DYSPROSIUM(III) ION-SELECTIVE ELECTROCHEMICAL SENSOR BASED ON 6-HYDRAZINO-1,5-DIPHENYL-6,7-DIHYDROPYRAZOLO-[3,4-*d*]PYRIMIDINE-4(5*H*)-IMINE

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Received September 9, 2006
Accepted December 12, 2006

A Dy(III) ion-selective electrode based on 6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo-[3,4-*d*]pyrimidine-4(5*H*)-imine (HDDPI) as an excellent sensing material was developed. The sensor exhibits a Nernstian behavior (a slope of 19.6 ± 0.3 mV per decade) over a wide concentration range (from 1.0×10^{-1} to 8.0×10^{-7} M Dy) with a detection limit of 4.2×10^{-7} M. The sensor response is independent of pH of the solution in the pH range 3.5–8.3. The sensor possesses the advantages of short conditioning time, fast response time (<10 s) and in particular, good selectivity and sensitivity to the dysprosium ion in the presence of a variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The sensor also showed a great enhancement in selectivity coefficients for dysprosium ions, in comparison with the formerly mentioned dysprosium sensors. The electrode can be used for at least 10 weeks without any considerable divergence in the potentials. The proposed electrode was successfully used as an indicator electrode in potentiometric titration of Dy(III) ions with EDTA. The membrane sensor was also used in the determination of concentration of F^- ions in some mouth washing solutions and in the Dy^{3+} recovery from solution.

Keywords: Potentiometry; Dysprosium sensors; ISEs; 6-Hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-*d*]pyrimidine-4(5*H*)-imine; Metal ions complexation.

At present, analysis and determination of lanthanides consist of essential issues, on the grounds that lanthanides show similar chemical and physical properties. For the determination of each one of them, first separation along with purification, and even sometimes preconcentration, are necessary steps[1]. Dysprosium is one of the lanthanides widely used as a fluorescence and magnetic material, magnetic material as well as in the field of life science. As already mentioned, the difficulty degree of the lanthanides determination is high. Therefore, a sensitive and selective method is required in order to gain a precise result. Several methods have been used for the Dy^{3+} determination like spectrometry[2–5], inductively coupled plasma[6,7]

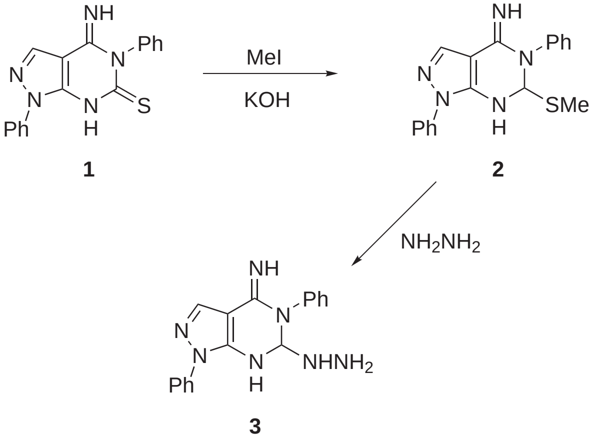
Collect. Czech. Chem. Commun. 2007, Vol. 72, No. 9, pp. 1189–1206

doi:10.1135/cccc20071189

(ICP), chromatography[8,9], electrochemistry[10,11], resonance light scattering[12] (RLS) and capillary zone electrophoresis coupled with cloud point extraction[13]. Despite the fact that these methods are precise and sensitive, they are also expensive and time-consuming. Another method for the determination of this element is the ion selective electrode (ISE) for Dy(III) potentiometric titration. The ISEs work fast and they are easily prepared without any special or expensive equipment.

We have currently developed some ISEs for the potentiometric determination of lanthanides, where polymeric membranes were prepared with increasingly selective ionophores, sensing analyte selectively. The ISEs include in particular; terbium(III)[14], ytterbium(III)[15], samarium(III)[16], lanthanum(III)[17], cerium(III)[18] and gadolinium(III)[19] sensors. Nevertheless, there is only a limited number of reports concerning the development of highly selective ionophores for dysprosium in literature[20–22].

This study describes another ion selective sensor for Dy(III) potentiometric determination based on 6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-*d*]pyrimidine-4(5*H*)-imine (HDDPI), as a novel neutral ionophore (Scheme 1, compound **3**). Three noticeable benefits demonstrated by this sensor are the fast response time, low detection limit and also great selectivity.



