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Cesium ion-selective electrodes based on 1,3-alternate thiacalix[4]biscrown-6,6

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Abstract

Four thiacalix[4]biscrown ethers with 1,3-alternate conformation were examined for the potentiometric responses in poly(vinyl chloride) membrane electrodes. Their potentiometric selectivities toward potassium and cesium ions over other alkali, alkaline earth, and transition metal ions were measured by the fixed interference method (FIM). Among the ionophores, 1,3-alternate thiacalix[4]biscrown-6,6 showed a high selectivity for cesium over potassium ion and so was optimized as a Cs^+-selective electrode. The electrode exhibited a linear response with a near Nernstian slope of 57.6 mV per decade in the concentration range of 1.0×10^{-6} to 3.2×10^{-2} M. It was suitable for use in aqueous solution in a wide range of pH 2.5–12.5 and had a fast response time of ca. 5 s. On the basis of 1,3-alternate thiacalix[4]biscrown-6,6, the electrode has a wide linear range and selectivity for cesium ion over potassium ion ($\log K_{Cs^+,K^+} = -3.7$) better than those previously reported with other ionophores.

Keywords: Thiacalix[4]biscrown ethers; Cesium ion-selective electrode; Potentiometry

1. Introduction

Since nuclear power has been extensively used as an important energy source, more radioactive wastes are now generated mostly from atomic power plants [1]. Therefore, techniques for disposing radioactive wastes safely and store them in as little space as possible became important and immediate issues. In order to dispose such wastes, of particular interest has been extractants that are capable of selectively separating heat-generating nuclides and long half-life nuclides, such as cesium or strontium ion [2]. Thus, if the cesium ion contained in radioactive wastes is selectively separated, a great effect can be brought about on the disposal of radioactive wastes in terms of stability and energy efficiency. Active and extensive research has been and continues to be directed toward the development of the extractants concerning cesium ion removal from the nuclear energy wastes.

Much attention has lately been paid to calixarene chemistry due to its great number of applications to selective separation of specific metal ion [3]. In particular, calix[4]arene crown-6 in which a pentaethylene glycol unit connects with 1,3-dialkyloxy calix[4]arene framework within 1,3-alternate type was known to give high cesium ion selectivity over other alkali metal ions [4–11]. This cesium ion selectivity is ascribed not only to size agreement of crown ether moiety based on electrostatic interaction between electron donor atom and metal cation but also to two rotated aromatic nuclei (cation/π-interaction) [4].

Although replacement of the CH_2 bridge of the calix[4]arene by heteroatoms such as NH, O, and S had been a challenge [12], synthetic difficulty retarded the emergence of heteroatom-bridged calixarenes. By contrast, in 1997, Miyanari et al. [13] reported the facile one-step synthesis of thiacalix[4]arene by simply heating a mixture of a *p*-tert-butylphenol and S_8 in the presence of a base. Soon after the ready production in substantial quantities, thiacalixarenes was noticed for its potential importance as a new member of the calixarene family. Lamare

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et al. [14] and Grün et al. [15] reported the synthesis of several 1,3-alternate thiacalix[4]crown ethers. While thiacalix[4]arene is able to form complexes with various transition metal ions [16], thiacalix[4]biscrown ethers could complex with alkali cations. Investigation of their complexing abilities toward alkali metal cations (Na^+, K^+, Rb^+, and Cs^+) showed lower extraction efficiencies than those for the related calix[4]biscrown ethers [17]. This result is explained by a larger thiacalix[4]arene cavity (about 0.5 Å) as determined from X-ray crystal structures [14] and weaker π-cation interactions between the metal ions and the aromatic rings [17].

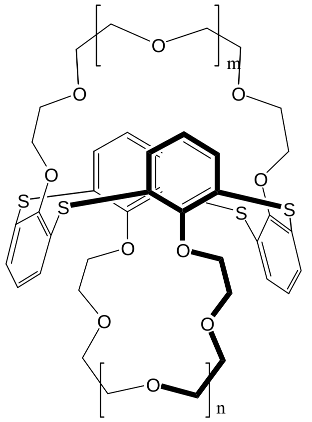
As one of the tools for rapid and inexpensive measurement of the concentration of the metal ion in aqueous solution, ion-selective electrodes (ISEs) have been well established. They are ideally suitable for on-site analysis, and nowadays are found to be applicable in the analysis of some biologically relevant ions, in the process control and environmental analysis [18–21]. There has been much attention in ISEs for alkali metal ions such as sodium [18–21] and potassium ions [22,23]. However, the development of cesium ion-selective electrodes has been scarcely investigated.

