Novel Calcium Sensor Based on [2-(2-Hydroxyphenyl)imino]-1,2-diphenylethanone

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Abstract

In this work, a novel calcium PVC-based membrane sensor based on 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone (HD) as a new ionophore is presented. The sensor displays a linear dynamic range between 1.0×10^{-1} and 1.0×10^{-6} M, with a near Nernstian slope of 28.5 ± 0.5 mV per decade and a detection limit of 8.0×10^{-7} M. The best performance was obtained with a membrane composition of 30% poly(vinyl chloride), 62% nitrobenzene, 5% sodium tetraphenyl borate and 3% HD. The potentiometric response of the proposed electrode is independent of the pH of the solution in the pH range of 4.0 –11.5. The sensor possesses the advantages of short conditioning time, fast response time (<20 s), and especially, very good selectivity towards alkali and alkaline earth, and some mono, di and trivalent cations, such as Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Cu^{2+}, Al^{3+}, La^{3+} and Ce^{3+} ions. The electrode can be used for at least 10 weeks without any considerable divergence in the potentials. It was used as an indicator electrode in potentiometric titration of Ca(II) ions with EDTA.

Key words: potentiometry, calcium sensor, PVC membrane, 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone

Introduction

Potentiometric sensors have been shown to be very effective tools for analysis of a wide variety of cations and anions. They are very simple to use, inexpensive, and capable of reliable responses in a wide concentration range.

A wide variety of chemically, clinically or environmentally important analytes are now routinely monitored using ion-selective sensors based on impregnated polymeric membranes.[1–3]

During the past decade, an extensive effort has been made in the synthesis and characterization of neutral ion carriers with high selectivities for specific cations to develop new potentiometric sensors for the monitoring of the respective cations in real samples.[3–5]

Literature survey revealed that a number of Ca(II) membrane sensor based on different ion carrier have been reported.[6–17] Most of these reported calcium sensors have one, two, or in some cases all following problems; A) relatively, high detection limit, B) narrow working concentration range, and finally, C) serious interfering from Na^+, K^+, Sr^{2+}, Ba^{2+},...ions.

We were interested in the preparation of a highly selective and sensitive sensor for determination of Ca(II). We have recently reported a number of highly selective and sensitive membrane sensors for various metal ions.[18–22] In this work, we report a novel Ca(II) membrane sensor base on a new selective ionophore HD (Figure 1).
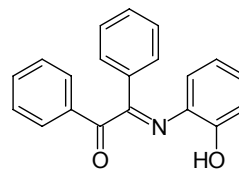

Figure 1. Structure of HD

Experimental

Reagents

Reagent grade benzyl acetate (BA), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF), and high relative molecular weight PVC (all from Merck and Aldrich) were used as received. The nitrate and chloride salts of all cations used (all from Merck and Aldrich) were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. Doubly distilled de-ionized water was used throughout.

Synthesis of HD

The procedure for the preparation of 2-[(2-hydroxyphenyl)imino]-1,2-diphenylethanone: A mixture of benzil (0.01 mol, 2.10 g), 2-aminophenol (0.01 mol, 1.09 g) and catalytic amount of toluene-4-sulfonic acid was refluxed in benzene (70 mL) for 6 h. Then the solvent was evaporated and the residue was crystallized from 95% ethanol as pale yellow crystals, mp 118–120 °C, 2.56 g, yield 85%; IR (KBr) (v_{max}/cm^{-1}): 3246 (br, OH), 1610 (C=O), 1474, 1450, 1344, 1259, 1232, 1092, 1042, 989, 933, 750, 694; MS, m/z (%): 301 (M$^+$, 2), 196 (10), 104 (23), 77 (100), 65 (89), 51 (77), 39 (56). Anal. Calcd. for $C_{20}H_{15}NO_2$: C, 79.72; H, 5.02; N, 4.65. Found: C, 79.7; H, 5.1; N, 4.7%. ^{1}H NMR (80 MHz, acetone-d_6): δ 7.40 (t, J = 7.7 Hz, 1H), 7.43 (t, J = 7.8 Hz, 1H), 7.60–7.90 (m, 8H), 8.00 (t, J = 7.5 Hz, 2H), 8.05 (t, J = 7.4 Hz, 1H), 8.30 (dd, J = 7.7, 2.0 Hz, 2H). ^{13}C NMR: δ 118.0, 122.4, 123.0, 128.6, 129.0, 129.7, 130.0, 130.9, 134.5, and 135.2 (10 CH), 136.5, 139.5, 140.9, and 154.3 (4 C), 163.2 (C=N), 182.1 (C=O).