SCHEME 1
General procedure for the HDDPI synthesis

EXPERIMENTAL

Reagents

Merck Chemical and the Aldrich Co. were the suppliers of the nitrate and chloride salts of all cations and the reagent grades of 2-nitrophenyl octyl ether (NPOE), dibutyl phthalate (DBP), nitrobenzene (NB), sodium tetraphenylborate (NaTPB), tetrahydrofuran (THF) and high-molecular-weight PVC. All reagents were used without any modification. Nitrates and chlorides of the employed cations were of the highest available purity. They were vacuum-dried over P_2O_5. Triply distilled deionized water was used in experiments.

HDDPI Synthesis

6-(Methylsulfonyl)-1,5-diphenyl-6,7-dihydropyrazolo[3,4-d]pyrimidine-4(5H)-imine (**2**): 4-iminio-1,5-diphenyl-4,5-dihydropyrazolo[3,4-*d*]pyrimidine-6(7*H*)-thione (**1**; 5 mmol) and methyl iodide (5 mmol) were dissolved in EtOH (20 ml) and H_2O (15 ml), contaning KOH (10 mmol). The reaction mixture was stirred at room temperature for 5 h. Then, the crude product was filtered off and recrystallized from ethanol to give compound **2** in 70% yield, m.p. 162–163 °C. ^{1}H NMR (DMSO-d_6): 2.7 (S, 3 H, CH_3); 7.2–8.1 (m, 11 H, arom.); 9.6 (s, 1 H, NH, exchangeable with D_2O). MS, *m/z*: 333 (M^+). For $C_{18}H_{15}N_5S$ (333.0) calculated: 64.84% C, 4.53% H, 21.01% N, 9.62% S; found: 64.87 C, 4.48 H, 20.97 N, 9.65% S.

6-Hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-d]pyrimidine-4(5H)-imine (**3**): 6-(methylsulfonyl)-1,5-diphenyl-6,7-dihydropyrazolo[3,4-*d*]pyrimidine-4(5*H*)-imine (**2**; 1 mmol) and hydrazine hydrate were heated at 60 °C in ethanol (10 ml) for 8 h. Then, the precipitate was filtered off and recrystallized from ethanol to give compound **3** in 62% yield, m.p. 221–223 °C. ^{1}H NMR (DMSO-d_6): 4.7 (s, 1 H, NH, exchangeable with D_2O); 6.8–8.2 (m, 11 H, arom.); 4.7 (s, 1 H, NH, exchangeable with D_2O); 9.2 (s, 1 H, NH, exchangeable with D_2O). MS, *m/z*: 317 (M^+). For $C_{17}H_{15}N_7$ (317.4) calculated: 64.34% C, 4.76% H, 30.90% N; found: 64.36% C, 4.72% H, 30.86% N.

Electrode Preparation

The PVC membrane preparation involved blending of the following compounds; 30 mg of powdered PVC, 63 mg of NPOE and 2 mg of NaTPB in 5 ml THF. To this solution, 5 mg of HDDPI was added and mixed well. Then, the resulting mixture was transferred into a glass dish of 2 cm in diameter. A Pyrex tube (5 mm o.d.) was dipped into the mixture for about 5 s, leading to the formation of a transparent membrane (about 0.3 mm in thickness). Afterwards, the tube was removed from the mixture, kept at room temperature for at least 12 h and filled with an internal filling solution (1.0×10^{-3} M $DyCl_3$). Eventually, the electrode was conditioned for 24 h by soaking in 1.0×10^{-2} M $DyCl_3$ [23–31]. A silver/silver chloride electrode was used as an internal reference electrode.

The emf Measurements

The equipment for the electromotive force (emf) measurements consisted of: (i) Ag–AgCl| internal solution, 1.0×10^{-3} M $DyCl_3$|PVC membrane|sample solution|$Hg–Hg_2Cl_2$, KCl (sat.), (ii) a Corning ion analyzer with a 250 pH/mV meter and (iii) a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. The potential measurements were performed at 25.0 °C.

Complexation Study

Conductivity measurements were carried out with a Metrohm 660 conductivity meter. A dip-type conductivity cell made of black platinum was used with a cell constant of 0.83 cm^{-1}. In all measurements, the cell was thermostatted at the desired temperature 25.0 °C, using a Phywe immersion thermostat.