With this in mind, we synthesized 1,3-alternate thiacalix[4]biscrown ethers with different sizes of crown ether ring and examined them with regard to the potentiometric response in poly(vinyl chloride) membrane electrodes. The results of sensitivity, selectivity over interfering ions, optimal experimental conditions, and sensing characteristics of poly(vinyl chloride) supported liquid membrane are now reported.

2. Experimental

2.1. Ligands and reagents

The ionophores L1∼L4 were synthesized according to published procedures [17], and their structures are shown in Fig. 1. High-molecular weight poly(vinyl chloride) (HMW-PVC) used as a membrane material, and tetrahydrofuran (THF) used as a solvent were obtained from Aldrich. Dioctyl sebacate (DOS) and 2-nitrophenyl octyl ether (*o*-NPOE) as plasticizers were purchased from Fluka and Aldrich, respectively. Potassium tetrakis(4-chlorophenyl) borate (KT*p*ClPB) used as a lipophilic salt and tris(hydroxymethyl)aminomethane (Tris) for buffer reagent were purchased from Fluka company. Nitrate salts of alkali, alkaline earth, and transition metal ions were of analytical reagent grade. Triply distilled deionized water was used throughout.



	n	m
L1 :	1	1
L2 :	1	2
L3 :	2	2
L4 :	3	3

Fig. 1. Schematic representation of ionophores.

2.2. Preparation of membranes and electrodes

The PVC matrix membrane contains 1.0 wt.% ionophore, 33.0 wt.% PVC and 66.0 wt.% plasticizer. Additional 25 mol% KT*p*ClPB (relative to the ionophore) was also used. The components are homogenized in 2 ml of THF by 6 h-stirring. The resulting mixture was poured to a glass ring (inner diameter 25.5 mm) placed on a petri dish. After evaporating solvent at room temperature, the resulting membrane was peeled off from the glass mould and discs of 6 mm inner diameter were cut out. Membrane disks were mounted on the Philips electrode bodies to measure the electromotive force (EMF). The electrode was finally conditioned by soaking in a 1.0×10^{-2} M internal filling solution of $CsNO_3$ for 48 h.

2.3. EMF measurements

All measurements were carried out with the following assembly

Internal reference electrode Ag/AgCl	Internal reference solution 0.01M $CsNO_3$	PVC membrane	Sample solution	External reference electrode Ag/AgCl, KCl (sat'd)

The external reference electrode was an Orion sleeve-type double junction Ag/AgCl electrode (Model 90-02). All measurements were carried out at room temperature, using a home-made multi-channel millivoltmeter connected to a personal computer. The cell potential was measured by immersing ion-selective electrode and the reference electrode in a cell containing 200 ml of the 0.05 M Tris–HNO_3 buffer (pH 7.4). The data were obtained every second while increasing the concentration of cesium nitrate solution stepwise from 10^{-8} to 10^{-1} M. The activity of cesium ions in aqueous solution was calculated from the Debye–Hückel approximation [24]. The influence of the pH on the response of the electrode was studied at the concentration of 10^{-3} M $CsNO_3$ solution. The pH was adjusted by HNO_3 and LiOH solutions. Potentiometric selectivity coefficients were determined by the fixed interference method (FIM) according to the IUPAC recommendations reported in 1976 [25].

3. Results and discussion

3.1. Potentiometric response of the electrodes based on L1∼L4

The composition of ligand was 1.0 wt.% ionophore, 33.0 wt.% PVC, and 66.0 wt.% DOS as a plasticizer. Figs. 2 and 3 show the potentiometric response of the electrode based on L1∼L4 toward potassium and cesium ion, respectively. L1 with crown-5 rings exhibits a near Nernstian response to K^+ activity (57.2 mV per decade) in the range of 3.2×10^{-5} to 3.2×10^{-2} M. L3 revealed the least sensitivity toward potassium ion, although L4 has the larger crown ether rings to the K^+ ion. This point will be explained later with respect to potentiometric selectivity. L3 showed the most sensitive response toward Cs^+ ion. On the whole, we observed near Nernstian behavior with a slope of 56.2 mV per decade and linear response in the activity of 3.2×10^{-6} to 3.2×10^{-2} M. L4 with crown-7 rings showed lower sensitivity toward alkali metal ions than did L1∼L3 obviously because the crown-7 ring is known to be too large to fit with most metal ions [26].

