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A Hydrogen Ion-Selective Poly(Vinyl Chloride) Membrane Electrode Based on Calix[4]arene as a Perchlorate Ion-Selective Electrode

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A hydrogen ion-selective electrode was prepared using 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyano-methoxy-calix[4]arene and the possibility of its use as a perchlorate ion-selective electrode was investigated using its characteristic of becoming perchlorate sensitive in acidic regions. The electrode of the optimum characteristic had a composition of 1% ionophore, 66% o-NPOE, and 33% PVC. This electrode exhibited a linear response over the range 1.0×10^{-1} - 1.0×10^{-5} M of perchlorate with a slope of 48.7 ± 0.5 mV per p[ClO₄]. The effects of the pH and the membrane composition were also investigated. The lifetime of the electrode was at least 4 months and its response time was 10-15 s. The selectivity coefficients of some anions were calculated by the matched potential method.

Key Words: Calix[4]arene, perchlorate, PVC membrane ion-selective electrode, potentiometry.

Introduction

It is a common strategy to measure the charged species using either ion sensors or chromatographic techniques such as high-performance liquid chromatography (HPLC). Potentiometric ion-selective electrodes (ISEs) are very valuable for direct ion analysis. However, ISE technology, especially that for anions, is still underdeveloped. Commercially available anion selective ISEs are very few, while research for the development of anion selective carriers is very tedious and laborious.¹⁻⁷ At the same time, the fact that anion selective ISEs are usually based on ionophore doped, liquid polymeric membranes limits the application possibilities of these sensors, especially those that require micro- or nano-sized sensors. Efforts to miniaturize ISEs started in the 1970s, using glass micropipette microelectrode⁸⁻¹⁰ systems that were fragile and very difficult to use. The use of coated wire electrodes was proposed as a solution to the classical ISEs.¹¹ These electrodes possess

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a longer lifetime and a higher mechanical stability, but they do not have an internal reference element and thus suffer from long-term signal stability.¹²

Anions play fundamental roles in a wide range of biological, medicinal, and environmental processes and because of their significance the development of synthetic receptors and sensors for anions has been growing in importance in recent years.^{13–15} Therefore, considerable effort has been devoted to the development and study of new solvent/polymeric membrane electrodes for the selective potentiometric detection of anionic species by using various new ionophores.^{16,17–19} Anion receptors use binding forces such as electrostatic interactions, hydrogen bonds, and covalent coordination to a suitable metal center.²⁰

Calix[4]arenes are well-known and widely applied compounds in ion recognition and ‘host-guest’ chemistry. The recognition of specific ions by these receptors is determined by the cavity size and the kind of functional groups attached to the aromatic rings. Because of the selective ion complexation, various derivatives of calix[4]arene have been used as ionophores in membrane electrodes that are selective towards different cations.^{21–24} There are few reports on the application of calix[4]arenes as electroactive components in membrane anion-selective electrodes.²⁵ Moreover, calixpyrroles (pyrrole-based tetraazacrown ethers) have also been noted for their anion binding properties and molecular recognition of anionic guests.^{18,26,27}

Various ionophores for PVC membrane perchlorate electrodes have been reported in the literature and are given in Table 1.^{25,28–44} Most of the reported ClO_4^- ion-selective electrodes are ion exchanger based (liquid) membranes, where the electroactive species including perchlorate ion-association complexes with cations and metal chelates. In these (liquid) membranes, ion-pair formation between ClO_4^- and the cationic site may occur with some selectivity but none of these electrodes can be considered to be carrier-based.

This study was carried out in order to investigate whether a hydrogen-selective electrode prepared using 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene (Figure 1) as a neutral carrier can act selectively against perchlorate ions in acidic regions. In the region of low pH, where acid is extracted from the sample solution, calix[4]arene is transformed into the cationic form. In this case, the potential is independent of the pH and is a function of the concentration of anions in the solution.²² In our previous studies this calix[4]arene was used in hydrogen- and thiocyanate-selective electrodes and they were found to give nearly Nernstian responses against these ions.^{23,24,45} It was stated earlier that the response of this hydrogen-selective electrode is distorted by various anions such as thiocyanate and perchlorate in acidic regions. It was also indicated that this response changes with the perchlorate concentration. Based upon this fact, this study was carried out in order to determine whether perchlorate ions that interfere with this hydrogen-selective electrode give a Nernstian response and whether this electrode can be employed as a selective electrode for this ion in acidic media. For this purpose, membranes with various combinations were prepared by changing the ratio of ionophore, PVC, and plasticizer in order to determine the optimum membrane composition. The response time and the lifetime of the electrode and its selectivity against some anions were investigated.