In a typical experiments, 25 ml of a cation nitrate solution (1.0×10^{-4} M) was placed in a water jacketed cell, equipped with a magnetic stirrer and connected to a water thermostat. In order to keep the electrolyte concentration constant during titrations, both the starting solution and the titrant had the same cation concentration. Then, a known amount of the HDDPI (1.0×10^{-2} M) solution was added stepwise using a calibrated micropipette. The solution conductance was measured after each addition. The HDDPI addition was continued until the desired HDDPI/cation mole ratio was achieved. The 1:1 binding of the cations with HDDPI can be expressed by the following equilibrium:

$$M^{n+} + L \xrightleftharpoons{K_f} ML^{n+}. \tag{1}$$

The corresponding equilibrium constant, K_f, is given by

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

where $[ML^{n+}]$, $[M^{n+}]$, [L] and f represent the equilibrium molar concentration of complexes, free cation, free HDDPI and the activity coefficient of the species indicated, respectively. Under the dilution conditions, the activity coefficient of the uncharged ligand, $f_{(L)}$ can be reasonably assumed as unity[32]. The use of Debye–Hückel limiting law for 1:1 electrolytes[33], leads to the conclusion that $f_{(M^{n+})} \approx f_{(ML^{n+})}$, so the activity coefficient in Eq. (2) is canceled out. Thus, the complex formation constant in terms of molar conductance Λ, can be expressed as[34]:

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

where

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

Here, Λ_M is the molar conductance of the cation before the HDDPI addition, 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 added HDDPI and C_M the analytical concentration of the cation salt. The complex formation constant, K_f, and the molar conductance of the complex, Λ_{ML}, were obtained by computer-fitting Eqs (3) and (4) to the molar conductance-mole ratio data, using a nonlinear least-squares program KINFIT[35].

RESULTS AND DISCUSSION

HDDPI Complexation with Some Cations in Acetonitrile

In primary experiments, the interaction of HDDPI (with seven nitrogen donor atoms) with a number of metal ions was investigated in an acetonitrile solution using the conductometric method. The associated results illustrated that the ligand/cation mole ratio is 1 in all cases. The formation constants (K_f) of the resulting 1:1 complexes were evaluated by computer-fitting the molar conductance-mole ratio data to the appropriate equations. The results are summarized in Table I. The obtained formation constants revealed that HDDPI could be used as an excellent ion carrier for the construction of a selective Dy(III) membrane sensor.

TABLE I
The formation constants of HDDPI–M^{n+} complexes

Cation	log K_f	Cation	log K_f
Dy^{3+}	5.46 ± 0.08	Na^+	<2
Ce^{3+}	2.93 ± 0.05	K^+	<2
La^{3+}	<2	Ca^{2+}	<2
Eu^{3+}	3.56 ± 0.01	Sr^{2+}	<2
Gd^{3+}	<2	Co^{2+}	<2
Sm^{3+}	2.65 ± 0.11	Ni^{2+}	<2
Nd^{3+}	<2	Cd^{2+}	<2
Cr^{3+}	2.83 ± 0.02	Cu^{2+}	2.14 ± 0.04
Fe^{3+}	<2	Zn^{2+}	2.21 ± 0.07

Response of the HDDPI-Based Sensors to Dy(III) Ions

HDDPI was used as a neutral ion carrier to prepare a number of membrane sensors for some metal ions. Then, their potential responses were measured the results are shown in Figs 1a, 1b and 1c. It can be seen that the HDDPI-based membrane displays a Nernstian response to the concentration of Dy(III) ions in a wide concentration range.

