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Novel Neodymium(III) Membrane Sensor based on *N*-(2-Furylmethylene)pyridine-2,6-diamine

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Através de nossos estudos, encontramos que *N*-(2-furilmetileno) piridina-2,6-diamina (FPD) pode ser usado como um excelente ionóforo na construção de um novo sensor baseado em membrana de poli(vinil cloreto) (PVC). Uma composição para a membrana, de 33% de PVC, 59% de nitrobenzeno (NB), 6% de FPD e 2% de borato de potássio tetrakis (*p*-clorofenil) (KTpClPB), levou a ótimos resultados. A seletividade do sensor frente a Nd(III), é relativamente boa em comparação com um grande número de íons de lantanídeos, tais como lantânio, cério, gadolínio, samário, térbio, európio, disprósio, e itérbio. A resposta do sensor é Nernstiniana (com inclinação de 19,6 ± 0,3 mV *per* década para íon carregado triplamente) em um largo intervalo de concentração ($1{,}0 \times 10^{-5}$ a $1{,}0 \times 10^{-2}$ mol L^{-1}) com limite de detecção de $7{,}0 \times 10^{-6}$ mol L^{-1}, tempo de resposta relativamente rápido em todo intervalo de concentração (<15 s), e um tempo de vida considerável, de no mínimo seis semanas no intervalo de pH de 4,0 a 8,0.

We found that *N*-(2-furylmethylene) pyridine-2,6-diamine (FPD) can be used as an excellent ionophore in the construction of a novel neodymium(III) poly(vinyl chloride) (PVC)-based membrane sensor. A membrane composition of 33% poly (vinyl chloride), 59% nitrobenzene (NB), 6% FPD, and 2% potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), led to the optimum results. The Nd(III)-selectivity of the sensor, is relatively good in comparison to a large number of lanthanide metal ions, such as lanthanum, cerium, gadolinium, samarium, terbium, europium, dysprosium, and ytterbium ions. The sensor response is Nernstian (with slope of 19.6±0.3 mV *per* decade for the triply charged ion) over a wide concentration range (1.0×10^{-5} to 1.0×10^{-2} mol L^{-1}) with a detection limit of 7.0×10^{-6} mol L^{-1}, a relatively fast response time, in the whole concentration range (<15 s), and a considerable life time of at least six weeks in the pH range of 4.0–8.0.

Keywords: neodymium(III), sensor, potentiometry, PVC, *N*-(2-furylmethylene) pyridine-2,6-diamine

Introduction

Neodymium is the most abundant of the rare earths, after cerium and lanthanum. It shows similar characteristics to the other trivalent lanthanides. Primary applications include lasers, glass coloring and tinting, dielectrics, and most importantly, as the fundamental basis for neodymium-iron-boron ($Nd_2Fe_{14}B$) permanent magnets. Neodymium has a strong absorption band centered at 580 nm, which is very close to the human eyes maximum level of sensitivity making it useful in protective lenses for welding goggles. Neodymium salts are used as catalysts in polymerization of 1,3-butadiene and isoprene.[1,2]

The common methods for determination of Nd^{3+} ion are spectrophotometry, atomic absorption spectroscopy (AAS), and inductively coupled plasma atomic emission spectroscopy (ICP AES).[3] The spectrometry method suffer from the lack of selectivity and the AAS and ICP AES have higher amounts of detection limit for lanthanide ions (in the case of Nd^{3+} ion, 60 ppm and 20 ppb for AAS and ICP AES respectively).

Solvent polymeric membrane based ion-selective electrodes (ISEs), prepared by the incorporation of new ionophores, have shown to be very useful tools for clinical, environmental and chemical analysis as well as for process monitoring. A great emphasis, in this field, has been focused on the development of new and highly selective ion-carriers, which can be used in the fabrication of a new ion-specific ISEs with high selectivities and

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sensitivities, wide linear concentration ranges, long lifetime, and good reproducibilities.

There have been many studies on ion-selective electrodes for transition and heavy metal ions.[4] Among these metal ions, a little attention has been paid to the development of lanthanide electrodes,[5-24] and especially Nd(III).[25] Although, this sensor has good sensitivity but in the case of selectivity has serious interferences (especially for Cu^{2+} and Yb^{3+}).

Due to the vital importance of neodymium in industry, and the need for an Nd(III)-selective electrode for the potentiometric monitoring of Nd(III), we were interested to prepare a novel sensor for the determination of Nd(III) ions based on *N*-(2-furylmethylene) pyridine-2,6-diamine (FPD) with higher selectivity than previously reported.

