Hydrogen Ion-Selective Poly(vinyl chloride) Membrane Electrode Based on a Calix[4]arene

Demet KURUOĞLU,* Esin CANEL,* Shahabuddin MEMON, Mustafa YILMAZ,** and Esma KILIÇ*†**

**Department of Chemistry, Faculty of Science, Ankara University, Ankara, Turkey*
***Department of Chemistry, Selçuk University, Konya, Turkey*

A hydrogen ion-selective poly(vinyl chloride) membrane electrode was constructed using 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene as a neutral carrier. The electrode showed an apparent Nernstian response in the 2 – 11.5 pH range with a slope of 54.0±0.2 mV/pH at 20±1˚C. This electrode showed a rapid response of the emf to changes in the pH, high ion selectivity with respect to lithium, sodium and potassium, and characteristics similar to those reported for the conventional pH glass membrane electrode. It can be used as a potentiometric indicator electrode in hydrofluoric acid solutions. The effects of iodide, thiocyanate, perchlorate and bromide on the characteristics of the electrode were also considered.

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Introduction

For more than 60 years, pH-glass electrodes have been widely used, and pH measurements in various samples are still made using these electrodes. They are very popular due to their high selectivity and dynamic pH range. However, in spite of the distinctive potential characteristic of pH-glass electrodes and their use in routine pH measurements for so many years, they have certain limitations, such as high resistance, brittleness, instability in hydrofluoric acid and fluoride-containing media. They also create problems in the construction of microelectrodes for biological applications and *in vivo* measurements. That is why studies related to the construction of nonglass pH electrodes have been gaining momentum. The construction of PVC pH electrodes based on neutral carriers will solve most of these problems. The facts that PVC electrodes have low electrical resistance and that they are easy to construct have increased interest in the implementation of these electrodes in place of glass membranes. These electrodes are of great practical importance, since they are solid and unbreakable. For example, there have been numerous studies about the use of pH-sensitive liquid membrane electrodes in clinical studies.[1] Le Blanc *et al*. prepared a liquid-membrane electrode with *p*-octadecyloxy-*m*-chlorophenylhydrazone-mesoxalonitrile (OCPH) as a proton carrier.[2] Simon *et al*. developed different PVC membrane pH electrodes based upon tri-*n*-dodecylamine, which gave good response characteristics.[3-8] Wu and Yu prepared a pH-sensitive electrode using methyldioctadecylamine (MDODA) as a neutral carrier.[9] Later, some authors continued similar research, and other compounds have been investigated as ionophores for hydrogen ions, many of which can be used for a very wide range of pH values.[10-23]

Calixarenes are metacylclophanes comprising phenolic and methylene units. They are very popular as attractive and excellent ionophores because they provide a platform for the attachment of convergent binding groups to create host molecules, mainly for the attraction of simple cations, anions and small molecules.[24-31] McKervey *et al*. first recognized that calixarenes with cations-complexing groups attached to the lower rim may possess the molecular requirements for the type of ionophore used in ion-selective electrodes (ISEs).[32,33] For example, the tetraesters of calix[4]arenes have been proved to be excellent ionophores for sodium in liquid membrane and PVC membrane electrodes. These types of electrodes based on such compounds were shown to be capable of measuring sodium in blood.[34,35] Some calixarenetetraesters are now commonly used in commercial blood electrolyte analyzers for sodium determination.

The purpose of this study was to develop a hydrogen ion-selective electrode using a macrocyclic compound of calix[4]arene as a neutral carrier and to determine its lifetime, response time, optimum working range and other response characteristics. The question whether this electrode can be used for other analytical purposes will also be investigated.

Experimental

Reagents and solutions

All of the chemical substances used were of reagent grade, and were used without further purification. Stock solutions (0.1 M) of metal ions were prepared using deionized water, and working solutions were obtained by dilution of the stock solutions with deionized water.

5,11,17,23-Tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxy-calix[4]arene was synthesized at the Department of Organic Chemistry of Selçuk University, using procedures developed in Refs. 36 and 37. The structure of the ionophore studied in this work is shown in Fig. 1. High-molecular-weight poly(vinyl chloride) (PVC), 2-nitrophenyloctylether (2-NPOE), bis-(2-

† To whom correspondence should be addressed.
E-mail: ekilic@scence.ankara.edu.tr

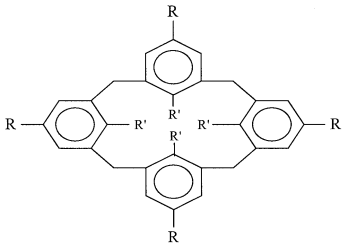

Fig. 1 Structure of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene.

ethylhexyl)sebacate and tetrahydrofuran (THF) were obtained from Fluka as selectophores. Potassium tetrakis(*p*-chlorophenyl)borate (KTpClPB) and sodium tetraphenylborate were purchased from Aldrich.

