

## Polymeric Membrane Cesium-Selective Electrodes Based on Quadruply-bridged Calix[6]arenes

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New quadruply-bridged calix[6]arenes (**I-V**) have been studied as cesium selective ionophores in poly(vinyl chloride) (PVC) membrane electrodes. PVC membranes were prepared with dioctyl sebacate (DOS) or 2-nitrophenyl octyl ether (*o*-NPOE) as the solvent mediator and potassium tetrakis(*p*-chlorophenyl)borate as the lipophilic salt additive. These ionophores produced electrodes with near-Nernstian slope. The selectivity coefficients for cesium ion with respect to alkali, alkaline earth and ammonium ions have been determined. The lowest detection limit ( $\log a_{\text{Cs}^+} = -6.3$ ) and the higher selectivity coefficient ( $\log k_{\text{Cs}^+,\text{Rb}^+}^{\text{pot}} = -2.1$  by SSM,  $-2.3$  by FIM for calix[6]arene **I**) for  $\text{Cs}^+$  have been obtained for membranes containing quadruply-bridged calix[6]arenes (**I, II, III**), which have no *para*-*t*-butyl substituents on the bridging benzene ring.

**Keywords:** Quadruply-bridged calix[6]arene, Ionophore, Cesium, Ion-selective electrode, Poly(vinyl chloride) membrane.

### Introduction

Polymeric carrier-based ion-selective electrodes (ISEs) are well-established analytical tools for determining the alkali metal ions due to the importance of lithium,<sup>1</sup> potassium<sup>2,3</sup> and sodium<sup>4-7</sup> in biological systems and the susceptibility of cesium and rubidium to neutron activation.<sup>8</sup> Cesium and the other alkali metal ions have been determined by either atomic spectrometry or inductively coupled plasma mass spectrometry.<sup>9</sup> Potentiometry involving ISEs is now widely used for simple and rapid measurements, particularly in clinical and environmental assays, for the determination of alkali metal ions.<sup>1-8</sup> Calixarenes have received considerable attention as an interesting class of ionic and molecular binding hosts.<sup>10,11</sup> Reports have indicated that various functionalized calixarenes are selective host molecules for cations and anions.<sup>12-19</sup> The ISE dynamic response is generated by selective complexation of the target or primary ion by neutral carrier molecules dispersed in a poly(vinyl chloride) (PVC) matrix. Polymeric membrane type ISEs provide one of the most versatile sensing methods because they allow the selection of various sensory elements, according to the structures of the target ion. Hence, polymeric membrane ISEs for inorganic metal cations have been extensively developed by the use of crown ethers, a related macrocyclic hosts and acyclic ligands.<sup>20-23</sup> Many of these ISEs exhibit excellent selectivity for metal cations as guests and are now commercially available. Recently cesium ISEs have received considerable attention for clinical and environmental analysis. In earlier work, ion-exchangers, tetraphenylborate derivatives and valinomycin were used for cesium ISEs.<sup>24,25</sup> Many macrocycles, including related calixarenes, have been synthesized for cesium recognition and ISEs.<sup>26-38</sup> The syntheses, structures and cation-binding properties of chemically modified calixarenes as a new class of macrocyclic molecular receptors have been reviewed recently.<sup>39-41</sup> This work has con-

