENTAL

Materials and reagents

All chemicals used for electrolyte solutions (LiCl, NaCl, KCl, RbCl, CsCl, NH_4Cl, $MgCl_2$, $CaCl_2$, and $BaCl_2$) were of analytical-reagent grade form and the solutions were prepared in deionized water. The membrane materials including the plasticizer (Scheme 2) [tris(2-ethylhexyl) phosphate (TOP), dibenzyl ether (DBE), di(2-ethylhexyl) sebacate (DOS), di(2-ethylhexyl) phthalate (DOP), di(2-*n*-octyl) adipate (*n*-DOA)], the lipophilic additive [potassium tetra-bis-*p*-chlorophenyl borate (KTpClPB)], poly(vinyl chloride) (PVC, n = 1100), and 1,2-dichloroethane were supplied by Tokyo Kasei Corp. of the highest purity available.

Details of the synthesis of the calix[4]arene ionophoric ligand **1** can be found in our previous paper.[8]



Scheme 2 Structures of the plasticizers.

Preparation of PVC membranes

The general procedure for the preparation of the polymeric membrane is as follows: PVC (50 mg), the plasticizer (100 mg), KTpClPB (1 mg), and the calix[4]arene ionophore (5 mg) were mixed and dissolved in 1,2-dichloroethane (3 mL). The resulting solution was poured into a Petri dish (diameter 3.0 cm) and the solvent was evaporated at room temperature (3 days) under N_2 in the dark to give an elastic and transparent membrane of *ca* 0.15 mm thickness.

Construction of photoswitched ion selective electrodes

A disk of 8 mm diameter was cut out from the PVC membrane and incorporated into one side of an electrode body of PVC tube (outer diameter 8 mm; inner diameter 4 mm, and height 6 cm). The tube was filled with 1×10^{-3} mol dm^{-3} of sodium chloride solution and the Ag/AgCl (5 cm × 3 mm) plate was inserted as a working electrode. The external reference electrode is a saturated Ag/AgCl electrode dipped in a saturated KCl solution with a 1×10^{-1} mol dm^{-3} lithium acetate electrolyte bridge. The both electrodes were connected to an electrometer (Advantest Co. R-8240). The composition of the electrochemical cell is as follows: Ag/AgCl | aq. NaCl (1×10^{-3} mol

dm^{-3}) | photoresponsive PVC membrane | measured solution | aq. lithium acetate (1×10^{-1} mol dm^{-3})| KCl (saturated) | Ag/AgCl.

Measurements of membrane potentials

All measurements were carried out at 25 °C in the dark or after 15 min direct irradiation with a high pressure mercury lamp equipped with a Toshiba UV35 cut-off filter. To determine the response slope of the electrodes, potentials were measured in six standard solutions of metal chloride over the range of 1×10^{-1} mol dm^{-3} to 1×10^{-6} mol dm^{-3}. Selectivity coefficients $\log K^{\mathrm{pot}}_{\mathrm{Na,M}}$ were calculated from the following expression (Eq 1)[1-3] by the separate-solutions method using the solutions of 1×10^{-1} mol dm^{-3} chloride salts of the cations involved,

$$\log K^{\mathrm{pot}}_{\mathrm{Na,M}} = Z_i F(E_j - E_i)/2.303RT - Z_i/Z_j \log a_i + \log a_j \qquad (1)$$

where $\log K^{\mathrm{pot}}_{\mathrm{Na,M}}$ is the selectivity coefficient relative to Na^+ ion, a_i and a_j are the activities of the primary ion (Na^+) and the interferring ions, E_i and E_j are the measured potentials of the primary ion and the interferring ions at equal activity (1×10^{-1} mol dm^{-3}) respectively, R is the gas constant, T is the absolute temperature, Z_i and Z_j are the charge on the primary or interferring ions, and F is the Faraday constant.

The potentials of monomer-**1** were measured according to the ordinary method. The values of dimer-**1** were determined as soon as possible after photoirradiation. In most cases the measurements were carried out within two minutes for one ion series. In this period of time the thermal splitting of dimer-**1** is negligible.