Electrode preparation

The general procedure to prepare the PVC membrane was to mix thoroughly 30 mg of powdered PVC, 62 mg of plasticizer NB, 5 mg of additive NaTPB, and 3 mg of ionophore HD 4 mL of fresh THF. The resulting mixture was transferred into a glass dish of 2 cm diameter. The solvent was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (3–5mm o.d.) was dipped into the mixture for about 10 s, so that a nontransparent membrane of about 0.3 mm thickness was formed. The tube was then pulled out from the mixture and kept at the room temperature for about 12 h. The tube was then filled with internal filling solution (1.0×10^{-3} M of CaCl$_2$). The electrode was finally conditioned by soaking in a 1.0×10^2 M CaCl$_2$ solution for 24 h.[23-25] A silver/silver chloride wire was used as an internal reference electrode.

The emf measurements

All emf measurements were carried out with the following assembly: Ag–AgCl | internal solution (1.0×10^{-3} M CaCl$_2$) | PVC membrane | sample solution | Hg–Hg$_2$Cl$_2$, KCl (satd.)

A Corning ion analyzer 250pH/mV meter was used for the potential measurements at 25.0 ± 0.1 °C.

Procedure of complexation study of HD and metal ions

Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell made of platinum black, with a cell constant of 0.84 cm^1 was used. In all measurements, the cell was thermostated at the desired temperature 25.0 ± 0.05 °C using a Phywe immersion thermostat. In typical experiments, 50 mL of a metal ion nitrate solution

(1.0×10^4 1.0×10^{-5} M) was placed in water jacketed cell equipped with magnetic stirrer and connected to the thermostat circulaing water at the desired temperature. In order to keep the electrolyte concentration constant during the titration, both the starting solution and titrant had the same metal ion concentration. Then, a known amount of the HD (1.0×10^{-2} – 1.0×10^{-3} M) solution was added in a stepwise manner using a calibrated micropipette. The conductance of the solution was measured after each addition. Addition of the HD was continued until the desired HD-to-metal ion mole ratio was achieved. The 1:1 binding of the metal ions with HD can be expressed by the following equilibrium:

$$M^{n+} + L \xrightleftharpoons{K_f} ML^{n+} \qquad (1)$$
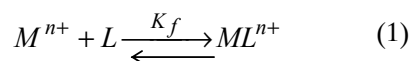
The corresponding equilibrium constant, K_f, is given by

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} \times \frac{f_{(ML^{n+})}}{f_{(M^{n+})} f_{(L)}} \qquad (2)$$

where $[ML^{n+}]$, $[M^{n+}]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free HD and the activity coefficient of the species indicated, respectively. Under the dilute condition we used, the activity coefficient of the unchanged ligand, $f_{(L)}$ can be reasonably assumed as unity.[26] The use of Debye–Hückel limiting law of 1:1 electrolytes,[27] lead to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in equation (2) is canceled out. Thus, the complex formation constant in terms of the molar conductances, Λ, can be expressed as:[28]

$$K_f = \frac{[ML^{n+}]}{[M^{n+}][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \qquad (3)$$

Where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})} \qquad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of HD, Λ_{ML} the molar conductance of the complexed, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the HD added, and C_M the analytical concentration of the metal ion salt. The complex formation constant, K_f and the molar conductance of the complex, Λ_{ML}, were obtained by computer fitting of equations (3) and (4) to the molar conductance-mole ratio data using a nonlinear least-squares program KINFIT.[29]

Results and discussion

Theoretical studies

Many experimental and theoretical investigations have been carried out to better understand the fundamental interaction between metal ions and neutral molecules and their relationship to molecular recognition. Computational models capable of reliably predicting ligand selectivity in a variety of cations have been shown to be valuable tools for the advancement of practical works.[1–4,30–33] In order to have a clear picture about the selectivity of (HD) for various metal ions, in this work, we investigated its binding to Li^+, K^+, Ba^{2+}, La^{3+}, Sr^{2+}, Rb^+, Be^{2+}, Cs^+, Pb^{2+}, Bi^{3+}, and Ca^{2+} ions by using the ab initio theoretical calculations. The influence of the nature, size and charge of metal ions on the complexation reaction with the neutral ligand is explained on the basis of the calculation of gas – phase binding energies.