Experimental

In our previous studies, we explained the general procedure to prepare PVC membrane electrodes and the reagents used.⁴⁵

All measurements were carried out with a cell of the following type: Double junction reference electrode/analyte solution/membrane/ 1.0×10^{-2} M HCl/Ag/AgCl.

Table 1. Properties of some PVC membrane perchlorate-selective electrodes in the literature.

Ionophore	Slope, mV/pClO ₄	Linear Range, pClO ₄	Response time	Lifetime	Selectivity Coefficients Log K	Ref.
Aliquat 336S	58	1-4		At least 3 month	Cl ⁻ : -2.40; NO ₃ ⁻ : -1.55; SO ₄ ²⁻ : <-3.0; ClO ₃ ⁻ : -1.41	28
Homogeneous cross-linked polystyrene	55-57	3-5	5 min	-	In nitrobenzene Cl ⁻ : -3.4; NO ₃ ⁻ : -2.4; Br ⁻ : -2.8; I ⁻ : -1.8; ClO ₃ ⁻ : -2.3 In o-dichlorobenzene Cl ⁻ : -3.7; NO ₃ ⁻ : -2.8; Br ⁻ : -3.0; I ⁻ : -1.4; ClO ₃ ⁻ : -2.3 In 1-decanol Cl ⁻ : -2.1; NO ₃ ⁻ : -1.1; Br ⁻ : -1.4; I ⁻ : -0.4; ClO ₃ ⁻ : -1.1 In chloroform Cl ⁻ : -3.1; NO ₃ ⁻ : -1.9; Br ⁻ : -2.2; I ⁻ : -0.6; ClO ₃ ⁻ : -1.8 Cl ⁻ : -3.18; NO ₃ ⁻ : -2.36; SCN ⁻ : -0.92; Br ⁻ : -2.92; I ⁻ : -1.59; AcO ⁻ : -3.58; IO ₄ ⁻ : 0.02; SO ₄ ²⁻ : -3.36; ClO ₃ ⁻ : -2.74; BrO ₃ ⁻ : -3.22; IO ₃ ⁻ : -2.85 Cl ⁻ : -3.20; NO ₃ ⁻ : -2.30; SCN ⁻ : -1.00; Br ⁻ : -2.74; I ⁻ : -0.75; AcO ⁻ : -; IO ₄ ⁻ : 0.18; SO ₄ ²⁻ : -3.64; ClO ₃ ⁻ : -2.55; BrO ₃ ⁻ : -3.24; IO ₃ ⁻ : -2.37	29
Nitron thiocyanate	53	1-4.5	<1 min	7 days		30
Without nitron thiocyanate	55	1-4.5	<1 min	7 days		
Ba complex of Schiff base ligand derived from condensation of 1,3-diamino-2-hydroxypropane with 2,6-diacetylpyridine (BaL ⁺ (ClO ₄) ₂ =C ₂₄ H ₃₄ BaCl ₂ N ₆ O ₁₂)	58	1-5.4	40 s	2 months	Cl ⁻ : -3.46; NO ₃ ⁻ : -3.27; F ⁻ : -3.09; Br ⁻ : -3.37; I ⁻ : -2.74; AcO ⁻ : -4.14; SCN ⁻ : -0.49; HSO ₃ ⁻ : -3.35; H ₂ PO ₄ ⁻ : -2.52	31
Aliquat 336S	52±0.5	2-4.7	2-3 min	-	Cl ⁻ : -2.85; NO ₃ ⁻ : -2.89; Br ⁻ : <-4; I ⁻ : -2.64; SO ₄ ²⁻ : <-4; AcO ⁻ : <-4	32
Silica gel functionalized with 1,4-diazabicyclo(2.2.2)octane(DABCO)	58.6±1.11	1-4	10 s	1 week	Cl ⁻ : -0.52; NO ₃ ⁻ : -2.34; AcO ⁻ : -2.20; IO ₄ ⁻ : -0.46; SO ₄ ²⁻ : -5.70; ClO ₃ ⁻ : -0.82; IO ₄ ⁻ : -0.45	33
Phosphadithiamacroyle ISE	56 ISE	2-6	< 10 s	>9 months	Cl ⁻ : -4.52; NO ₃ ⁻ : -3.02; Br ⁻ : -3.82; I ⁻ : -1.92; SCN ⁻ : -1.03; HSO ₃ ⁻ : -4.55; HPO ₄ ²⁻ : -4.96; BF ₄ ⁻ : -1.22; NO ₂ ⁻ : -4.04; HCO ₃ ⁻ : -4.14; CO ₃ ²⁻ : -4.82; SO ₄ ²⁻ : -4.42	34, 35
Phosphadithiamacroyle CHEMFET	54 CHEMFET	2-6.2	< 4 s	2 months	Cl ⁻ : -4.9; NO ₃ ⁻ : -3.4; Br ⁻ : -4.5; I ⁻ : -2.9; SCN ⁻ : -1.0; NO ₂ ⁻ : -3.9; BF ₄ ⁻ : -2.0; CO ₃ ²⁻ : -4.5; HCO ₃ ⁻ : -4.4; HPO ₄ ²⁻ : -5.0; HSO ₃ ⁻ : -5.2; SO ₄ ²⁻ : -4.60	
Phosphadithiamacroyle MEMFET	54 MEMFET	2-6.2	< 4 s	2 months	Cl ⁻ : -4.74; NO ₃ ⁻ : -3.49; Br ⁻ : -4.53; I ⁻ : -2.54; SCN ⁻ : -1.14; HSO ₃ ⁻ : -4.08; HPO ₄ ²⁻ : -4.79; BF ₄ ⁻ : -2.10; NO ₂ ⁻ : -4.88; HCO ₃ ⁻ : -4.30; CO ₃ ²⁻ : -4.47; SO ₄ ²⁻ : -4.60	