RESULTS AND DISCUSSION

Principle

"One ligand responds to one specific target ion"—this is the basic principle of ISEs. We now extend this concept to the electrodes incorporating interchangeable chemical species as the ligands into the matrix membrane. This can be established by the utilization of the well-known stationary state shifting principle. The general mechanism can be understood as below: at the stationary state species **A** can be reversibly converted to new species **B** (Eq 2) by various external factors. Because of the different intrinsic chemical characteristics of **A** and **B**, which here can be defined as the metal ion binding ability, the stationary state shift should induce the change in the ion selectivity at the electrode.

$$\mathbf{A} \xrightleftharpoons{\text{Light or electrical signals}} \mathbf{B} \qquad (2)$$

For simplicity, the most convenient way is to use a light signal as the control force. The photoresponsive unit chosen here is the well-known photodimerization of anthracene.[5] The photoresponsive ionophoric cavity is constructed on the calix[4]arene skeleton which serves as an excellent platform for the Na^+-binding.[7,8,10-15] Synthetic methods of calixarene derivatives have been well established by several groups, and the metal ion recognition behaviors have also been extensively studied.[16] The results show that calix[4]arenes usually exhibit a notable affinity for Na^+. These molecules form a polar cavity with optimum dimensions for Na^+ complexation and display excellent selectivity against other alkali and alkaline earth metal ions either in solvent extraction or in plasticized membrane electrodes (ISEs).[7,8,10-19]

Here, we introduce a unique one working electrode system in which the selectivity can be switched reversibly from Li^+ to Na^+ or from Cs^+ to Na^+ by photoirradiation. Our interest in these three ions is also related to the production of radioactive cesium during nuclear processes and the possible use of lithium as a fusion fuel in nuclear industry.

Photoswitched ion selectivity

In the experiments, we found that in general the electrochemical performance characteristics of the SISEs with ligand **1** are comparable to the ordinary ISEs. For example, the Nernstian or near-Nernstian responses were observed in the metal chloride concentration range of 1×10^{-1} to 1×10^{-4} mol dm^{-3}. The Nernstian slope values calculated are in the range of 50 to 62 mV decade^{-1}. The response speed of the electrode was excellent: it took only 5 to 10 seconds to reach the stationary voltage. At the same time, the SISEs also displayed several promising properties superior to the conventional ISEs. First, as we have expected, the photoswitching of the selectivity from one target ion to other target ions was successfully achieved. The selectivity coefficients relative to Na^+ ($\log K^{\mathrm{pot}}_{\mathrm{Na,M}}$) summarized in Table 1 indicate that the electrode plasticized with tris(2-ethylhexyl) phosphate (TOP) showed Li^+ preference in the dark with the affinity decreasing in the order of $\mathrm{Li}^+(1.82) > \mathrm{NH}_4^+(0.83) > \mathrm{Na}^+(0.00) > \mathrm{K}^+(-0.32) > \mathrm{Rb}^+(-0.53) > \mathrm{Cs}^+(-0.59)$. On the other hand the excellent Na^+ selectivity was obtained after 15 min irradiation at 365 nm (under these conditions 81% of monomer-**1** was converted to dimer-**1**):[8] the selectivity coefficients ($\log K^{\mathrm{pot}}_{\mathrm{Na,M}}$) were in a pattern of $\mathrm{Na}^+(0.00) > \mathrm{K}^+(-3.06) > \mathrm{Li}^+(-4.02) = \mathrm{NH}_4^+(-4.02) > \mathrm{Rb}^+(-4.37) > \mathrm{Cs}^+(-5.20)$. The reversion of the Li^+–Na^+ couple ions selectivity can be more clearly illustrated in Figure 1. In the dark,

Table 1 Selective coefficients (log $K^{pot}_{Na,M}$) for the electrodes based on the photoresponsive calix[4]arene. Values obtained by the separate solution method in 1×10^{-1} mol dm^{-3} solutions of each metal ion (all chlorides) at 25 °C.