The molecular structures of the uncomplexed ligand and its complexes with a number of metal ions were optimized using the lanl2mb basis set for all atoms at restricted Harfree Fock (RHF) level. No molecular symmetry constraint was applied. Rather, full optimization of all bond lengths, angles and torsion angles was carried out using the Gaussian 98 program.[34] The binding energy (ΔE) was calculated with the enlarged basis sets using equation (1):

$$\Delta E = E_{complex} - (E_{ligand} - E_{cation}) \qquad (1)$$

Where, $E_{complex}$, E_{ligand} and E_{cation} are the total energies of the complex, uncomplexed HD and metal ion, respectively.

Optimization of the uncomplexed HD was also carried out with the semi-empirical PM_3 method using Hyper Chem software (Version 6.01). No adequate parameterization of the metal ions was available in PM_3, so that semi-empirical calculations could not be carried out on the complexes.

Table 1 summarizes the theoretical data relating the stability of the HD complexes with Li^+, K^+, Ba^{2+}, La^{3+}, Sr^{2+}, Rb^+, Be^{2+}, Cs^+, Pb^{2+}, Bi^{2+}, and Ca^{2+} ions. Inspection of Table 1 reveals that the cation binding energy with HD shows a pronounced dependence on the nature of metal ions used. In fact, the stability of the resulting complexes is expected to decrease in the order $Ca^{2+} > La^{3+} > Sr^{2+} > K^+ > Ba^{2+} > Rb^+ > Cs^+ > Be^{2+} > Li^+ > Bi^{3+} > Pb^{2+}$.

The optimized structures of free HD and its Ca^{2+} complexes are shown in Figure 2 and some of their selected geometric parameters are summarized in Table 2.

As can be seen from Figure 2b, in the complexed form, the benzo groups are not coplanar. It is immediately obvious that while the optimized of free

Table 1. Binding energy of HD with various metal ions.

Metal ion	Total energy of Metal ion /Hartree	Total energy of the complex /Hartree	Binding energy (ΔE) [a]/kcalmol^{-1}
Ca^{2+}	–35.6102894	–994.0233323	–44842.29757
La^{3+}	–29.5417988	–988.287661	–37435.18598
Sr^{2+}	–29.5354119	–987.9049245	–37191.01105
K^+	–27.6277966	–985.8765068	–34721.15034
Ba^{2+}	–24.3878965	–982.7080712	–30699.91969
Rb^+	–23.4435331	–981.6778679	–29460.87908
Cs^+	–19.4792122	–977.7001223	–24477.23235
Be^{2+}	–13.439758	–972.4282974	–17379.40472
Li^+	–7.1354476	–965.5392815	–9100.592466
Bi^{3+}	–3.5615768	–962.5547625	–4985.202866
Pb^{2+}	–2.6011289	–961.1170647	–3480.366439