Table 1. Continued.

5,11,17,23-tetrakis-(1,1-dimethylethyl)-25,26,27,28-tetrakis [(dimethylthiocarbamoyl)methoxy]-calix[4]arene	56.5	1-5	30 s		SO ₄ ²⁻ : -5.1; Cl ⁻ : -3.4; NO ₃ ⁻ : -3.3; Br ⁻ : -2.2; Sal ⁻ : -2.1 (FIM) SO ₄ ²⁻ : -5.7; Cl ⁻ : -4.0; NO ₃ ⁻ : -3.1; Br ⁻ : -1.8; Sal ⁻ : -1.4 (SSM)	25
Octylammonium chloride	57.3	1-5	13-15 s	>10 months	SO ₄ ²⁻ : -4.10; I ⁻ : -1.20; Br ⁻ : -1.40; Cl ⁻ : -1.89; F ⁻ : -2.50; NO ₃ ⁻ : -1.60; NO ₂ ⁻ : -2.10; ClO ₃ ⁻ : -1.50; IO ₄ ⁻ : -0.08	36
Bis[tri-(p-metoxypheyl)phosphine]gold(I) perchlorate	56.7	2-5.3	≤10-14 s	>2 months	Cl ⁻ : -5.0; NO ₃ ⁻ : -3.2; AcO ⁻ : -5.2; Br ⁻ : -4.0; I ⁻ : -2.0; SCN ⁻ : -1.4; NO ₂ ⁻ : -4.4; PO ₄ ³⁻ : -5.1; SO ₄ ²⁻ : -5.0; HCO ₃ ⁻ : -4.7; ClO ₃ ⁻ : -3.9	37
Aliquat-336S supported on poly(ethylene-co-vinyl-acetate) copolymer(EVA)	54.0±0.4	1-5	<1 min	150 days	Cl ⁻ : -0.44; NO ₃ ⁻ : -0.55; AcO ⁻ : -1.92; IO ₄ ⁻ : -0.21; SO ₄ ²⁻ : -1.39; BrO ₃ ⁻ : -1.68; CO ₃ ²⁻ : -1.06; SO ₄ ²⁻ : -1.39	38
1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane -Cu(II) complex	67 (BEHS)	1-4.3	3 s	30 days	BEHS → ClO ₄ ⁻ > SCN ⁻ > I ⁻ > NO ₃ ⁻ > AcO ⁻ > Br ⁻ > HCO ₃ ⁻ > Cl ⁻ > HPO ₄ ²⁻	39
	55 (DBP)	1-4.3	3 s	30 days	DBP → ClO ₄ ⁻ > SCN ⁻ > I ⁻ > AcO ⁻ > NO ₃ ⁻ > Br ⁻ > Cl ⁻ > HCO ₃ ⁻ > HPO ₄ ²⁻	
	66 (NPOE)	1-4.3	3 s	15 days	NPOE → ClO ₄ ⁻ > SCN ⁻ > I ⁻ > NO ₃ ⁻ > Cl ⁻ > Br ⁻ > HCO ₃ ⁻ > AcO ⁻ > HPO ₄ ²⁻	
Ni(II)-Hexaazacyclotetradecane complex	59.3	1-6.3	<7 s	7 weeks	AcO ⁻ : -4.5; SO ₄ ²⁻ : -4.1; SO ₃ ²⁻ : -4.1; Cl ⁻ : -4.6; HCO ₃ ⁻ : -4.3; NO ₃ ⁻ : -3.4; Br ⁻ : -4.3; NO ₂ ⁻ : -4.1; I ⁻ : -3.3; SCN ⁻ : -2.1; IO ₄ ⁻ : -2.3; MnO ₄ ⁻ : -1.0	40