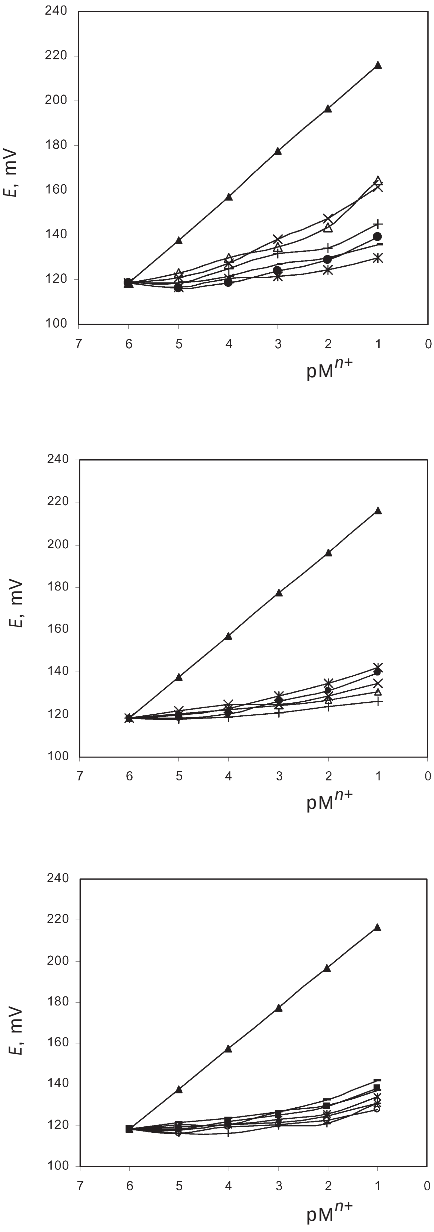


FIG. 1

Potential responses of various ion-selective electrodes based on HDDPI. a: ▲ Dy, ● Nd, × Eu, ∗ Gd, △ Sm, | Ce, - La; b: ▲ Dy, △ Co, × Zn, ∗ Cu, ● Cd, | Ni; c: ▲ Dy, ■ Pb, × Na, ○ Mg, | Ca, - Fe, – Cr

Membrane Composition Effect on the Potential Response of the HDDPI-Based Dy(III) Sensor

Since the sensitivity and selectivity for a given ionophore depend significantly on the membrane ingredients, the nature of the solvent mediator and the additive[36–46], the influence of membrane composition on the potential response of the Dy(III) sensor was investigated. The data reported in Table II demonstrate that an ionophore amount increase up to 5% in the presence of 2% NaTPB and 63% polar solvent (NPOE) results in the achievement of the optimum sensitivity. Generally speaking, the presence of lipophilic anions in a cation-selective membrane based on a neutral carrier not only diminishes the ohmic resistance and enhances the response behavior and selectivity, but also, in cases where the extraction capability is poor, increases the membrane electrode sensitivity[46–50]. However, the membranes with the composition 30% PVC, 5% HDDPI, 2% NaTPB and 63% NPOE show a Nernstian potential response.

TABLE II
Optimization of membrane composition (wt.%)

Sensor No.	PVC	Plasticizer	HDDPI	NaTPB	Slope mV/decade	Dynamic linear range mol/l
1	30	NPOE,68	2	0	7.3 ± 0.4	$4.3 \times 10^{-2} - 1.0 \times 10^{-4}$
2	30	NPOE,66	2	2	12.5 ± 0.6	$5.0 \times 10^{-1} - 1.0 \times 10^{-5}$
3	30	NPOE,64	4	2	17.3 ± 0.7	$1.0 \times 10^{-1} - 2.5 \times 10^{-6}$
4	30	NPOE,63	5	2	19.6 ± 0.3	$1.0 \times 10^{-1} - 8.0 \times 10^{-7}$
5	30	NPOE,62	5	3	18.2 ± 0.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
6	30	NPOE,62	6	2	17.9 ± 0.4	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
7	30	NB,63	5	2	17.5 ± 0.6	$1.0 \times 10^{-1} - 1.0 \times 10^{-6}$
8	30	DBP,63	5	2	16.7 ± 0.7	$1.0 \times 10^{-1} - 5.0 \times 10^{-6}$

Calibration Graph and Statistical Data

The potential response of the developed HDDPI-based sensor (composition No. 4) shows a linear response to the concentration of Dy ions in the range 8.0×10^{-7}–1.0×10^{-1} M Dy (Fig. 2). The results may be summarized as follows. The calibration graph slope is 19.6 ± 0.3 mV per decade of the Dy(III) concentration. The detection limit of the sensor, as determined from the intersection of the two extrapolated segments of the calibration graph, is 4.2 × 10^{-7} M. The standard deviation of eight replicate measurements is ±0.4 mV.

It should be noted that the observed detection limits are usually affected by the presence of other interfering ions or impurities. So, if metal buffers are used to eliminate such effects, which lead to the contamination of very dilute solutions, the detection limit can be enhanced down to 10^{-10} M.

Recently, it was shown that the lower detection limit is not an inherent property of ISEs, and is determined by a small flux of primary ions from the organic sensing membrane into its aqueous surface layer[51–53]. As a consequence, a constant low activity, a_{ilim}, of the primary ion (i) is maintained in this surface layer even when the activity of (i) in the sample, a_{i}, is lower than a_{ilim} [54–56]. This small flux of the target ions has been successfully eliminated by choosing an internal solution with a constant low activity of (i) and a high one of an interfering ion (j)[57–59].