[a] The total energy of the uncomplexed ligand is –809.625146 Hartree.
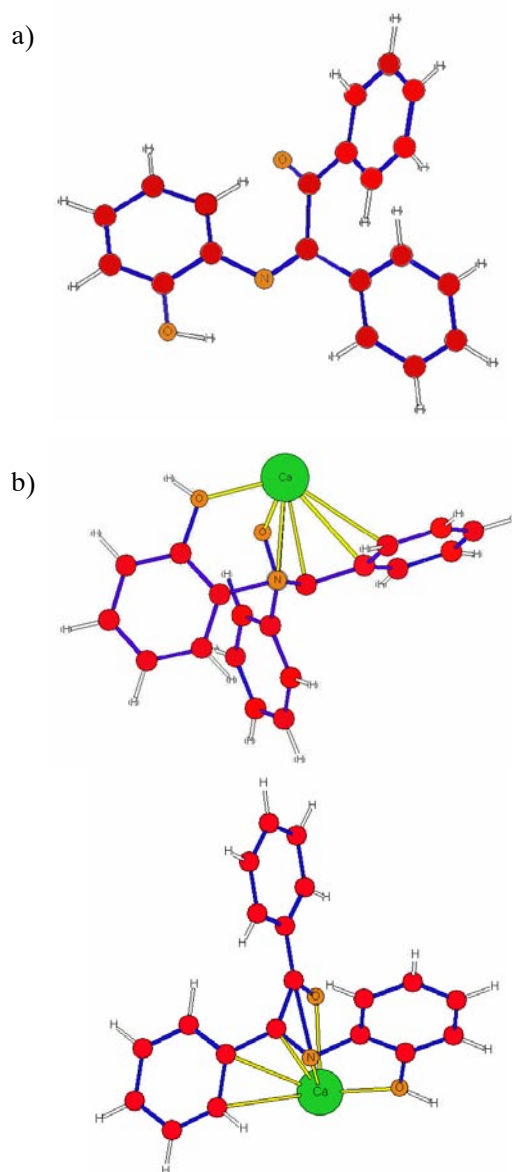
a)

b)

Figure 2. Optimal comformation of HD before (a) and after (b) complexation with Ca^{+2}.

Table 2. Selective Geometric Parameters for Free, and its Ca^{+2} Complex of HD.[a]

	<OCC	<CNC	Torsion angle of <NCCN	Atomic Charge N	Atomic Charge O	N − Ca	O − Ca	<CNCa	<COCa
Ligand Free	120.745	122.072	120.594	−0.265793	−0.060799 −0.208153	−	−	−	−
Complex with a^{+2}	118.103	118.954	107.612	−0.283667	−0.084466 −0.287324	2.5862	2.3357 2.48349	107.022 81.4151	118.088 47.9106

[a] Distances in Å, angles in degrees.

HD structure reveled the N group and the two = O-groups on are far enough from each other to minimize the possible intermolecular repulsive forces.

So that all three donating atoms of the HD will be in suitable proximity of the central metal ion for proper binding interactions. Of course, the contribution of a change in solvation-desolvation energies of the metal ions, in both aqueous and membrane phases on the stability order of the deferent metal ions complexes with HD and can not be ignored. The obtained results revealed that among the different alkaline and earth alkaline ions, Ca^{2+} posses the energy changes for HD.

Stability of various complexes of HD-Metal ions in acetonitrile solution

The stability of the complexes of HD and common alkali and alkalin earth cations were evaluated by conductometric method in acetonitrile solution at 25.0 ± 0.05 °C. The stability constants of the resulting 1:1 complexes are determined by computer fitting of equations (3) and (4) to the molar conductance-mole ratio data using a nonlinear least-squares program KINFIT.[29] The resulted formation constants are illustrated in Table 3. As it is immediately obvious from Table 3, among cations tested, the interaction between HD is very stronger than other common alkali and alkaline earth cations. Thus, it seems may be act as a selective ion carrier in construction of a Ca(II) membrane sensor.

Table 3. The formation constants of $HD - M^{n+}$ complexes.

Cation	Log K_f
Ca^{2+}	4.92 ± 0.08
Mg^{2+}	2.55 ± 0.07
Sr^{2+}	2.65 ± 0.10
Ba^{2+}	2.66 ± 0.12
Na^{+}	2.43 ± 0.09
K^{+}	2.19 ± 0.11