Phosphorus(V)-tetraphenylporphyrin complex	57.8±0.4	0.8-5 (PME)	Very fast	2 months	SCN ⁻ : -2.0; I ⁻ : -1.50; Br ⁻ : -3.0; NO ₂ ⁻ : -3.3; Cl ⁻ : -3.7; SO ₄ ²⁻ : -4.2; AcO ⁻ : -2.80; NO ₃ ⁻ : -3.8; CN ⁻ : -2.9; F ⁻ : -4.1	41
	53.6±0.4	1.5-6 (CGCE)			SCN ⁻ : -2.6; I ⁻ : -1.9; Br ⁻ : -3.7; NO ₂ ⁻ : -3.9; Cl ⁻ : -4.4; SO ₄ ²⁻ : -4.7; AcO ⁻ : -3.2; NO ₃ ⁻ : -4.2; CN ⁻ : -3.5; F ⁻ : -4.4	
1,4,8,11-tetra(n-octyl)-1,4,8,11-tetraazacyclotetradecane	52.5	1-5.3		60 days	I ⁻ : -2.12; NO ₃ ⁻ : -3.02; Br ⁻ : -2.23; Cl ⁻ : -2.92; HCO ₃ ⁻ : -2.73; AcO ⁻ : -3.20; HPO ₄ ²⁻ : -3.74; SO ₄ ²⁻ : -4.02; Cr ₂ O ₄ ²⁻ : -4.12	42
	51.3	1-4.6	3 s	7 days	I ⁻ : -2.12; NO ₃ ⁻ : -3.02; Br ⁻ : -2.23; Cl ⁻ : -2.92; HCO ₃ ⁻ : -2.73; AcO ⁻ : -3.20; HPO ₄ ²⁻ : -3.74; SO ₄ ²⁻ : -4.02; Cr ₂ O ₄ ²⁻ : -4.12	
		54.3	1-4.6		15 days	
2,2'-[1,2-ethanediy]bis(nitriolethylene)-bis-phenolato uranil	60.6±1.0	1-6	≤10 s	>2 months	SCN ⁻ : -2.6; Cl ⁻ : -1.5; F ⁻ : -1.3; Br ⁻ : -2.5; I ⁻ : -2.5; NO ₂ ⁻ : -1.7; CN ⁻ : -2.2; AcO ⁻ : -2.5; SO ₄ ²⁻ : -3.5; NO ₃ ⁻ : -2.5	43
Cobaloxime	56.8	1-6	<15 s	>4 months	IO ₄ ⁻ : -5.6; SCN ⁻ : -2.3; NO ₂ ⁻ : -3.1; SO ₄ ²⁻ : -2.1; AcO ⁻ : -4.8	44
5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene	48.7	1-5	10-15 s	>4 months	I ⁻ : 1.14; SCN ⁻ : -0.99; F ⁻ : -1.90; Br ⁻ : -3.04; NO ₂ ⁻ : -2.44; NO ₃ ⁻ : -2.97; HPO ₄ ²⁻ : -1.69; H ₂ PO ₄ ⁻ : -1.47; AcO ⁻ : -1.62; SO ₃ ²⁻ : -1.17; HSO ₃ ⁻ : -2.98	This work