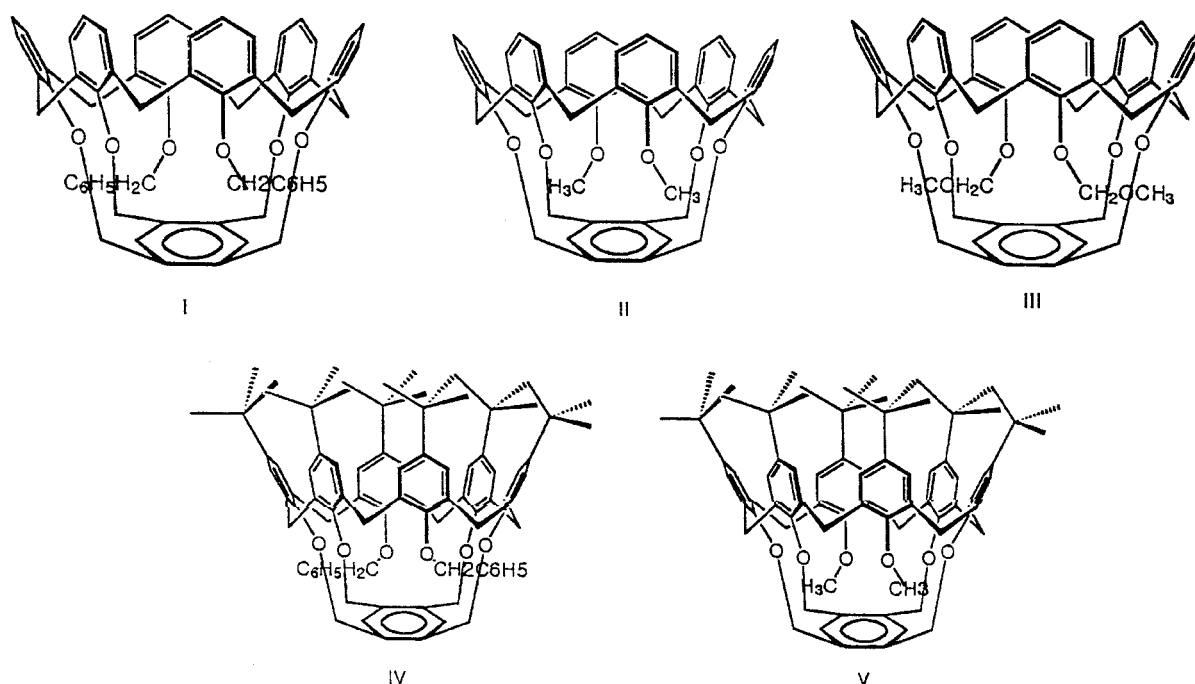
firmed the ionophoric behaviour of many calixarene esters, ethers and ketones.<sup>12-16</sup>

In the present study, PVC polymeric membrane ISEs have been prepared from the five quadruply-bridged calix[6]arenes **I-V** (Fig. 1) as cesium selective ionophores and used to study the selectivity coefficients for cesium with respect to alkali, alkaline earth and ammonium ions. The sensory element quadruply-bridged calix[6]arenes have a well-defined cavity, which is capable of incorporating cesium ion. The characteristic selectivities of the calixarene electrode were correlated with the recognition of steric shapes of nonpolar moieties by the inclusion of cation guests into the calix[6]arene cavity.

### Experimental Section

**Reagents.** Five quadruply-bridged calix[6]arenes (**I-V**) tested as cesium ionophores are shown in Figure 1. Two quadruply-bridged calix[6]arenes (**I, II**) were prepared according to our literature procedure, and the other quadruply-bridged calix[6]arenes (**III-V**) were synthesized by similar method.<sup>42,43</sup> High molecular weight PVC, dioctyl sebacate (DOS), 2-nitrophenyl octyl ether (*o*-NPOE), potassium tetrakis(*p*-chlorophenyl)borate (KTPCIPB) and tetrahydrofuran (THF), which were obtained from Fluka, were used to prepare the PVC membranes. Analytical grade chlorides of cesium, rubidium, potassium, sodium, lithium, magnesium, calcium and ammonium were used. Doubly distilled water in a quartz apparatus was used to prepare all aqueous electrolyte solutions.