Potential response of the sensors based on HD

The existence of two donating oxygen atoms, as well as one nitrogen-group, in the structure of HD was expected to increase both the stability and selectivity of its complexes with alkali and alkaline earth metal ions, rather than transition and heavy metal ions. Thus, in order to check the suitability of HD as an ion carrier for different metal ions, in preliminary experiments,

it was used to prepare PVC membrane ion-selective electrodes for a wide variety of cations, including alkali, alkaline earth and transition metal ions, the potential response of the most sensitive ion-selective electrodes based on HD are shown in Figure 3.
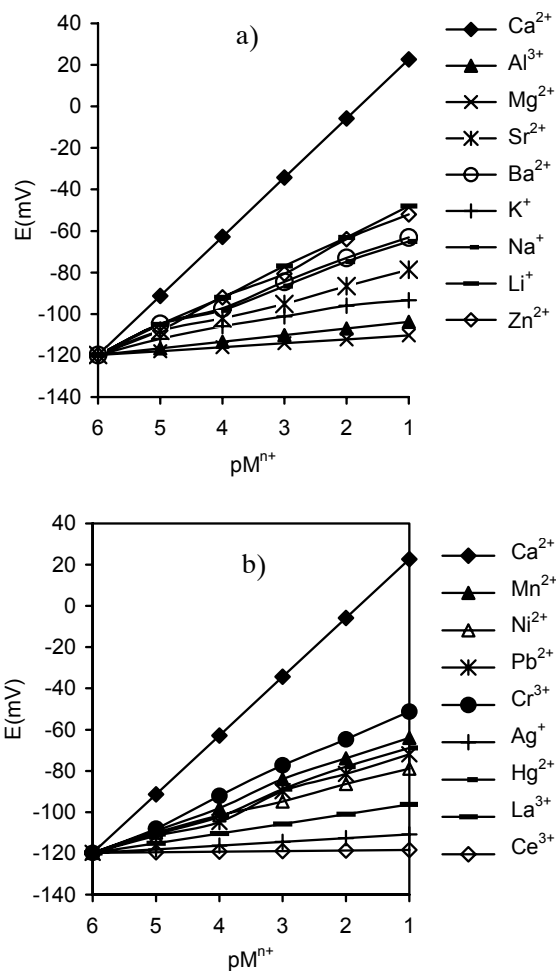
Figure 3. Potential responses of various ion-selective electrodes based on HD.

As can be seen, with the exception of Ca(II) ions, show stronger responses to the HD-based membrane sensors in comparison with the other cations tested. Comparison between the resulting data that shown in Figure 3, and given in Table 3, revealed that, there is a good correlation between the selectivity of HD and its stability complexes.

Table 4. Optimization of membrane ingredients.

No.	Composition (wt.%)				Linear range	Slope (mV/decade)
	PVC	Plasticizer	Ligand	NaTPB		
1	30	NB,68	2	–	$1.0 \times 10^{-2} – 1.0 \times 10^{-6}$	12.5 ± 0.4
2	30	NB,67	3	–	$1.0 \times 10^{-2} – 1.0 \times 10^{-6}$	14.3 ± 0.6
3	30	NB,66	4	–	$1.0 \times 10^{-2} – 1.0 \times 10^{-6}$	13.2 ± 0.3
4	30	NB,65	3	2	$1.0 \times 10^{-1} – 1.0 \times 10^{-6}$	25.6 ± 0.4
5	30	NB,64	3	3	$1.0 \times 10^{-1} – 1.0 \times 10^{-6}$	26.6 ± 0.3
6	30	NB,63	3	4	$1.0 \times 10^{-1} – 1.0 \times 10^{-6}$	27.9 ± 0.8
7	30	NB,62	3	5	$1.0 \times 10^{-1} – 1.0 \times 10^{-6}$	28.5 ± 0.5
8	30	NB,61	3	6	$1.0 \times 10^{-1} – 1.0 \times 10^{-6}$	28.3 ± 0.6
9	30	BA,62	3	5	$1.0 \times 10^{-2} – 1.0 \times 10^{-6}$	23.5 ± 0.5
10	30	NB,65	–	5	$1.0 \times 10^{-2} – 1.0 \times 10^{-6}$	5.5 ± 0.7

Influence of membrane composition on the potential response of the Ca(II) sensor based on HD

The PVC-based membrane sensor based on HD generated stable potential response in aqueous solutions containing calcium ions after conditioning for about 12 h in a 1.0×10^{-2} calcium chloride solution. Table 4 shows the data obtained with membranes having various ratios of different constituents. The potential responses of all of the membrane sensors were studied in a wide range of concentrations of calcium chloride solution. Table 4 shows that the total potentiometric response of the electrode towards Ca(II) ions is dependent on the concentration of the HD that incorporated within the membrane. As can be seen from Table 4, increasing the amount of HD up to 3% resulted in the membranes (No. 2 and 7) that display larger slopes. A maximum slope of 28.5 mV per decade of calcium concentration was observed for the membrane No. 7 with 3% of HD.