Britton–Robinson (BR) buffer solutions (pH 2 – 12) with a 0.1 M Na_2SO_4 were used to investigate the performance of the prepared hydrogen ion-selective electrode. BR buffer solutions were prepared by mixing boric acid, acetic acid and phosphoric acid; the pH values of these solutions were adjusted by means of a combined glass pH-electrode by the addition of sodium hydroxide to stock buffer solutions. For the determination of the potentiometric selectivities of the electrode to lithium, sodium and potassium ions, all buffer solutions were prepared according to Ref. 16.

Preparation of electrode

The membrane contained 1 wt% calix[4]arene, 66 – 67.5 wt% plasticizer and 31.5 – 33 wt% PVC. The membrane components, 425 mg in total, were dissolved in 5 mL of THF. This solution was placed in a glass ring of 35 mm i.d. resting on a glass plate. After overnight solvent evaporation, the resulting membrane was peeled off from the glass mold and discs of 7 mm i.d. were cut out. Membrane discs were mounted in a glass tube. After filling the internal filling solution containing 1.0×10^{-2} M HCl and contacting with an AgCl-coated Ag wire, the prepared PVC pH-electrode was conditioned in pure water for 12 h. The electrode was instantly ready for use.

Potential measurements

All measurements were carried out with a cell of the type Ag/AgCl/analyte solution/membrane/1.0×10^{-2} M HCl/Ag/AgCl. Potential measurements were carried out with an ORION 720 A Model pH-ionmeter. The reported potential values are given against the saturated Ag/AgCl reference electrode (ORION 90-01). Measurements were made with the electrodes immersed to a depth of 1.5 cm in the sample solution and with the solution being stirred by a magnetic stirrer. All of the experimental work was carried out at 20±1˚C and the pH values were determined using a combined glass-pH electrode (Ingold 1 0.402.3311).

Results and Discussion

According to the literature, the most commonly used composition in the preparation of PVC matrix neutral carrier membrane electrodes is as follows: 1 – 7% macrocyclic compound (ionophore), 28 – 33% PVC (internal matrix), 60 – 69% plasticizer, 0.03 – 2% lipophilic anion.[38] Using these values, the optimum membrane composition was defined by changing the ratios of the ionophore, PVC, plasticizer and lipophilic anion. The slope and the working range of the electrode were determined by changing the percentage of PVC between 31.5 and 33.2 and the percentage of 2-nitrophenyloctyl ether between 66 – 67.5%. The obtained data are tabulated in Table 1.

Table 1 Effect of the membrane composition on the performance of the proposed hydrogen ion-selective electrode

No.	Mass% (total mass 425.4 mg)			Slope
	2-Nitrophenyloctyl ether	PVC	Ionophore	
1	66	33	1	41.1±0.5
2	66.5	32.5	1	48.5±0.3
3	67	32	1	54.0±0.2
4	67.5	31.5	1	49.7±0.3
5	66.3	31.7	2	46.2±0.4
No.	Mass% (total mass 200 mg)			Slope
	2-Nitrophenyloctyl ether	PVC	Ionophore	
1	66	33	1	40.2±0.5
2	67	32	1	38.2±0.3

Effect of the membrane composition and thickness

The table indicates that the best slope value was obtained from an electrode which contained 32% PVC and 67% 2-NPOE in its membrane. These values were taken in this PVC: 2-NPOE ratio when investigating the other parameters. In order to determine the effect of the ionophore ratio upon the overall performance of the electrode, the ionophore concentration was increased to 2%. This caused a decrease in the slope of the electrode (Table 1). It is stated in the literature that the complex stoichiometry between the macrocyclic compound and the analyte ion is of great importance regarding the selectivity and the slope of the electrode. It is claimed that the decrease in the concentration of the macrocyclic compound in the membrane caused an enlargement of the linear working range of the electrode and changed its slope.[38]