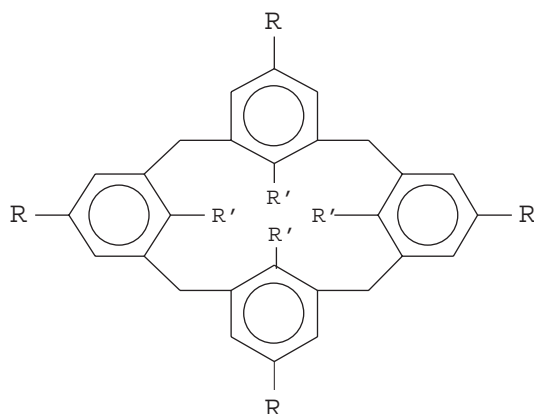


Figure 1. The structure of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene ($R' = -OCH_2CN$; $R = -C(CH_3)_3$).

Potential measurements were carried out with an ORION 720 A Model pH-ionmeter. The potential values reported are given against the saturated Ag/AgCl double junction reference electrode (ORION 9700BN). Measurements were obtained with the electrodes immersed to a depth of 1.5 cm in sample solution and with the solution stirring by a magnetic stirrer. All the experimental work was carried out at 20 ± 1 °C and the pH values were determined using a combined glass-pH electrode (Ingold 10.402.3311).

Results and Discussion

Effect of membrane composition

The hydrogen ion-selective electrode prepared with the use of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene as an ionophore that showed the best Nernstian response for hydrogen ion was the one with a membrane containing 67% 2-nitrophenyloctyl ether, 32% poly(vinyl chloride), and 1% ionophore.²³ In this study the first step was the preparation of such an electrode and to check its response against perchlorate ions. The electrodes containing this membrane are electrodes 3, 4, and 5 listed in Table 2. Since the slopes and working ranges of these electrodes were not very satisfactory for perchlorate, electrodes with 3 different membrane compositions were also prepared by varying the ratio of PVC to plasticizer, and their slopes, working ranges, and suitable working pH values are listed in Table 2.

As seen in Table 2, when the plasticizer percent changed from 66% to 68%, variation in the performance of the electrode occurred. A reasonable explanation cannot be given for this variation observed in the slope.

Working ranges and slopes of electrodes

The emf response of the proposed ClO_4^- electrodes based on 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene in varying concentrations of perchlorate ion at pH 2.0 (Figure 2 and Table 2) indicates a linear range from 1.0×10^{-5} M to 1.0×10^{-1} M for electrodes 1, 2, 5, 7, and 8; from 3.0×10^{-5} M to 1.0×10^{-1} M for electrode 4; and from 1.0×10^{-4} M to 1.0×10^{-1} M for electrodes 3 and 6. Using the linear portion of these calibration curves, the slopes of the electrodes were determined to be 48.7-44.5 mV/pClO₄. It is seen that the electrode with the best slope and working range was electrode 1. The response of this electrode

was compared with those for perchlorate with different neutral carriers (Table 1). Although the electrode does not give a full Nernstian response, its slope is very close to the Nernstian value. In the literature, it is stated that the electrodes with such values could be used for analytical purposes.⁴⁸⁻⁵⁰ Moreover, electrodes with a slope of 55 mV at 25 °C are considered to give a Nernstian response. The limit of detection, as determined from the intersection of the 2 extrapolated segments of calibration curve, was 5.0×10^{-6} M for electrode 1.

Table 2. Effect of the membrane composition on the characteristics of the proposed perchlorate-selective electrode.