Plasticizer		Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Mg^{++}	Ca^{++}	Ba^{++}
TOP	dark	1.82	0.00	−0.32	−0.53	−0.59	0.83	−1.11	−0.87	−1.20
	light	−4.02	0.00	−3.06	−4.37	−5.20	−4.02	−4.02	−3.50	−4.20
DOP	dark	0.07	0.00	1.34	1.45	1.78	0.73	−1.09	−0.79	−0.38
	light	−6.58	0.00	−1.61	−2.56	−3.56	−6.54	−6.27	−5.57	−5.18
DOS	dark	−0.82	0.00	0.61	0.62	0.83	—	—	—	—
	light	−2.75	0.00	−1.25	−1.75	−1.86	—	—	—	—
n-DOA	dark	−0.49	0.00	0.10	0.85	0.07	−0.25	−1.93	−1.42	−1.18
	light	−0.53	0.00	0.17	−0.17	−0.32	−0.46	−0.51	−0.31	−0.14
DBE	dark	−1.22	0.00	−0.37	−0.58	−0.27	−0.39	−3.04	−2.93	−3.13
	light	−0.19	0.00	−0.69	−0.95	−0.90	−0.37	−0.14	−0.03	−0.20

[a] Ligand 1: 5 mg; light: irradiated at 365 nm for 15 min at 25 °C.

[b] TOP: tris(2-ethylhexyl) phosphate; DOP: di(2-ethylhexyl) phthalate; DOS: di(2-ethylhexyl) sebacate; *n*-DOA: di(*n*-octyl) adipate; DBE: dibenzyl ether.

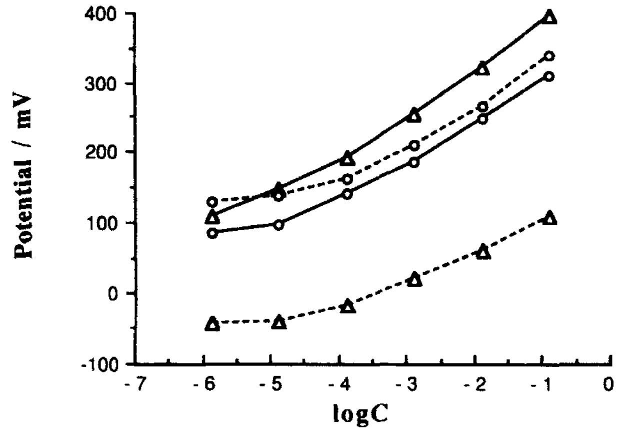


Figure 1 Response of the PVC membrane plasticized with TOP to Na$^+$ (○) and Li$^+$ (△) chloride solutions before (—) and after (---) 15 min irradiation at 365 nm.

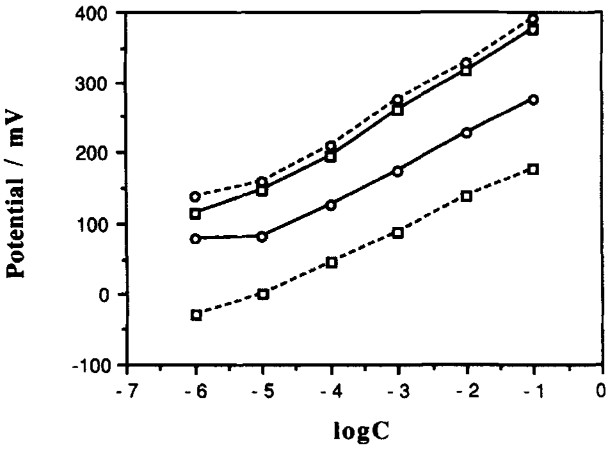


Figure 2 Response of the PVC membrane plasticized with DOP to Na$^+$ (○) and Cs$^+$ (□) chloride solutions before (—) and after (---) 15 min irradiation at 365 nm.

the response to Li$^+$ ion is the top curve, but it turns down to the bottom one after irradiation. At the metal chloride concentration of 1×10^{-1} mol dm^{-3}, the observed potential difference ($E_{Li^+} - E_{Na^+}$) changed from +107 mV in the dark to −237 mV after irradiation, indicating the reverse of the ion affinity from Li$^+$ to Na$^+$ and the increasing in Na$^+$ selectivity.