**Preparation of ion-selective membranes.** PVC-based cesium-selective membranes were prepared according to the literature method. The typical composition of PVC-based cesium-selective membranes was 33 mg PVC, 66 mg plasticizer DOS or *o*-NPOE, 1 mg ionophore and KTPCIPB (50 mol% of ionophore if needed). Table 1 summarizes the com-



**Figure 1.** Five quadruply-bridged calix[6]arenes tested as ionophores in this study.

positions of the cesium-selective membranes employed in this study. The ionophore, plasticizer and PVC were dissolved in the appropriate volume of THF and mechanically stirred. All membrane cocktails were cast in glass rings placed on glass plates for conventional ion-selective electrodes. Solvent from the PVC membrane was allowed to evaporate for at least 24 hours at room temperature. The thickness of the resulting membrane was about 0.3 mm.

**Potentiometric measurements.** The electrochemical properties of the cesium-selective membranes were investigated in the conventional configuration. Small disks were punched from the cast membranes and mounted in Philips electrode bodies (IS-561). For all electrodes, 0.1 M KCl was used as an internal filling solution. The external reference electrode was an Orion sleeve-type double-junction Ag/AgCl reference electrode (Model 90-02). The electrochemical potential was measured by a home-made 16-channel potentiometer coupled to a computer. The dynamic response curves were obtained by adding standard solutions of cations to magnetically stirred buffer solution (0.05 M Tris-HCl, pH 7.2). The selectivity coefficients ( $K_{Cs^+}^{pot}$ ) were determined by both the separate solution method (SSM), using 0.1 M chloride salts of the cations involved, and the fixed interference method (FIM), using 0.1 M solutions of the interfering ions. The fixed interference selectivity coefficient for  $Cs^+$  in the presence of 0.1 M  $Rb^+$  or  $Na^+$  was obtained from calibration plots, according to IUPAC recommendation. Detection limits were obtained from the intersection of two linear lines in the plot of the concentration of  $Cs^+$  and the potential difference.

## Results and Discussion

New lipophilic quadruply-bridged calix[6]arenes have been

synthesized and employed as the selective ionophores for cesium ion. In calixarene crown-ethers, quadruply-bridged calix[6]arenes likely have six oxygens, which function as well-defined convergent binding sites for the metal ions that sterically fit well with the pseudocavity constructed by these oxygens. Especially, the calixarene structure is used as a rigid support for the six oxygens that function as convergent binding sites for the metal ions. A bridged benzene ring in quadruply-bridged calix[6]arenes should also produce the binding interaction with the target cations. Actually, quadruply-bridged calix[6]arenes have been shown to display selectivities for cesium ion, in a complexation/extraction/transport experiments.<sup>43</sup> The quadruply-bridged calix[6]arenes showed excellent ion transport ability with efficiency decreasing in the order  $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ . Among them, quadruply-bridged calix[6]arenes (I-III) exhibited the best extractibility of alkali metal ions. The phase transfer experiments represent a simple ion transfer system from an aqueous to an organic phase and provide a swift method for evaluating the selectivity of ionophores for the guest ions. However, because the polymeric membrane ISEs are a more complex ion transfer system and the conditions under which the selectivity of the ISE is examined are vary widely, the phase transfer results should be regarded only as a consulted data for ISE selectivity.

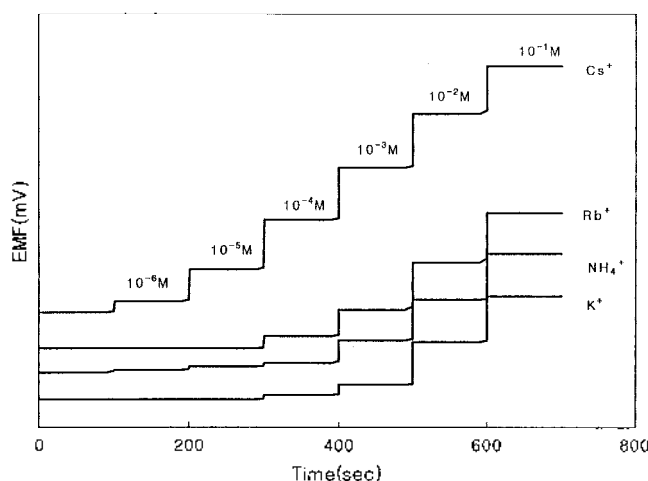
The potentiometric response properties of these polymeric membrane ISEs were examined for alkali metal and ammonium ions. An electrode with a membrane containing no specific selective ionophore shows negligible response to all the alkali and alkaline earth metal ions employed. The ion exchanger *KTpCIPB* in these experiments have been shown to exhibit some cesium sensor activity in PVC-NPOE membranes containing no ionophore because of an ion-exchange