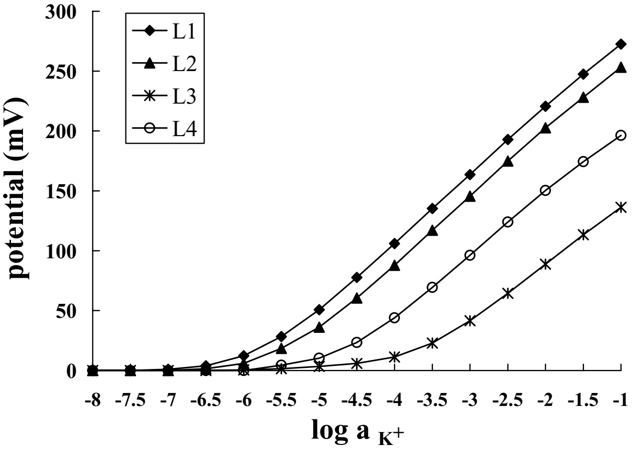


Fig. 2. Potentiometric response of the electrodes based on L1∼L4 toward K^+ activity.

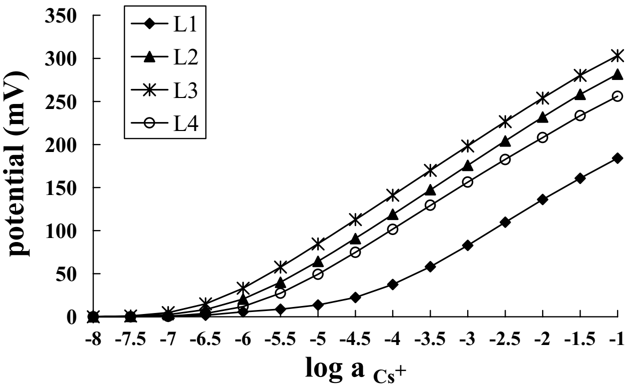


Fig. 3. Potentiometric response of the electrodes based on L1∼L4 toward Cs^+ activity.

3.2. Potentiometric selectivity of the electrodes with L1∼L4

The potentiometric selectivity coefficients ($\log K^{\mathrm{Pot}}_{\mathrm{Cs^+},\mathrm{M^+}}$) were measured by fixed interference method (FIM) at 1.0×10^{-2} M of interfering ions. Potassium nitrate was used as a primary ion for L1 and L2, and cesium nitrate for L3 and L4. Fig. 4 shows potentiometric selectivity of the electrode based on L1∼L4 for alkali metal ions and alkaline earth metal ions.

The potentiometric selectivity coefficients for K^+ (L1 and L2) or Cs^+ (L3 and L4) versus alkaline earth metal ions are much smaller than those toward alkali metal ions due to the difference in charge density. In the case of the electrode based on L1, the most interfering ions are Rb^+ (1.49 Å) and NH_4^+ (1.59 Å), sizes of which are similar to that of K^+ (1.33 Å). For L3, the selectivity coefficients showed $Rb^+ > K^+ > Na^+ > Li^+$ consistent with the cation size, indicating that ion size and the charge density are the most important factors affecting selectivity coefficients in alkali and alkaline earth metal ions in the ligand–metal ion complexation.

Fig. 5 shows potentiometric selectivity coefficients of the electrode with L1∼L4 for transition metal ions. Of all ligands, Ag^+ (1.15 Å) and Pb^{2+} (1.19 Å) ions are the most interfering ions.

Herein, L3 exhibits Nernstian response toward Cs^+ and remarkable cesium selectivity over potassium ion as well as shows a wide linear range. Results with L3 led us to optimize it as a cesium ion-selective ionophore in poly(vinyl chloride) membrane.