The addition of a lipophilic anion to neutral carrier membranes improves almost all of the electrode characterictics, since it stabilizes the membrane operating conditions, decreases the membrane resistance, and significantly reduces the response times.[38] We prepared electrodes by using sodium tetraphenylborate and potassium tetrakis(*p*-chlorophenyl)borate as a lipophilic anion with 1% ionophore, 67% 2-NPOE and 32% PVC, but the hydrogen-ion selectivity was observed to diminish. This does not comply with the literature, since it is claimed that the addition of lipophilic anion to the membrane phase improves the performance of the electrode. This may be attributed to the fact that sodium and potassium ions which then form ion-pairs with tetraphenylborate and tetrakis(*p*-chlorophenyl)borate settle in the cavity of the calix[4]arene and decrease the number of active sites in the membrane.

It is also known that the type of plasticizer used has a significant effect upon the performance of the membrane electrodes. There have been numerous studies to address this phenomenon. In our study, in order to investigate this phenomenon, the plasticizers used were bis(2-ethylhexyl)-sebacate and bis(2-ethylhexyl)phthalate instead of 2-nitrophenyloctyl ether. The ratios of PVC, plasticzer and

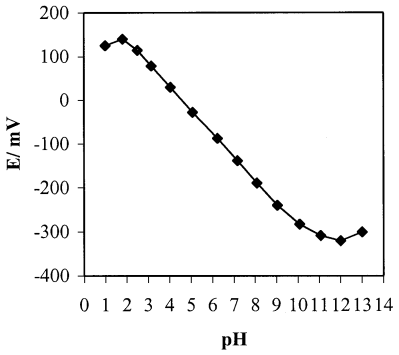

Fig. 2 Calibration curve of the hydrogen ion-selective electrode based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxy-calix[4]arene.

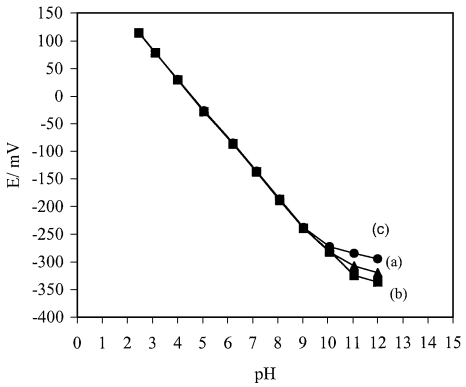

Fig. 3 Effect of the nature of background electrolyte on the electrode response of pH-ISE based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene: calibration curves with (a) 0.1 M sodium, (b) 0.1 M lithium, (c) 0.1 M potasium.

ionophore were 32%, 67% and 1%, respectively. However, an electrode prepared with the membrane containing these plasticizers did not give satisfactory results. It is stated in the literature that the dielectric constant of the plasticizer has a marked effect upon the selectivity and the response time of the membrane; it is emphasized that much more detailed research and experimental data are needed to determine the optimum conditions. 2-Nitrophenyloctyl ether is said to be the best membrane plasticizer for ion-selective electrodes prepared by using macrocyclic compounds.[38] The thickness of the membrane appears to be of secondary importance due to the surface layer, which plays an important role during the recognition of ions. The effect of the thickness of the membrane upon the performance of the electrode is tabulated in Table 1. It is observed that the slope of electrode decreases as the thickness of the membrane decreases. However, no clear explanation can be given for this decrease in the slope.

After all these studies related to the composition of the electrode, a hydrogen ion-selective electrode containing 1% calix[4]arene, 67% 2-nitrophenyloctyl ether and 32% PVC in its membrane was finally prepared, the performance of which was investigated as follows.

The performance of the electrode was checked using 1.0×10^{-2} M HCl and a citrate buffer with a pH of 5.6 as an internal filling solution. The slope of the electrode was the same for both filling solutions. Therefore, all of the studies were carried out using 1.0×10^{-2} M HCl as an internal filling solution.