**Table 1.** Compositions of PVC-based Cesium Selective Membranes<sup>a</sup>

| Ionophore | No. | PVC | DOS | <i>o</i> -NPOE | KTpCIPB <sup>b</sup> | Ionophore |
|-----------|-----|-----|-----|----------------|----------------------|-----------|
| I         | 1   | 33  | 66  |                |                      | 1         |
|           | 2   | 33  | 66  |                | 50                   | 1         |
|           | 3   | 33  |     | 66             |                      | 1         |
|           | 4   | 33  |     | 66             | 50                   | 1         |
| II        | 5   | 33  | 66  |                |                      | 1         |
|           | 6   | 33  | 66  |                | 50                   | 1         |
|           | 7   | 33  |     | 66             |                      | 1         |
|           | 8   | 33  |     | 66             | 50                   | 1         |
| III       | 9   | 33  | 66  |                |                      | 1         |
|           | 10  | 33  | 66  |                | 50                   | 1         |
|           | 11  | 33  |     | 66             |                      | 1         |
|           | 12  | 33  |     | 66             | 50                   | 1         |
| IV        | 13  | 33  | 66  |                |                      | 1         |
|           | 14  | 33  | 66  |                | 50                   | 1         |
|           | 15  | 33  |     | 66             |                      | 1         |
|           | 16  | 33  |     | 66             | 50                   | 1         |
| V         | 17  | 33  | 66  |                |                      | 1         |
|           | 18  | 33  | 66  |                | 50                   | 1         |
|           | 19  | 33  |     | 66             |                      | 1         |
|           | 20  | 33  |     | 66             | 50                   | 1         |
| none      | 21  | 33  | 66  |                |                      | 1         |
|           | 22  | 33  | 66  |                | 50                   | 1         |
|           | 23  | 33  |     | 66             |                      | 1         |
|           | 24  | 33  |     | 66             | 50                   | 1         |

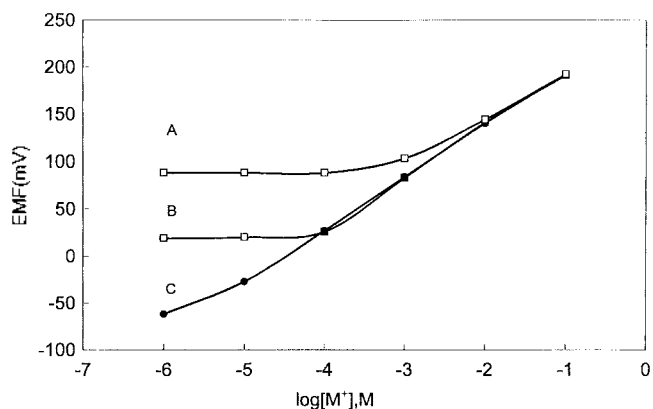
<sup>a</sup>In wt %. <sup>b</sup>mol% relative to the ionophore