3.3. Optimization of membrane composition with L3

Besides the critical role of the nature of ionophore, some other important features of the PVC membrane such as the

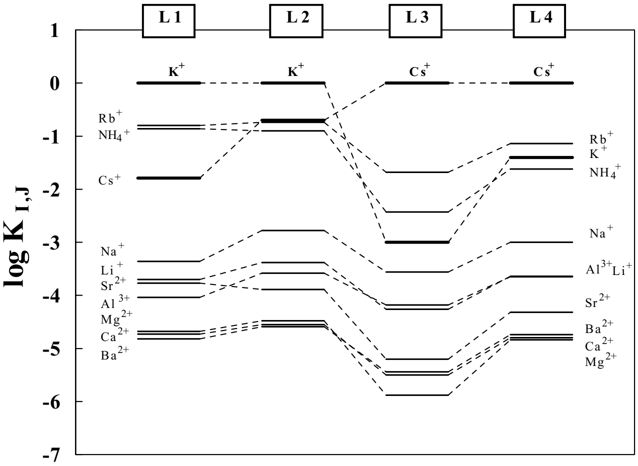


Fig. 4. Potentiometric selectivity of the electrodes based on L1∼L4 toward alkali and alkaline earth metal ions (0.01 M).

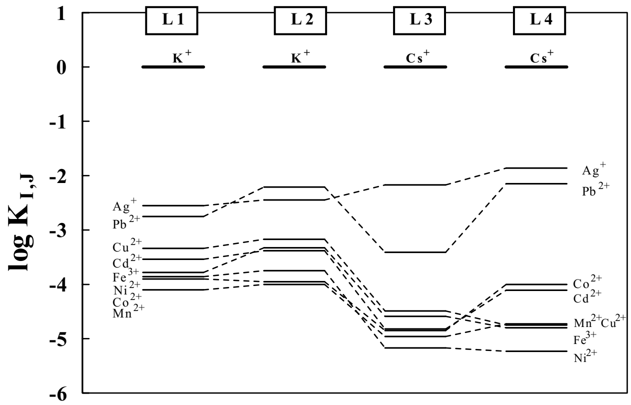


Fig. 5. Potentiometric selectivities of the electrodes using L1∼L4 toward transition metal ions (0.01 M).

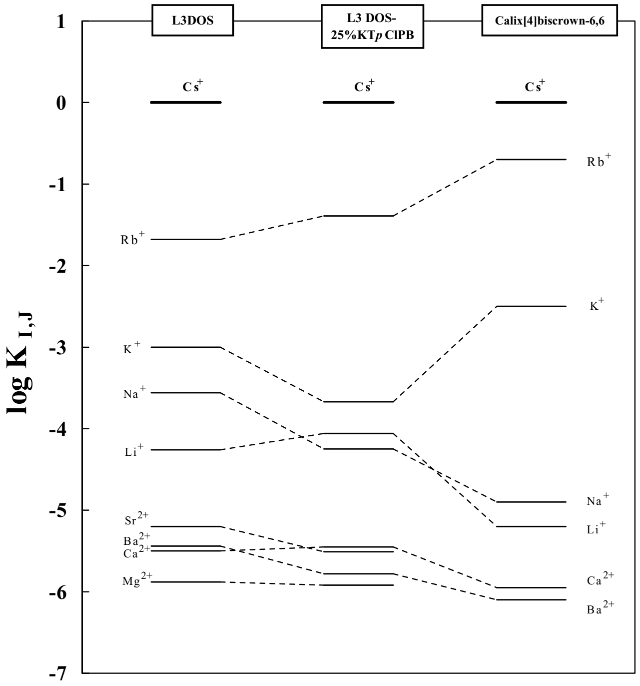


Fig. 6. Potentiometric selectivity of L3 in presence and absence of 25 mol% KT*p*ClPB and calix[4]biscrown-6,6.

nature of plasticizer and additives are known to significantly influence the sensitivity and selectivity of ion-selective electrodes [27]. Membranes incorporated with different plasticizers, lipophilic salts, e.g., KT*p*ClPB were therefore prepared. The effect of composition on the performance of the membranes was investigated, and their behaviors toward cesium ion in terms of slope, linear range, and detection limit are summarized in Table 1. To begin with, the effect of the plasticizer based on L3 was investigated by using two kinds of plasticizers, *o*-NPOE (dielectric constant, $\epsilon = 24$) and DOS (dielectric constant, $\epsilon = 4$). As seen from Table 1 (M1 and M2), DOS is more effective solvent mediator than NPOE. The electrodes made with DOS show a bit better linear dynamic range and slope. It is known that in sensors for monovalent cations the use of relatively nonpolar membrane materials can improve the cation response [28,29].