Working range and slope of the electrode

The potential of the electrode was read by using a series of pH buffer solutions in the cell depicted above. These potentials were plotted against the pH values of the buffer solutions in order to obtain the calibration curve of the electrode (Fig. 2). The linear portion and the slope of this calibration curve gave the working range and the slope of the electrode. The slope of the electrode prepared was 54.0±0.2 mV/pH. The electrode was found to give a linear response against hydrogen ions in the pH range of 2 – 11.5. This electrode was found to have a longer working range than those of most of the reported electrodes.[9,10,21,22,39] Egorov and Sin'kevich have noticed that introducing calix[4]arene and *p-tert*-butylcalix[4]arene into the anion-exchange membrane was accompanied by the appearance of pH-dependence.[21] The linear working pH ranges of these electrodes were 4 – 10 and 5 – 12, respectively. The working pH range of our pH-ISE based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxy-calix[4]arene was unexpectedly wider (approximately 2 – 3 pH units wider) than that of the electrodes proposed by Egorov *et al.* The existence of the cyanic group would be especially important to make a strong response to hydrogen ion, because we did not obtain any responses to hydrogen ion when calix[4]arene and *p-tert*-butylcalix[4]arene were used as ionophores to construct pH-ISE without using an anion-exchanger. The slope of the electrode was observed to be close to that of the Nernstian behavior. Although the electrode does not display a full Nernstian behavior, it is stated in the literature that the electrodes with these slope values can conveniently be employed in analytical studies.[40-42] Also, those electrodes giving a slope value of 55 mV or more at 25˚C are accepted to be Nernstian in the literature. The reason why the calibration curve deviates from the linearity in regions lower than pH 2 and higher than pH 12 can be explained as follows. The distorting effect in the region with a pH value lower than 2 is most probably because of the sulfate anion which was added to the medium in order to adjust the ionic strength. On the other hand, the deviation in regions higher than pH 12 may stem from the sodium anions present in the solution.

Response time of the electrode

The response time of the electrode 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 high to low pH values. This response time was a few seconds. These results were within the limit of the results obtained by many hydrogen electrodes, giving a linear response within the same pH range.[5,9,19,20] In conclusion, the response time of the electrode which we prepared is compatible with most similar electrodes reported in the literature.

Lifetime of the electrode

The lifetime of the electrode was determined by reading the potential values of the calibration solutions and plotting the calibration curves for a period of four months. The slope of the electrode (54 mV/pH) was observed to show a gradual decrease after 110 days. After 120 days, the slope reached approximately 47 mV/pH. We can therefore conclude that the lifetime of the proposed electrode prepared by the use of calix[4]arene is at least 4 months.

Interference studies

A survey of the literature showed that the working range of

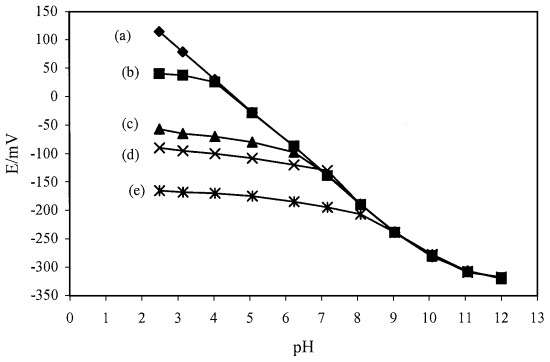

Fig. 4 Effect of the nature of background electrolyte on the electrode response of pH-ISE based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene: calibration curves with (a) 0.1 M sulfate, (b) 0.1 M bromide, (c) 0.1 M thiocynide, (d) 0.1 M perchlorate and (e) 0.1 M iodide.

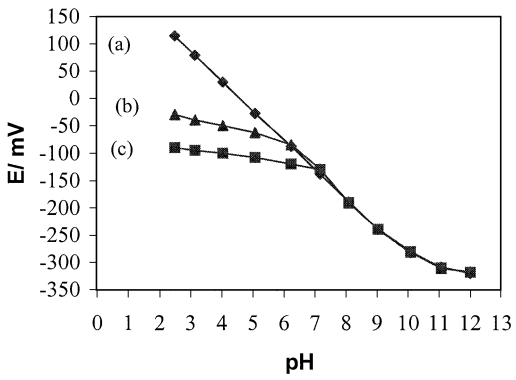

Fig. 5 Effect of the concentration of anion on the electrode response of pH-ISE based on 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetracyanomethoxycalix[4]arene: calibration curves (a) without $NaClO_4$, (b) with 0.01 M $NaClO_4$ and (c) with 0.1 M $NaClO_4$.