Originally, internal solutions with ion buffers (e.g., EDTA) were used for this purpose. Obviously, this is not feasible with cations such as alkali metal and ammonium ions as well as many anions for which no appropriate complexing agents are available. Another method to avoid leaching of primary ions from the membrane into the sample makes use of an externally applied current that generates a steady flux of cations toward the inner compartment of the ISE [60]. Although this method does not require any

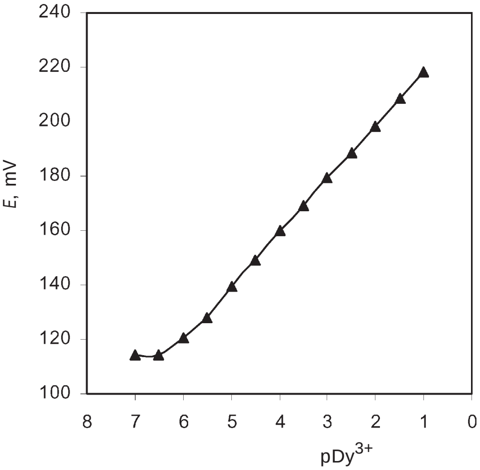


FIG. 2
Calibration curve of the dysprosium electrode based on HDDPI

complexing reagents, it needs more sophisticated instrumentations and measurement procedures and is, therefore less appropriate for routine applications.

Ions leaching from the membrane into the sample not only influences the lower detection limits of ISEs, but also bias the selectivity coefficients since they may be potential determining even if measurements are taken in pure solutions of a strongly discriminated ion[61–66]. It was found that the thus-obtained selectivity coefficients represent upper limits rather than true (thermodynamic) values, which may be better by many orders of magnitude than those determined by conventional methods[61].

Pretsch et al. added a cation-exchange resin to the internal solution of ISEs to keep the primary ion activity at a constant low level. The results showed that the lower detection limit is improved and true selectivities are obtained for a valinomycin-based K^+-ISE. The general applicability of the method is demonstrated by improving the lower detection limits of NH^{+4}, Pb^{2+}, Cd^{2+} and Ca^{2+}-ISEs [67]. Michalska et al. reduced the detection limit of a conducting polymer (CP) poly(pyrrole)-based potentiometric chloride-selective electrode over three orders of magnitude by appling anodic current of density in the range of microamperes per centimeter squared[68].

In 2003, Pretsch et al. devised a new technique for improving the detection limits of ISEs, by the incorporation of liphophilic particles such as silica gel 100 C18-reversed phase 40–63 μm (230–400 mesh ASTM) into the sensing membrane of ion-selective membrane sensors that strongly influences the uptake of ions from the sample solution. The apparent super-Nernstian response of ISEs caused by a strong flux of the target ions from the sample to the inner filling solution can be completely suppressed. The mentioned effect opens up new possibilities for the trace-level detection of ions. Figure 10 in ref.[69] shows the optical microscope images of the two sides of a typical ion-selective membrane sensor with 16 wt.% of silica gel focusing on the particles through the transparent membrane again shows that they are closely packed[69].

Life-Time Study

The stability and life-time evaluation of the recommended membrane sensor required four electrodes. They were tested for a period of 12 weeks, during which the electrodes were used extensively (one hour per day)[70,71]. After 10 weeks, a slight gradual decrease in the slopes (from 19.6 to 17.8 mV per decade) was observed.

pH Effect on the Electrode Response

For the study of the pH effect on the sensor performance, the potentials were determined in the pH range 2.0–11.0 (pH was adjusted with concentrated NaOH or HCl) at the concentration of the Dy(III) solution 1.0×10^{-3} M. The resulting data are depicted in Fig. 3. Evidently, the potential response of the sensor remains constant in the pH range 3.5–8.3. At pH values lower than 3.5, a potential increase was noticed. This phenomenon is attributed to the membrane response to hydronium ion (protonation of nitrogen atoms in acid media). At pH values greater than 8.3, a potential decrease took place, owing to the formation of insoluble dysprosium hydroxide.

Dynamic Response Time of the Dy(III) Sensor

Generally, dynamic response time is a significant parameter for any ion-selective electrode. In this research, the practical response time of the recommended sensor was recorded by changing the dysprosium ion concentration in a series of solutions from 1.0×10^{-6} to 1.0×10^{-1} M. The presented data in Fig. 4 illustrate that the sensor reaches its equilibrium response quickly (<10 s) in the whole concentration range.