It is well established that the presence of lipophilic anions in cation-selective membrane electrodes diminishes the ohmic resistance, enhances the response behavior and selectivity, and increases the sensitivity of the membrane electrodes.[35–39] As can be seen from Table 4, the slope of the sensor in the absence of NaTPB is lower than the expected Nernstian value (membranes nos. 1–3), while, addition of 5% NaTPB will increase the sensitivity of the electrode response considerably, so that the membrane electrode demonstrates a near Nernstian behavior (membrane no. 7). However, the membrane sensor with composition of 30% PVC; 62% NB; 5% NaTPB, and 3% HD exhibits the best performance.

Calibration graph and statistical data

The optimum responses of the sensors based on HD were evaluated after conditioning of the membranes with same composition, for different periods of time in 0.01 M calcium chloride solution. The slope obtained using 12 h of conditioning was closer to the theoretically expected slopes, on the basis of the Nernst equation. Longer conditioning times produced no further improvements in the response. The optimum conditioning solution was determined to have a concentration of about 0.01 M.

The potential response of the Ca(II) PVC-based membrane sensor at varying concentrations of calcium chloride (Figure 4) indicates a linear working concentration range from 1.0×10^{-1} to 1.0×10^{-6} M. The slope of the calibration graph was 28.5 ± 0.5 mV per decade of calcium ions concentration. The detection limit of the sensor that determined from the intersection of the two extrapolated segments of the calibration graph was 8.0×10^{-7} M (32 ng per mL). The standard deviation for ten replicate measurements was ± 0.5 mV.
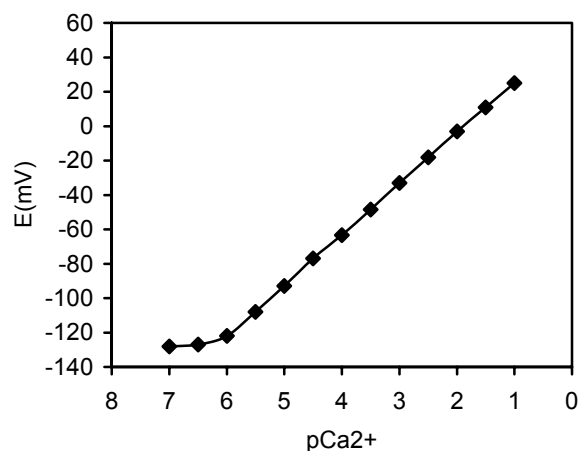
Figure 4. Calibration curve of the calcium electrode based on HD.

Life-time study

For evaluation of stability and lifetime of the proposed membrane sensor, four same electrodes were chosen and tested over a period of 12 weeks. During this period, the electrodes were used over extended period of time (one hour per day). After 10 weeks, a slight gradual decrease in the slopes (from 28.5 to 25.7 mV per decade) was observed.

Effect of pH of solution on the response of the sensor

The pH dependence of the membrane electrode was evaluated over a pH range of 1.0 – 12.5 at a 1.0×10^{-3} M of calcium ion concentration and the results are depicted in Figure 5. As can be seen, the potential remains fairly constant in the pH range of 4.0 – 11.5 (the pH of the solutions was adjusted by either HNO_3 or NaOH solutions). Beyond this range, a gradual change in the potential was detected. The observed potential drift at the higher pH values could be due to the formation of some hydroxyl complexes of Ca(II) and insoluble calcium hydroxide, that in both cases, the concentration of free Ca(II) reduces in the solution. At the lower pH values than 4, the potentials increase, indicating that the membrane sensor responds to hydrogen ions protonation of nitrogen atom in structure of HD.
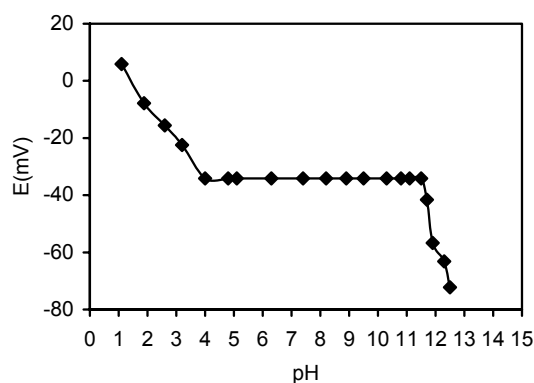
Figure 5. The effect of the pH of the test solution on the potential response of the calcium sensor.