electrodes prepared by using of macrocyclic compounds is adversely affected by the presence of anions and cations. It is known that cations, such as lithium, sodium and potassium, decrease the lower detection limit (at high pH), and that anions, such as bromide, chloride, iodide, perchlorate and thiocyanate, decrease the upper detection limit (at low pH); thus, the working range of the electrode decreases.[10,21] Therefore, the working range of the proposed electrode varies depending on the cation and anion background used in the buffer samples. The prepared hydrogen ion-selective electrode was tested in view of its sensitivity towards lithium, sodium and potassium ions, and its selectivity coefficients were evaluated by the fixed interference method (Fig. 3). The selectivity coefficients for the calix[4]arene based hydrogen ion-selective electrode are less than 10^{-11} for lithium, 7×10^{-11} for sodium and 2×10^{-9} for potassium. In the region of high pH, where the hydrogen-ion concentration is very low, but the alkali metal ion concentration is high, alkali metal ions (K^+, Na^+ and Li^+) are extracted from the sample solution and the potential is independent of the pH.[21] These results concerning the selectivity of this electrode indicated that the common ions of alkali metals would not cause any significant interference, unless they are present in very high concentrations. These results are compatible, and sometimes better than those given for similar electrodes described in the literature.[5,20,22,39]

The effect of the above-mentioned anions (0.1 M) on the pH response was also investigated (Fig. 4). The following sequence of anion interference was observed:[10] $I^- > ClO_4^- > SCN^- > Br^- > Cl^-$. The working range in the solutions containing 0.1 M Cl^- was pH = 2 – 11.5. This range was decreased to pH = 4 – 11 for 0.1 M Br^-, pH = 6.5 – 11 for 0.1 M SCN^-; pH = 7 – 11 for 0.1 M ClO_4^- and pH = 8.5 – 11 for 0.1 M I^-. The effect of the nature of the anion on this electrode was most in I^-, SCN^- and ClO_4^-, and the least in Br^-, Cl^-. The interference imposed limitations on their use in acidic solutions, because it was formed as a more stable complex, as noted in Ref. 12. The effect of the anion concentration upon the working range also was investigated. The anion concentration was changed from 0.1 M to 0.01 M and the calibration curves plotted (Fig. 5). The decrease in the working range was observed to be smaller with a decrease in the anion concentration. The results were as fol1ows: pH = 3 – 11 for 0.01 M Br^-, pH = 4 – 11 for 0.01 M SCN^-, pH = 6 – 11 for 0.01 M ClO_4^- and pH = 7 – 11 for 0.01 M I^-. 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.[21]

Application to an end-point indication of the electrode

The proposed hydrogen ion-selective electrode can be used for end-point indication. For this purpose, the titrations of acetic, hydrochloric and hydrofluoric acid solutions were titrated with sodium hydroxide. Figure 3 shows the titration curve obtained for the hydrofluoric acid as an example. The expected end-points are identical for the proposed electrode and an Orion combined glass pH electrode for acetic and hydrochloric acids. It was observed that there is no erosion effect of hydrofluoric acid on the prepared membrane. After a measurement of this electrode in hydrofluoric acid, the working range and the Nernstian slope remained the same. We can say that the electrode prepared could be successfully employed in acid-base titrations.

Conclusion

The conclusions which can be drawn from this study are the following. Calix[4]arene can be successfully used as an ionophore in hydrogen ion-selective electrodes. The proposed electrode can be a good alternative for a glass electrode employed as a potentiometric indicator electrode in various acid-base titrations; it has been successfully used in fluoride-containing media. The electrode has a lower sensitivity towards lithium, sodium and potassium ions than the glass electrode. The advantages of this electrode are its simplicity of preparation, fast response time and long lifetime. The proposed electrode has shown the best Nernstian slope and the widest response range. As a result, it is possible to prepare a PVC micro pH electrode using the composition determined in this study.

Acknowledgements

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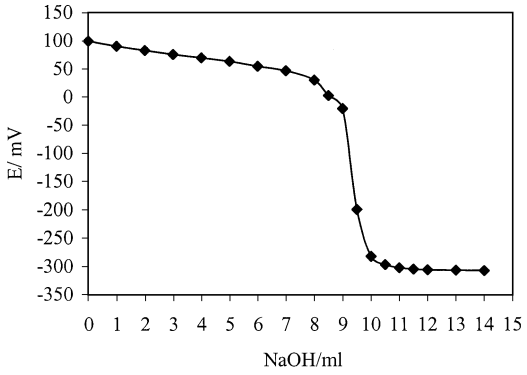

Fig. 6 Titration of 0.1 M HF with 0.1 M NaOH by the use of the hydrogen ion-selective electrode as a potentiometric indicator electrode.

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