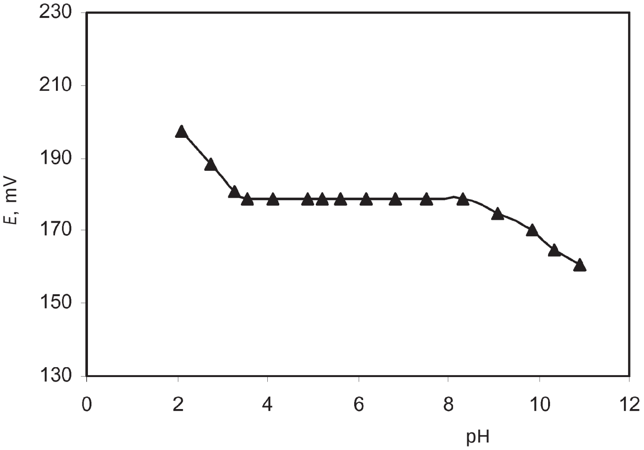


FIG. 3
The pH effect of test solutions (1.0×10^{-3} M) on the potential response of the dysprosium sensor

Dy(III) Electrode Selectivity

The influence of interfering ions on the response behavior of any ion-selective sensor is usually described in terms of selectivity coefficients, K_{sel}. In this work, selectivity coefficients were determined by the matched potential method (MPM)[72–76]. According to this method, a specified activity (concentration) of primary ions (A, 5.0×10^{-5} M Dy ions) is added to a reference solution (1.0×10^{-6} M Dy) 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 the primary ions addition. The matched potential method selectivity coefficient, K^{MPM}, is then given by the ratio of activities (concentration) of the resulting primary ion to those of interfering ion $K^{MPM} = a_A/a_B$.

The resulting potentiometric selectivity coefficients values are summarized in Table III. For all diverse ions, the selectivity coefficients of the electrode are of the order of 1.0×10^{-3} or smaller, indicating that they would not significantly disturb the function of the Dy(III) selective membrane sensor. Table III also shows the selectivity coefficient of the membrane without ionophore. In the absence of the ionophore in the membrane the

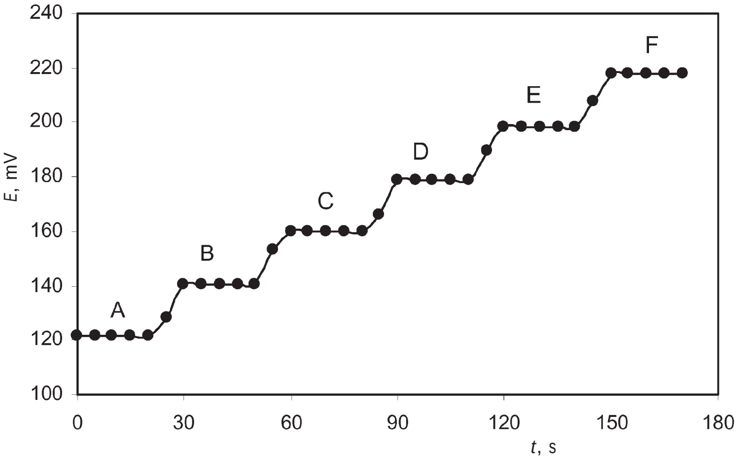


FIG. 4
Dynamic response time of the dysprosium electrode for step changes in the Dy^{3+} concentration (in M): A 1.0×10^{-6}, B 1.0×10^{-5}, C 1.0×10^{-4}, D 1.0×10^{-3}, E 1.0×10^{-2}, F 1.0×10^{-1}

selectivity coefficients are very high, which is due to the ability of the interfering ions to extract from aqueous solution into the organic layer by interaction with the additive. It is also worth noticing that the Dy(III) sensor response was found to be insensitive to the nature of the used anions.