With another plasticizer di(2-ethylhexyl) phthalate (DOP), Cs$^+$–Na$^+$ couple ions selectivity turnover behavior was also achieved. As shown in Figure 2 and Table 1, the selectivity for Na$^+$ ion was increased after irradiation and the selectivity for Cs$^+$ was decreased greatly at the same time. The value of ($E_{Cs^+} - E_{Na^+}$) at the salt concentration of 1×10^{-1} mol dm^{-3} shifted from +175 mV to −210 mV. The log $K^{pot}_{Na,M}$ order in the dark is Cs$^+$(1.78) > Rb$^+$(1.45) > K$^+$(1.34) > NH$_4^+$(0.73) > Li$^+$(0.07) > Na$^+$(0.00). In sharp contrast, it changed to Na$^+$(0.00) > K$^+$(−1.61) > Rb$^+$ (−2.56) > Cs$^+$(−3.56) > NH$_4^+$(−6.54) > Li$^+$(−6.58) upon of 365 nm light.

Examination of Table 1 reveals another important result: unusually high Na$^+$ ion selectivity was obtained after photoirradiation with most of the plasticizers tested in our experiment. For example, with plasticizer TOP, the selectivity coefficient values for Na$^+$ respect to other alkali metal cations or alkaline earth metal ions are in the range of −3.06 to −5.20. This is one of the best results currently obtained from neutral carrier type ISEs.[20] These results demonstrate that this is a novel and promising way to obtain high ion selectivity with the specific metal ion complexing species produced by photoreaction.

The remarkable increase in the Na$^+$ selectivity can be understood by the formation of a rigid, highly preorganized cavity in dimer-1 by photoirradiation. As discussed in our previous paper,[7] photodimer-**1** showed the high Na$^+$ binding ability whereas the parent monomer-**1** showed the poor selectivity toward Na$^+$ in solvent extraction experiments. We believe that the Li$^+$ selectivity with plasticizer TOP and the

Cs^+ selectivity with plasticizer DOP in the dark are attributed to the nature of the plasticizer. Control experiment indicated that the electrode plasticized with TOP or DOP in the absence of ligand **1** showed certain affinity toward Li^+ or Cs^+, respectively. As illustrated in Figures 1 and 2, it was observed that with ligand **1** at the metal chloride concentration of 1×10^{-1} mol dm^{-3} the Li^+ or Cs^+ potential response decreased from 402 mV or 375 mV in the dark to 98 mV or 175 mV after irradiation with plasticizer TOP or DOP, respectively, indicating the significant decrease of the Li^+ or Cs^+ ion affinity on electrodes. However, we could not observe such a dramatic change in solvent extraction experiments: monomer-**1** and dimer-**1** showed a remarkable difference in the affinity toward Na^+, but the affinities toward Li^+ and Cs^+ were only slightly changed. Possibly, this inconsistency is ascribed to a change in the microstructure or local property of ion selective membranes such as ion permeability, degree of photodimerization of anthracene, etc. The details of the plasticizer effects are not specified at the present stage. From the results obtained herein, however, we realized that the observed ion selectivity by electrodes is dominated by several associated effects including the properties of ligands and plasticizers. Further studies to elucidate the origin of the plasticizer effects are now in progress.

Optimization of measurement conditions

Initial studies were focused on the optimization of the measurement conditions with respect to the type of plasticizer, ligand concentration, and irradiation time. In Table 1 we compared five plasticizers: among the plasticizers used here the largest change in ion selectivity were observed for DOP, TOP, and DOS. In contrast, only slight difference on selectivity was observed for *n*-DOA and DBE as the plasticizer. Although the details of the nature of the plasticizer are not yet fully understood as mentioned above, it seems that the solubility of the ligand in the plasticizer plays an important role.

We varied the weight of ligand **1** in PVC membrane from 1 mg to 7 mg. The results listed in Table 2 show that under photoirradiation, Na^+ selectivity against Cs^+ was increased with the increase in the percentage of ligand **1**. It was almost saturated once the ligand weight was over 5 mg. In the dark, the selectivity coefficients $\log K^{pot}_{Na,Cs}$ were kept almost unchanged even the ligand percentage was increased. This indicates that the major contribution to ion selectivity in the dark is derived from TOP plasticizer but not from the ligand.