mechanism between the positive cesium ion and the large bulky negative anion, but the cesium sensitivity with the addition of KTpCIPB in PVC-DOS membrane containing no ionophore is largely decreased. The polymeric membrane ISEs have been investigated to measure the ability of the ionophores to act as neutral carriers in the absence of the ion exchanger. Figure 2 shows potentiometric response curves for alkali metal and ammonium ions, obtained at pH 7.2 (0.05 M Tris-HCl buffer) by electrode no. 1 (PVC membrane containing DOS as a plasticizer) based on quadruply-bridged calix[6]arene I. Electrode no. 1 displays a near-Nernstian response to Cs<sup>+</sup> in CsCl solution over the range  $1 \times 10^{-6}$ – $1 \times 10^{-1}$  M. The strongest response was observed for Cs<sup>+</sup> ion with a detection limit less than  $10^{-6}$  M. A linear response with a slope of 55.6 mV/decade, close to the theoretical value, according to the Nernst equation (59.16 mV/decade at 25 °C), started from *ca.*  $10^{-6}$  M to  $10^{-1}$  M. Nernstian responses were also observed for Rb<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions, starting from *ca.*  $10^{-3}$  M. The response to Na<sup>+</sup> ion was much weaker and the response to Li<sup>+</sup> ion was almost negligible. The responses to all the alkaline earth metal ions (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup>) were negligible. The selectivity of potentiometric responses by electrode no. 1 was in the order of Cs<sup>+</sup> > Rb<sup>+</sup> > K<sup>+</sup> NH<sub>4</sub><sup>+</sup> >> Na<sup>+</sup> ~ Li<sup>+</sup> >> Mg<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup>, Ba<sup>2+</sup> (no response). The responses of cesium selective electrodes membrane no. 1 to Cs<sup>+</sup> in the absence and presence of 0.1 M Rb<sup>+</sup> or Na<sup>+</sup> in pH 7.2 are shown in Figure 3 for determining the selectivity coefficients by FIM. The selec-



**Figure 2.** The potentiometric response curves for alkali metal and ammonium ions by electrode no. 1 based on quadruply-bridged calix[6]arene I at pH 7.2 (0.05 M Tris-HCl buffer).

tivity coefficients ( $K_{Cs^+,j}^{pot}$ ) determined by SSM and FIM are summarized in Table 2. The  $K_{Cs^+,j}^{pot}$  values for the electrode with a membrane containing no specific selective ionophore are also listed in Table 2. Electrode no. 1 based on the quadruply-bridged calix[6]arene I showed excellent selective response for cesium ion. The other quadruply-bridged calix[6]arenes (II, III), which have no *para t*-butyl substituents, showed a similar response order and gave similar  $K_{Cs^+,j}^{pot}$  values for most of the metal ions employed. Figure 4 shows potentiometric response curves for Cs<sup>+</sup> at pH 7.2 (0.05 M Tris-HCl buffer) by electrodes no. 1, 5, 9, 13, 17, as illustrated in Table 1 (all PVC-DOS membranes). The quadruply-bridged calix[6]arenes (I–V) employed are of two categories: One is the quadruply-bridged calix[6]arenes (I, II, III), which have no *para t*-butyl substituents, and the other is the quadruply-bridged calix[6]arenes (IV, V) which have *para t*-butyl substituents. Based on PVC-DOS-ionophore membranes in the absence of the ion exchanger, the quadruply-bridged calix[6]arenes (I, II, III), which have no *para t*-butyl substituents, provided the lowest detection limit, the highest selectivity coefficient for Cs<sup>+</sup>, and slopes in

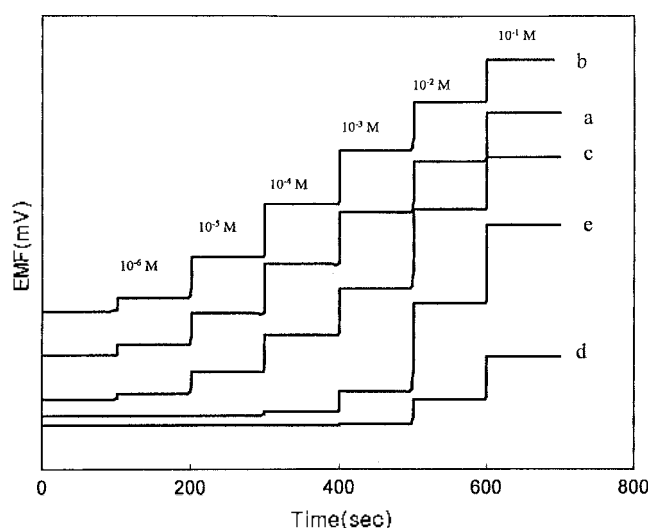


**Figure 3.** Dynamic Response of cesium ion selective electrodes membrane no. 1 to Cs<sup>+</sup> in the presence of 0.1 M Rb<sup>+</sup> (A), 0.1 M Na<sup>+</sup> (B), and in the absence of any cations (C).