TABLE III
Selectivity coefficients of various interfering ions for the membrane (sensor No. 4)

Ions	$K^{\mathrm{MPM}}_{\mathrm{Dy}^{3+},\mathrm{B}}$ [a]	$K^{\mathrm{MPM}}_{\mathrm{Dy}^{3+},\mathrm{B}}$	Ions	$K^{\mathrm{MPM}}_{\mathrm{Dy}^{3+},\mathrm{B}}$ [a]	$K^{\mathrm{MPM}}_{\mathrm{Dy}^{3+},\mathrm{B}}$
Eu^{3+}	7.3×10^{-1}	1.3×10^{-3}	Cd^{2+}	1.2×10^{-1}	5.6×10^{-4}
Nd^{3+}	8.5×10^{-1}	2.7×10^{-4}	Cu^{2+}	1.3×10^{-1}	6.2×10^{-4}
Sm^{3+}	6.0×10^{-1}	1.0×10^{-3}	Zn^{2+}	3.5×10^{-1}	2.9×10^{-4}
Gd^{3+}	4.0×10^{-1}	1.0×10^{-5}	Ni^{2+}	2.2×10^{-1}	1.0×10^{-4}
La^{3+}	4.8×10^{-1}	2.8×10^{-4}	Pb^{2+}	2.1×10^{-1}	5.8×10^{-4}
Ce^{3+}	6.0×10^{-1}	1.0×10^{-4}	Na^{+}	1.3×10^{-2}	2.5×10^{-4}
Cr^{3+}	5.3×10^{-1}	7.3×10^{-4}	K^{+}	2.1×10^{-2}	2.1×10^{-4}
Fe^{3+}	4.7×10^{-1}	6.4×10^{-4}	Mg^{2+}	2.2×10^{-1}	1.6×10^{-4}
Co^{2+}	4.1×10^{-1}	2.3×10^{-4}	Ca^{2+}	3.5×10^{-1}	1.5×10^{-4}

[a] The selectivity coefficients for the membrane without ionophore.

Furthermore, Table IV compares the selectivity coefficients of the Dy(III) sensor with those of the best formerly Dy(III) electrodes in the literature[20–22]. From the reported data in Table IV, it is instantly clear that the concentration range, response time, detection limit of the proposed electrode and also selectivity coefficients of the sensor are superior to those found by other researchers.

Analytical Application

The developed Dy^{3+} ion-selective electrode was found to work well under laboratory conditions. It was used as an indicator electrode in the titration of 1.0×10^{-4} M dysprosium ions solution with a standard 1.0×10^{-2} M EDTA. The resulting titration curve is shown in Fig. 5. Evidently, the sensor is capable of monitoring the dysprosium ion amount.

This electrode was also effectively used in the direct dysprosium detection in tap water and river water. The 10.0 ml wastewater was taken and di-

TABLE IV
Comparison of selectivity coefficients (MPM), linearity range, detection limit and response time of the Dy(III) electrode and the previously reported Dy(III) PVC-membrane sensors

Ion	Ref.[20]	Ref.[21]	Ref.[22]	This work
Eu^{3+}	4.0×10^{-4}	–	–	1.3×10^{-3}
Nd^{3+}	3.5×10^{-4}	–	–	2.7×10^{-4}
Sm^{3+}	2.0×10^{-4}	2.1×10^{-2}	–	1.0×10^{-3}
Gd^{3+}	1.0×10^{-5}	2.5×10^{-2}	–	1.0×10^{-5}
La^{3+}	3.0×10^{-4}	1.7×10^{-2}	–	2.8×10^{-4}
Ce^{3+}	1.5×10^{-4}	1.8×10^{-2}	–	1.0×10^{-4}
Cr^{3+}	–	–	–	7.3×10^{-4}
Fe^{3+}	–	–	–	6.4×10^{-4}
Co^{2+}	–	3.9×10^{-3}	–	2.3×10^{-4}
Cd^{2+}	–	–	–	5.6×10^{-4}
Cu^{2+}	1.5×10^{-5}	6.3×10^{-3}	–	6.2×10^{-4}
Zn^{2+}	–	–	–	2.9×10^{-4}
Ni^{2+}	–	4.1×10^{-3}	2.99×10^{-4}	1.0×10^{-4}
Pb^{2+}	8.0×10^{-4}	5.0×10^{-3}	–	5.8×10^{-4}
Na^{+}	2.0×10^{-3}	–	2.99×10^{-4}	2.5×10^{-4}
K^{+}	–	–	2.17×10^{-4}	2.1×10^{-4}
Mg^{2+}	3.0×10^{-5}	–	3.13×10^{-4}	1.6×10^{-4}
Ca^{2+}	–	–	2.17×10^{-4}	1.5×10^{-4}
Response time, s	<20	<20	~10	<10
Linearity range, mol/l	1.0×10^{-6}–1.0×10^{-2}	1.0×10^{-5}–1.0×10^{-1}	8.0×10^{-6}–1.0×10^{-1}	8.0×10^{-7}–1.0×10^{-1}
Limit of detection, mol/l	8.0×10^{-7}	6.0×10^{-6}	2.0×10^{-6}	4.2×10^{-7}

luted with distilled water in a 25.0 ml volumetric flask. The potential of this solution was measured by the proposed sensors. The resulting data are summarized in Table V. It was found that the accuracy of dysprosium detection in different solution samples is almost quantitative.