Dynamic response time of the Ca(II) sensor

Dynamic response time is an important factor for any ion-selective electrode. In this study, the practical response time was recorded by changing the concentration of calcium ion in solution in the range of 1.0×10^{-6} to 1.0×10^{-1} M and the results are shown in Figure 6. As can be seen, in the whole concentration range the electrode reaches its equilibrium response, very fast (<20 s).

Selectivity of the sensor

Potentiometric selectivity coefficients of the sensor were determined by the matched potential method.[38] According to this method, a specified activity (concentration) of primary ions (A, 5.0×10^{-5} M of calcium ions) is added to a reference solution (1.0×10^{-6} M of calcium ion) and the potential is measured. In a separate experiment, interfering ions (B, 1.0×10^{-1} M) are successively added to an identical reference solution, until the measured potential matches the one obtained before adding primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K^{MPM} = a_A/a_B$.
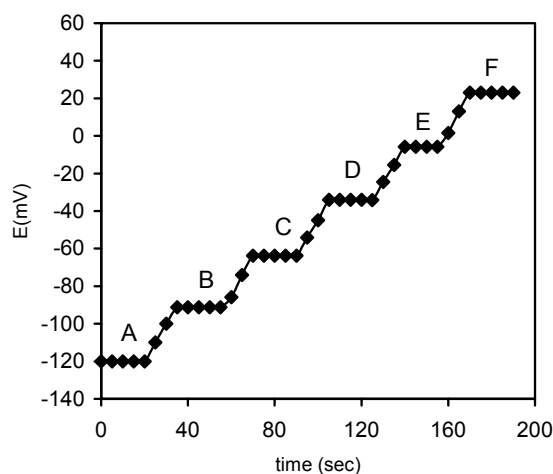
Figure 6. Dynamic response time of the calcium electrode for step changes in the concentration of Ca^{2+}: A) 1.0×10^{-6} M, B) 1.0×10^{-5} M, C) 1.0×10^{-4} M, D) 1.0×10^{-3} M, E) 1.0×10^{-2} M, F) 1.0×10^{-1} M.

The resulting potentiometric selectivity coefficients values are summarized in Table 5. The data given in Table 5, revealed that the proposed Ca(II) membrane sensor is highly selective with respect to most of alkali and alkaline earth ions. The surprisingly high selectivity of the membrane electrode for calcium ions over other cations used, most probably arises from the strong tendency of the carrier molecules for calcium ions.

Table 5. Selectivity coefficients of various interfering ions.

| Ions	$K^{MPM}_{Ca^{2+},M}$	Ions	$K^{MPM}_{Ca^{2+},M}$
Mg^{2+}	2.5×10^{-5}	Mn^{2+}	7.0×10^{-4}
Sr^{2+}	3.5×10^{-4}	Ni^{2+}	1.0×10^{-4}
Ba^{2+}	7.5×10^{-4}	Pb^{2+}	5.4×10^{-4}
Li^+	3.1×10^{-3}	Cr^{3+}	2.1×10^{-4}
Na^+	8.2×10^{-4}	Ag^+	3.5×10^{-4}
K^+	1.1×10^{-4}	Hg^{2+}	6.1×10^{-4}
La^{3+}	2.5×10^{-4}	Al^{3+}	3.0×10^{-5}
Ce^{3+}	2.1×10^{-5}	Zn^{2+}	1.1×10^{-3}

Table 6 compared the selectivity coefficients of the proposed sensor with those of the best previously reported calcium sensors. It is immediately obvious, the selectivity coefficients of the electrode for all cations, is superior to those reported for the calcium ion-selective membrane electrodes.[6–15]

Analytical application

The selective calcium membrane sensor was used as an indicator electrode in titration of 1.0×10^{-4} M solution of calcium ions with a standard 1.0×10^{-2} M EDTA and the resulting titration curve is shown in Figure 7. As can be seen from Figure 7, the sensor can monitor the amount of calcium ions.