It is also known that the nature and amount of lipophilic additive strongly influence the response of an ion-selective electrode. The additive lowers the electrical membrane resistance [30,31] as well as the activation barrier for the cation-exchange reaction at the membrane/solution interface, reduces the response time after an activity step and gives rise to significant changes in the selectivity [32,33]. The effect of the variable amounts of KT*p*ClPB (anionic additive) was examined in the PVC membrane electrode using 1.0 wt.% ionophore (L3), 33 wt.% PVC, and 66 wt.% DOS. The responses according to the amount of KT*p*ClPB, i.e. 0, 25, 50, 75, 100, 125, 150 mol%, with respect to the ionophore content are given in Table 1 (M3∼M8). Membranes in the presence of KT*p*ClPB show an improved slope compared with the membranes without KT*p*ClPB. The slope of the electrodes increases a bit to 100 mol% KT*p*ClPB, but the linear range becomes narrow and the value of detection limit rises with the amount of KT*p*ClPB.

3.4. Potentiometric selectivity of L3 containing lipophilic additives

The potentiometric selectivity of L3 in the presence of KT*p*ClPB was examined in order to assess the practical utility as a sensor. LogK_{Cs^+,K^+} of the electrodes containing

Table 1
Optimization of membrane ingredients based on L3

Membrane	Composition (% w/w)				Slope (mV per decade)	Linear range (M)	Detection limit (M)
	Ionophore L3	Plasticizer	PVC	KT*p*ClPB (mol% of ionophore)			
M1	1	*o*-NPOE, 66	33	–	52.0	1.8×10^{-6} to 5.6×10^{-2}	2.5×10^{-7}
M2	1	DOS, 66	33	–	56.2	1.0×10^{-6} to 3.2×10^{-2}	2.4×10^{-7}
M3	1	DOS, 66	33	25	57.6	1.0×10^{-6} to 3.2×10^{-2}	3.8×10^{-7}
M4	1	DOS, 66	33	50	58.0	1.8×10^{-6} to 1.8×10^{-2}	5.6×10^{-7}
M5	1	DOS, 66	33	75	58.1	1.8×10^{-6} to 1.0×10^{-2}	6.0×10^{-7}
M6	1	DOS, 66	33	100	58.5	3.2×10^{-6} to 5.6×10^{-3}	7.2×10^{-7}
M7	1	DOS, 66	33	125	58.4	3.2×10^{-6} to 5.6×10^{-3}	9.7×10^{-7}
M8	1	DOS, 66	33	150	58.0	3.2×10^{-6} to 5.6×10^{-3}	9.9×10^{-7}

Table 2
Comparison of a Cs^+-selective electrode based on L3 with those previously reported in literature

Cs^+-Ionophore	Slope (mV per decade)	Linear range (M)	Selectivity coefficient: $\log K_{Cs^+,K^+}$					
			Rb^+	K^+	Na^+	NH_4^+	Ca^{2+}	Mg^{2+}
Thiacalix[4]biscrown-6	57.6	1.0×10^{-6} to 3.2×10^{-2}	−1.4	−3.7	−4.3	−2.5	−5.5	−5.9
Calix[4]biscrown-6 [39]	57.5	1.0×10^{-6} to 2.0×10^{-3}	−0.7	−2.5	−4.9	–	−5.9	–
Bis(benzo-18-crown-6) [40]	57.0	5.0×10^{-5} to 7.9×10^{-2}	−1.9	−1.0	−2.0	−1.7	–	–
Calix[6]arene haxaester [41]	51.0	–	−1.9	−2.7	−3.9	−2.8	−3.4	−4.0

25, 50, 75, 100, 125, 150 mol% of KT*p*ClPB were also examined by FIM. There was no considerable difference on potentiometric selectivity toward alkali, alkaline earth, and transition metal ions. The membrane containing 25 mol% KT*p*ClPB (M3) however showed the best potentiometric selectivity of these membranes (M3∼M8). If excess amount of KT*p*ClPB is added, the selectivity for the primary ion decreases because KT*p*ClPB acts as a cation exchanger in its anionic form (T*p*ClPB⁻) [34].

The membrane with 25 mol% KT*p*ClPB was found to be effective in improving Cs^+ selectivity over K^+ and Na^+ compared with the membrane in the presence and absence of KT*p*ClPB. (Fig. 6) The selectivity differences might be partly explained by direct interactions between the complexed cations and the counter-anion sites in the ion-selective membrane. Counter-anion site such as sulfonate and sulfate anions are known to be already present as impurities in PVC with relatively low concentration. The interactions of cations with these counter-anions could be different from those with the lipophilic, bulky KT*p*ClPB anions [35–37].