**Table 2.** Electrochemical Properties of PVC-based Cesium Selective Membranes

| Ionophore | No. | slope<br>(mV/decade) | detection limit<br>(log $a_{Cs^+}$ ) | SSM<br>$-\log k_{Cs^+,j}^{pot}$ |              |           |            |            | FIM<br>$-\log k_{Cs^+,j}^{pot}$ |            |
|-----------|-----|----------------------|--------------------------------------|---------------------------------|--------------|-----------|------------|------------|---------------------------------|------------|
|           |     |                      |                                      | $j = Rb^-$                      | $j = NH_4^+$ | $j = K^+$ | $j = Na^+$ | $j = Li^-$ | $j = Rb^-$                      | $j = Na^-$ |
| I         | 1   | 55.6                 | -6.3                                 | 2.1                             | 2.4          | 2.7       | 4.1        | 4.1        | 2.3                             | 3.0        |
|           | 2   | 51.7                 | -3.3                                 | 0.3                             | 0.6          | 0.5       | 1.0        | 1.0        |                                 |            |
|           | 3   | 42.0                 | -3.9                                 | 1.5                             | 1.8          | 2.1       | 2.0        | 2.0        |                                 |            |
|           | 4   | 56.0                 | -4.8                                 | 0.7                             | 1.4          | 1.3       | 3.3        | 3.3        |                                 |            |
| II        | 5   | 56.8                 | -6.3                                 | 2.1                             | 2.4          | 2.8       | 3.5        | 3.4        | 2.0                             | 3.1        |
|           | 6   | 47.5                 | -3.2                                 | 0.9                             | 1.2          | 1.1       | 2.6        | 1.5        |                                 |            |
|           | 7   | 32.5                 | -4.1                                 | 1.1                             | 1.4          | 1.6       | 1.6        | 1.6        |                                 |            |
|           | 8   | 55.5                 | -4.8                                 | 0.7                             | 1.4          | 1.3       | 3.0        | 3.3        |                                 |            |
| III       | 9   | 54.0                 | -5.5                                 | 2.2                             | 2.3          | 2.7       | 3.3        | 3.8        | 2.0                             | 3.2        |
|           | 10  | 59.5                 | -3.5                                 | 0.7                             | 0.8          | 0.9       | 1.3        | 1.7        |                                 |            |
|           | 11  | 57.9                 | -4.3                                 | 0.4                             | 1.4          | 1.0       | 2.6        | 3.0        |                                 |            |
|           | 12  | 63.8                 | -5.0                                 | 1.1                             | 1.8          | 2.0       | 2.9        | 3.6        |                                 |            |
| IV        | 13  | 48.0                 | -2.6                                 | 0.8                             | 0.5          | 1.0       | 1.2        | 1.2        | 1.0                             | 1.4        |
|           | 14  | 54.0                 | -3.2                                 | 0.4                             | 0.6          | 0.6       | 1.7        | 1.5        |                                 |            |
|           | 15  | 40.0                 | -3.2                                 | 0.0                             | 0.2          | 1.4       | 1.1        | 1.0        |                                 |            |
|           | 16  | 70.5                 | -4.0                                 | 0.8                             | 1.7          | 1.5       | 2.8        | 3.3        |                                 |            |
| V         | 17  | 91.0                 | -3.4                                 | 1.8                             | 1.4          | 2.0       | 2.9        | 2.9        | 1.1                             | 1.5        |
|           | 18  | 51.5                 | -3.1                                 | 0.3                             | 0.5          | 0.4       | 0.8        | 1.0        |                                 |            |
|           | 19  | 37.0                 | -2.4                                 | 0.8                             | 0.7          | 0.9       | 1.0        | 1.0        |                                 |            |
|           | 20  | 62.0                 | -4.3                                 | 0.6                             | 1.5          | 1.2       | 2.7        | 3.2        |                                 |            |
| none      | 21  | 53.7                 | -2.9                                 | -0.2                            | 0.4          | -0.1      | 0.9        | 1.4        |                                 |            |
|           | 22  | 46.0                 | -2.8                                 | 0.1                             | 0.0          | 0.0       | 0.3        | 0.6        |                                 |            |
|           | 23  | 8.6                  | -2.6                                 | 0.1                             | -0.1         | 0.1       | 0.2        | 0.2        |                                 |            |
|           | 24  | 58.0                 | -3.9                                 | 0.6                             | 1.2          | 1.0       | 2.3        | 2.8        |                                 |            |