Table 6. Comparison of the selectivity coefficients of different Ca(II) electrodes.

Ref	Method	$\log K^{MPM}_{Ca^{2+},M}$							
		Mg²⁺	Sr²⁺	Ba²⁺	Na⁺	Li⁺	K⁺	NH₄⁺	H⁺
6	SSM	–	–	–	+0.5	–0.3	+1.4	–	+2.1
7	SSM	–0.4	+0.1	+0.4	–0.8	–1.3	+0.2	–	–
8	FIM	–1.5	–	–	–1.2	–	–2.1	–	–
9	FIM	–1.3	–0.8	–0.1	–0.2	–0.8	–0.2	–	–
10	FIM	–0.4	–0.2	–0.2	–0.2	–0.4	–0.1	–	–
11	FIM	–1.6	–	–	–	–	–	–	–
12	FIM	–1.7	–	–	–4.5	–4.9	–	–4.5	–
13	SSM	–4.3	–	–	–5.8	–5.7	–6.7	–	–3.1
14	SSM	–5.0	–	–	–4.1	–4.1	–4.4	–	–3.6
15	FIM	–4.8	–	–	–2.3	–	–3.2	–	–
This work	MPM	–4.6	–3.5	–3.1	–3.1	–2.5	–4.0	–	–
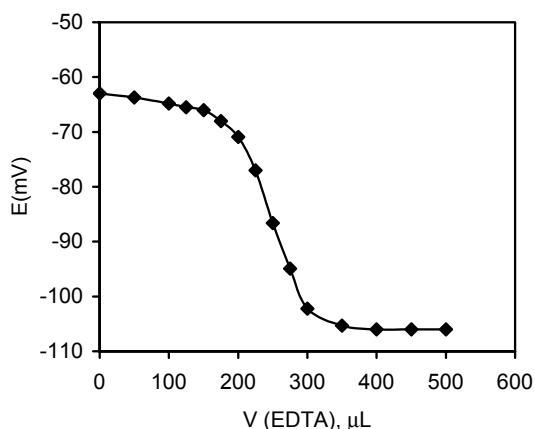
Figure 7. Potentiometric titration curve of 25.0 mL 1.0×10^{-4} M solution of Ca^{2+} with 1.0×10^{-2} M of EDTA.

Acknowledgements

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Povzetek

V delu predstavljamo nov membranski senzor za kalcijeve ione, ki temelji na PVC membrane z ionoforom 2-[(2-hidroksifenil)imino]-1,2-difeniletanonom (HD). Senzor se linearno odziva v območju med $1,0 \times 10^{-1}$ in $1,0 \times 10^{-6}$ M, z naklonom $28,5 \pm 0,5$ mV na dekado in mejo določljivosti $8,0 \times 10^{-7}$ M. Optimalne lastnosti smo dosegli z membrano naslednje sestave: 30% poli(vinil klorida), 62% nitrobenzene, 5% natrijevega tetrafenilborata in 3% HD. Potenciometrični odziv elektrode je neodvisen od pH v območju 4,0 – 11,5. Čas kondicioniranja je kratek, odzivni čas je <20 s, selektivnost v primerjavi z vrsto ionov alkalijskih in zemeljsko alkalijskih kovin ter nekaterih mono, di in trivalentnih kationov (Li^+, Na^+, K^+, Mg^{2+}, Sr^{2+}, Ba^{2+}, Ag^+, Cu^{2+}, Al^{3+}, La^{3+} in Ce^{3+}), je primerna. Uporabnost kolone je najmanj 10 tednov po pripravi. Uporabili smo jo kot indikatorsko elektrodo pri potenciometrični titraciji Ca(II) ionov z EDTA.