Taking these aspects such as slope, linear range, and selectivity into account, the optimal result was obtained with a membrane containing 1.0 wt.% L3, 33.0 wt.% PVC, and 66.0 wt.% DOS as a plasticizer and 25 mol% KT*p*ClPB.

3.5. Effect of pH and response time

The pH dependence of the Cs^+-selective electrode based on L3 with DOS plasticizer was tested over the pH range of 1.0–13.0 at a fixed concentration of cesium ion (1.0×10^{-3} M). It was observed that the potentiometric response of the electrode was pH independent from 2.5 to 12.5 as shown in Fig. 7. It is expected that at lower pH, protons start contributing to the charge transport process of the membrane, thereby causing interference and increasing potential. On the contrary, at lower pH (<2.5), the potential was observed to decrease, indicating that Donnan failure [38] took place by the nitrate anions formed by nitric acid. At higher pH (>12.5), the potential increase might be resulted from the response toward lithium ion.

Dynamic response time is an important factor for ion-selective electrodes. In this study, the practical response time ($t_{95\%}$) of the electrodes was tested by measuring the time required to achieve a 95% value of steady potential, when cesium concentration jumped from 1.0×10^{-3} to 1.0×10^{-2} M. The actual potential versus time traces are shown in Fig. 8. As can be seen, the electrode reaches the equilibrium response in a very short time (<5 s).

3.6. Comparison of performance characteristics

Thiacalix[4]biscrown ethers are macrocycles connected in the *ortho* position by sulfur bridges instead of the methylene bridges of calix[4]biscrown ethers, and it is necessary to compare L3 with the corresponding calix[4]biscrown-6,6 (Fig. 6 and Table 2). In addition, the response characteristics of the electrode based on L3 are compared with those of the best Cs^+-selective electrodes reported previously (Table 2). In Table 2, the performance of the cesium ion-selective electrode with L3 is comparable to those previously reported with other ionophores. So, we found that L3 is superior in linear range and selectivity for Cs^+ over K^+ to other organic ligands.

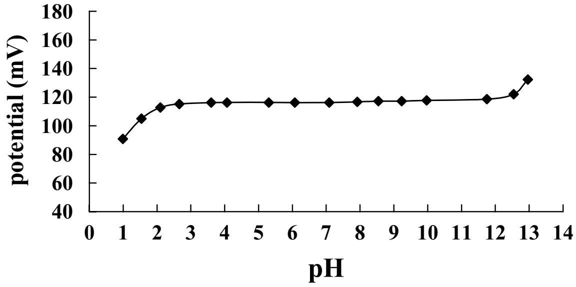


Fig. 7. pH response of the electrode using L3 with 10^{-3} M $CsNO_3$. The pH was adjusted with HNO_3 and LiOH.

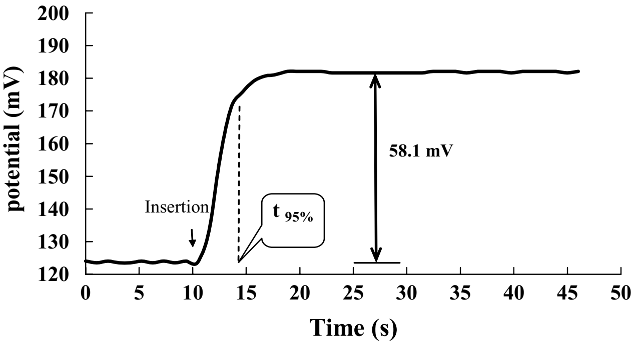


Fig. 8. Response time of the electrode using L3 with 25 mol% KT*p*ClPB by increasing from 10^{-3} to 10^{-2} M of $[Cs^+]$.

4. Conclusions

1,3-Alternate thiacalix[4]biscrown-6,6 exhibited linear response with a near Nernstian slope of 57.6 mV per decade within the concentration range of 1.0×10^{-6} to 3.2×10^{-2} M, and the limit of detection was determined as 3.8×10^{-7} M. The electrode was suitable for use in aqueous solutions in wide pH range of 2.5–12.5. It also has a fast response time of ca. 5 s. The cesium ion selectivity over potassium ion $\left(\log K_{\mathrm{Cs}^+,\mathrm{K}^+} = -3.7\right)$ was better than those previously reported with other ionophores.

Acknowledgements

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