excess of 50 mV/decade change in appropriate cesium concentrations. But the quadruply-bridged calix[6]arenes (IV, V), which have *para t*-butyl substituents, gave the lowest selectivity coefficient for  $Cs^+$ . The potentiometric selectivity of the quadruply-bridged calix[6]arene electrodes reflects the selectivity observed in the complexation, extraction, or transport of these ions. The preference for  $Cs^+$  ion can be reasonably explained by a good steric fit with the pseudocavity constructed by the six ether oxygens and bridged benzene ring. However, the cesium selectivity and sensitivity were reduced in PVC-DOS-ionophore membranes in the presence of *KTpCIPB* as an additive reagent (see electrodes no. 2, 6, 10, 14, 18 in Table 2). Meanwhile, the cesium selectivity and sensitivity are also reduced in PVC-NPOE-ionophore membranes regardless of the presence of *KTpCIPB* as an additive reagent (see Table 2). In general, ion exchangers such as *KTpCIPB* are accommodated into PVC membrane systems in small controlled amounts to reduce anion interference, enhance the selectivity characteristics, improve electrical properties and lower the membrane resistance by increasing the cation extraction efficiency. Examination of the selectivity data for the electrodes employed in the present study indicated that the major factor determining the selectivity was the presence or absence of the quadruply-bridged calix[6]arene ionophores, but not *KTpCIPB* as an additive. And the other factor determining the selectivity was the kind of plasticizer used in the PVC

**Figure 4.** The potentiometric response curves for cesium ion by electrodes (a) no. 1, (b) no. 5, (c) no. 9, (d) no. 13, and (e) no. 17.

membranes. The addition of the additive to PVC membranes containing an excess of ionophore greatly reduced the selectivity of all metals employed, and had no beneficial effect on selectivity. All the electrodes responded rapidly to change in cesium concentration with time constants on the order of a few seconds. The rate of response was limited only by the speed of stirring and the injection technique.

Lifetime studies gave a stability of at least 1 month for their electrodes.

### Conclusion

The present study is the first report on the usefulness of quadruply-bridged calix[6]arenes as ionophores in the development of cesium selective electrodes with excellent selectivity. Polymeric cesium ion-selective electrodes based on quadruply-bridged calix[6]arenes were prepared and exhibited high selectivity over alkali metal, alkaline earth metal and ammonium ions. The polymeric electrodes combined with the quadruply-bridged calix[6]arenes (**I**, **II**, **III**) having no *para*-*t*-butyl substituents had superior characteristics to those combined with the quadruply-bridged calix[6]arenes (**IV**, **V**) having *para*-*t*-butyl substituents. Quadruply-bridged calix[6]arenes (**I**, **II**, **III**) as new ionophores demonstrated a cesium/rubidium selectivity that is higher than reported previously. Especially, the selectivity coefficients of cesium ion ( $K_{Cs^+,Rb^+}^{pot}$ ) against rubidium were -2.1 by SSM, -2.3 by FIM for calix[6]arene **I**. The detection limit and the selectivity were dependent upon the ionophore as well as the plasticizer.

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