Membrane I 1% Ionophore, 66% o-NPOE, 33% PVC (Total mass of 425.4 mg)						
Electrode Number	pH	Slope (mV/pClO ₄)	Working range (M)	Detection limit (M)	Lifetime (month)	Response time (s)
1	2.5	48.7 ± 0.5	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	5.0 × 10 ⁻⁶	3-4	10-15
2	2.1	46.2 ± 0.5	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	3.6 × 10 ⁻⁴	3-4	10-15
Membrane II 1% Ionophore, 67% o-NPOE, 32% PVC (Total mass of 425.4 mg)						
Electrode Number	pH	Slope (mV/pClO ₄)	Working range (M)	Detection limit (M)	Lifetime (month)	Response time (s)
3	2.8	44.5 ± 0.7	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁴	2.5 × 10 ⁻⁵	3-4	10-15
4	2.5	46.7 ± 0.5	1.0 × 10 ⁻¹ -3.0 × 10 ⁻⁵	5.0 × 10 ⁻⁶	3-4	10-15
5	2.1	45.8 ± 0.6	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	2.5 × 10 ⁻⁵	3-4	10-15
Membrane III 1% Ionophore, 68% o-NPOE, 31% PVC (Total mass of 425.4 mg)						
Electrode Number	pH	Slope (mV/pClO ₄)	Working range (M)	Detection limit (M)	Lifetime (month)	Response time (s)
6	2.9	45.7 ± 0.5	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁴	2.5 × 10 ⁻⁵	3	10-15
7	2.5	47.0 ± 0.5	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	2.5 × 10 ⁻⁵	3	10-15
8	2.0	46.2 ± 0.4	1.0 × 10 ⁻¹ -1.0 × 10 ⁻⁵	1.0 × 10 ⁻⁶	3	10-15

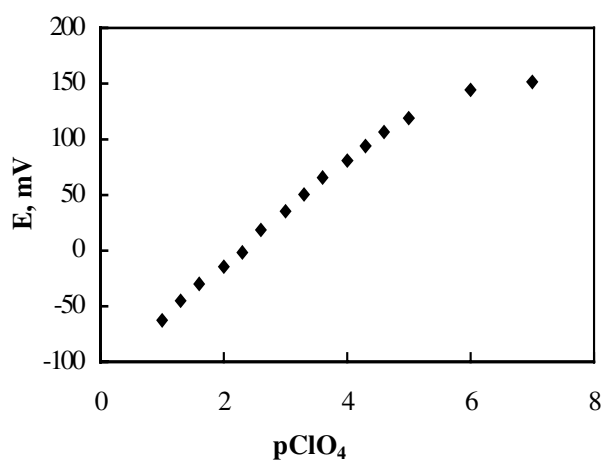


Figure 2. The calibration curve of perchlorate-selective electrode 1.

Effect of pH

The calibration curves of 3 different membrane electrodes prepared by the use of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene as ionophore were plotted between pH 2.0 and 4.0 in order to determine the pH range at which the electrodes gave the best response against perchlorate ions. The pH range was chosen as 2.0-3.0 since the range 3.0-4.0 was found to be unsuitable. The results obtained are tabulated in Table 2. The best slopes were obtained at pH 2.5 for the 3 membrane compositions. Therefore, all studies were carried out at the pH range of 2.0 and 2.9. The reason for obtaining the best response for perchlorate ions in acidic media is attributed to the fact that only in this medium can perchlorate ion attach to the protonated ionophore to form an ion pair reversibly.

Response time and lifetime of the electrode

The response time of an ion-selective electrode is important in analytical applications and it depends slightly on the concentration change. Therefore, it was determined by recording the time elapsed to reach a stable potential value after the electrode and the reference electrode were immersed in calibration solutions from low to high perchlorate ion concentrations. If the concentration of perchlorate was changed from 1.0×10^{-6} to 1.0×10^{-5} M, the response time was 15-20 s, but, at concentrations higher than 1.0×10^{-5} M, the response time decreased to 10-15 s. These periods are shorter than those that give a linear response in a similar concentration range.