Furthermore, the electrode was used in the potentiometric determination of fluoride ions in two mouthwash samples. 1.0 g of each sample was taken and diluted with distilled water in a 100 ml flask and titrated with a Dy^{3+} solution (1.0×10^{-3} M) and the results of triplicate measurements are sum-

TABLE V
Dy(III) determination in tap water and river water with the recommended electrode

Sample	Added, mg/ml	Found[a], mg/ml	Recovery, %
River water	0.3	0.35 ± 0.03	116.6
	0.5	0.54 ± 0.04	108
Tap water	0.3	0.34 ± 0.02	103.3
	0.5	0.54 ± 0.03	108

[a] Results of three measurements.

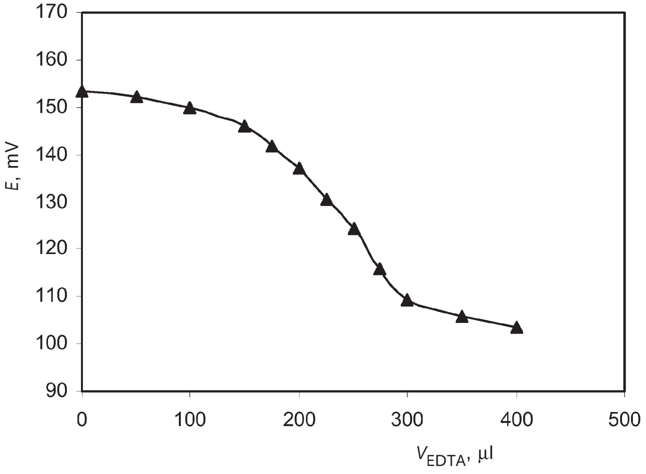


FIG. 5
Potentiometric titration curve of 25.0 ml 1.0×10^{-4} M Dy^{3+} with 1.0×10^{-2} M EDTA

marized in Table VI. The measurement principle for the determination of fluoride ions is based on the monitoring of the Dy^{3+} ion concentration. At the beginning of the titration, the concentration of the Dy^{3+} is zero. By addition of Dy^{3+} to the solution containing $F^–$ ions, the insoluble TbF_3 is formed and the potential during the titration remains almost constant. This is due to the formation of insoluble DyF_3 and changes in the potential are belongs to the K_{sp} of DyF_3. After total $F^–$ ions converted to DyF_3, by addition of Dy^{3+} ions, the potential of the solution will change sharply. The beginning point of sharp changes is the end point of titration. As it is seen, there is a satisfactory agreement among the declared fluoride content and the determined values by the sensor and commercial solid fluoride. The associated data from triplicate measurements are displayed in Table VI. It is clear that there is a satisfactory agreement between the declared fluoride content and the values determined by the commercial solid fluoride sensor and the proposed electrode.

TABLE VI
Determination of fluoride ions in mouth wash solutions

Mouth wash Manufactures	Labeled mg/ml	Found[a] mg/ml	Commercial Fluoride ISE, mg/ml
Aquafresh, Brentford, U.K.	1.35	(1.37 ± 0.04)[b]	(1.33 ± 0.02)[b]
Eurodont, DuroDont GmbH	1.45	(1.48 ± 0.03)[b]	(1.44 ± 0.02)[b]

[a] ISE with proposed Dy^{3+} sensor. [b] Based on three measurements.

CONCLUSION

This research demonstrated that ISEs, constructed on 6-hydrazino-1,5-diphenyl-6,7-dihydropyrazolo[3,4-*d*]pyrimidine-4(5*H*)-imine (HDDPI), exhibited dysprosium selectivity with low interference of common alkali, alkaline earth, transition and heavy metal ions. The recommended sensor displayed a short response time (<10 s) and its potential responses were pH-independent in the range of pH 3.5–8.3. Moreover, it was successfully used as an indicator electrode in the cadmium ion titration with EDTA as well as in the dysprosium ion detection in solution.

The authors gratefully acknowledge the financial support from the Research Council of the Quchan University.

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