Since photoirradiation time determined the concentration of dimer species in the membrane, the ion selectivity was significantly time-dependent (Table 3). With DOP plasticizer, the Na^+ selectivity coefficient $\log K^{pot}_{Na,Cs}$ against Cs^+ increased from -2.87 to -3.56 upon 5 and 15 min irradiation and then stabilized at around -3.55 even irradiated longer. It has already shown that photodimerization of ligand **1** within PVC membrane was completed in 15–20 min.[8] The concurrence between the photoreaction time in membranes and the time-dependent ion selectivity demonstrates that the selectivity change upon photoirradiation was mainly derived from the ligand composition change rather than other effects.

REVERSIBILITY

Very interestingly, the turnover of the ion selectivity from one sample ion to other ions can be realized reversibly. As shown in Figure 3, after irradiation, high Na^+ selectivity was obtained with the electrode plasticized with TOP, and the selectivity gradually returned to Li^+ after about 24 h in the dark because of the thermal splitting process from dimer-**1** to monomer-**1**. Such a cycle can be repeated several times

Table 2 Effect of the weight of ligand **1** in PVC membrane on the selectivity of Na^+ against Cs^+.[a]

Ligand **1** *(mg)*		*0*	*1*	*2*	*3*	*5*	*7*
$\log K^{pot}_{Na,Cs}$	Dark	−0.48	−0.52	−0.59	−0.45	−0.59	−0.62
	Light[b]	−0.55	−1.65	−2.88	−3.56	−5.20	−5.31

[a] Plasticizer: TOP.
[b] Irradiated at 365 nm for 15 min.

Table 3 Effect of irradiation time on the selectivity of Na^+ against Cs^+.[a]

hv/min	*0*	*2*	*5*	*15*	*25*	*30*
$\log K^{pot}_{Na,Cs}$	1.78	1.18	−2.87	−3.56	−3.57	−3.46

[a] Plasticizer: DOP, ligand **1**: 5 mg.

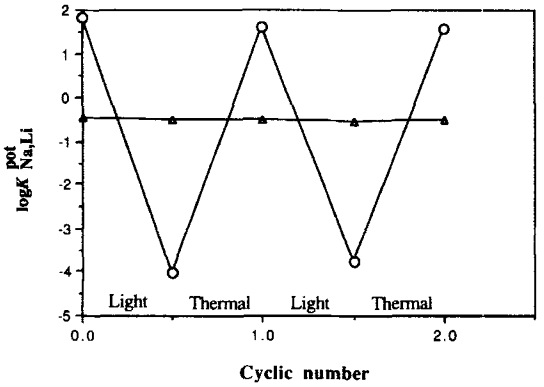


Figure 3 Plots of selectivity coefficient log $K^{pot}_{Na,Li}$ vs. cycling number of Li^+-Na^+ couple ions selective electrodes plasticized with TOP (○) and *n*-DOA (△). One cycle includes irradiation at 365 nm for 15 min and allowed to stand for 24 h in the dark at 25 °C.

without losing the initial ion selectivity. The cycling behavior was strongly dependent on the nature of plasticizer: as shown in Figure 3, we observed that the electrode plasticized with *n*-DOA is almost light silent and no detectable change of ion selectivity could be obtained upon photoirradiation.

CONCLUSION

Recent research and development of ISEs technique have focused on the elucidation of the relationships between ligand structure and ion selectivity, and the purpose is directly related to the achievement of higher ion selectivity and lower detection limit. On the other hand, little attention has been paid to the extension of the traditional ISEs concept itself. Our approach demonstrated that by using external disturbance, the switching of ion selectivity from one target ion to other ions is feasible. This conveys the possibility to design and fabricate the novel versatile ion selective electrodes which can respond to several chemical species. To the best of our knowledge, this is the first time to present the concept of Switch-functionalized Ion Selective Electrodes (SISEs). Undoubtedly, SISEs technique can be used as a guide for the further development of chemical sensors. Further investigations in this laboratory are directed toward the production of a wide range of new and more efficient ionophores with responsive functions for SISEs.

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