The lifetime of the electrode was determined by recording its potentials at an optimum pH value and by plotting its calibration curves for each day. It was observed that there was no significant change in the slope and working range of the electrode for a period of 4 months (Figure 3). However, after 120 days, a gradual decrease was seen in the slope of the electrode. According to our observations, the lifetime of the electrode prepared by the use of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene is at least 4 months. In conclusion, the response time and the lifetime of the proposed electrode are compatible with most similar perchlorate-selective electrodes reported in the literature.^{28-34,37-44}

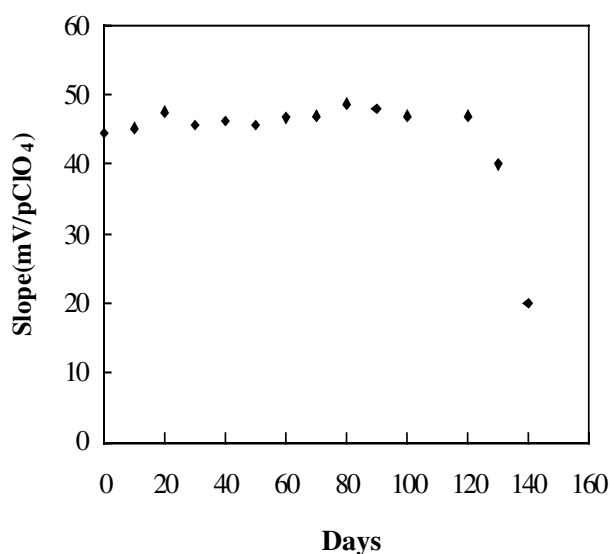


Figure 3. The lifetime of perchlorate-selective electrode 1.

Selectivity of the electrode

The most important characteristic of an ISE is its selectivity against the analyte ion of interest over other ions in solution. The selectivity of the proposed perchlorate-selective electrode against other anions such as nitrate, thiocyanate, fluoride, bromide, iodide, nitrite, acetate, and dihydrogen phosphate was calculated by the matched-potential method. This is a procedure recommended by the IUPAC that eliminates the limitation of the corresponding methods based on the Nicolsky-Eisenman equation for the determination of the potentiometric selectivity coefficients. These limitations include non-Nernstian behavior of interfering ions, inequality of charges of any primary and interfering ions, and activity dependence of potential values.⁵¹ These values are listed in Table 3. The ions interfering most are iodide. This is also the case for the commercially available electrodes and the electrodes reported in the literature (Table 1).

Table 3. Selectivity coefficients of perchlorate-selective electrodes obtained by matched potential method.

Electrode No	I ⁻	SCN ⁻	HPO ₄ ²⁻	SO ₃ ²⁻	H ₂ PO ₄ ⁻	AcO ⁻	F ⁻	NO ₂ ⁻	NO ₃ ⁻	HSO ₃ ⁻	Br ⁻
1	1.143	-0.988	-1.688	-1.174	-1.465	-1.618	-1.898	-2.440	-2.968	-2.978	-3.035
4	0.796	-0.984	-1.306	-1.117	-1.499	-1.634	-1.843	-2.547	-2.881	-2.982	-3.206
7	0.697	-0.997	-1.326	-1.395	-1.371	-1.728	-2.234	-2.731	-2.707	-3.009	-3.119

Thus, it can be concluded that this electrode could be used for the determination of perchlorate in solutions not including iodide ions.

The fact that the interference effect of the chloride ions on the response of the hydrogen ion-selective electrode prepared in this study is very low was also shown in our previous study.²³ Therefore, the lower interfering effect of chloride, a universal contaminant, is an important advantage.

The reason that the selectivity coefficients of this electrode do not comply with the Hofmeister series⁵² and that they show an anti-Hofmeister behavior is thought to be the possible formation of new structures that depend upon the hydrogen binding of anions.

As a result, Table 1 lists the response characteristics of other PVC membrane perchlorate-selective electrodes based on different ionophores together with those obtained from this work. Clearly, the response characteristics of the proposed electrode, including working range, detection limit, response slope, lifetime, selectivity, and response time, were comparable with those of these PVC membrane ISEs.

Conclusions

- The perchlorate-selective electrodes prepared by the use of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene as an ionophore is sensitive towards perchlorate ions in acidic media.
- The perchlorate-selective electrode prepared in this study can be an alternative for most perchlorate PVC membrane selective electrodes reported in the literature as regards ion selectivities, lifetime, and response time.
- PVC micro-electrodes using calix[4]arene can be constructed for the determination of perchlorate ions.
- The hydrogen-selective electrodes prepared by the use of 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetracyanometoxy-calix[4]arene can be used not only for hydrogen ions but also for perchlorate and thiocyanate ions in acidic media.

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