Experimental

Reagents

Reagent grade dibutyl phthalate (DBP), benzyl acetate (BA), acetophenon (AP), nitrobenzene (NB), potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), tetrahydrofuran (THF), and high relative molecular weight PVC were purchased from Merck and used as received. Neodymium chloride and the nitrate salts of neodymium and other cations used (all from Merck, Aldrich and Fluka), were of the highest purity available and used without any further purification except for vacuum drying over P_2O_5. 2-furaldehyde, 2,6-diaminopyridine, acetic acid, ethanol and methanol (all from Merck), were of the highest purity available. Triply distilled de-ionized water was used throughout.

Synthesis of FPD

For the preparation of *N*-(2-furylmethylene)pyridine-2,6-diamine, a mixture of 2-furaldehyde (0.01 mol, 0.96 g), 2,6-diaminopyridine (0.01 mol, 1.09 g) and catalytic amount of acetic acid, was refluxed for 1 h in absolute ethanol (20 mL). Then the mixture was cooled to the room temperature. The resulted pale yellow precipitate was filtered, washed with ethanol, and dried under reduced pressure.

mp 230 ºC (decomp), 1.6 g, yield 89%; IR (Schimadzu IR-460 Spectrometer, KBr) ν_{max}/cm^{-1}: 3342 and 3196 (NH_2), 1589 (C=N), 1468, 1429, 1354, 1232, 1123, 997, 777, 764. MS (FINNIGAN-MATT 8430 at 20 eV), *m/z* (%): 187 (M^+, 100), 164 (24), 88 (17), 28 (15). Anal. Calc. for $C_{10}H_9N_3O$ (187.20): C, 64.16; H, 4.85; N, 22.45. Found: C, 64.3; H, 4.9; N, 22.3%. ^1H NMR (250.1 MHz Bruker, DMSO-d_6 solution): δ 6.28 (1 H, d, *J* 6.9 Hz, CH), 6.42 (1 H, dd, *J* 3.7 Hz and *J* 1.5 Hz, CH), 6.66 (1 H, dd, *J* 3.7 Hz and *J* 1.0 Hz, CH), 6.84 (1 H, d, *J* 7.0 Hz, CH), 6.99 (1 H, d, *J* 6.8 Hz, CH), 7.36 (1 H, dd, *J* 1.5 Hz and *J* 1.0 Hz, CH), 7.95 (1 H, s, N=CH), 8.20 (2 H, br, NH_2); ^{13}C NMR: δ 107.36, 108.21, 113.52, 117.98, 131.029, and 145.54 (6 CH), 157.87, 158.46, and 159.23 (3 C), 160.18 (CH).

Electrode preparation

33 mg of powdered PVC, 59 mg of NB, 6 mg FPD and 2 mg of KTpClPB were dissolved and mixed in 5 mL of fresh THF, in order to prepare a membrane of optimum composition and behavior. The resulted mixture was transferred into a glass dish of 2 cm in diameter, and its solvent was slowly evaporated, until an oily concentrated mixture was obtained.

A final membrane of about 0.3 mm thickness was formed on the tip of a Pyrex tube (3-5 mm i.d.), by dipping the tube into the mixture for 10 s, pulling it out of the mixture and keeping it at room temperature for 12 h.

The tube, containing the membrane, was filled with internal filling solution (1.0×10^{-3} mol L^{-1} $NdCl_3$) in the next step. The resulting membrane electrode was finally conditioned for 24 h by soaking in a 1.0×10^{-2} mol L^{-1} solution of neodymium nitrate. For a comparative study, a membrane containing no active component was also prepared. The ratio of different membrane ingredients, concentration of equilibrating solution and the time of contact were optimized to provide membranes, which result in reproducible, noiseless and stable potentials.

Emf measurements

All emf measurements were carried out with the following assembly:

Ag–AgCl| internal solution (1.0×10^{-3} mol $L^{-1}NdCl_3$) | PVC membrane| sample solution| $Hg\text{-}Hg_2Cl_2$, KCl (satd.)

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

Results and Discussion

Potential responses

Some neutral ion carriers, containing nitrogen and sulfur donor atoms have been reported to use in the construction of the highly selective transition and heavy metal ion membrane sensors, lately.[12-19]

FPD (Figure 1), having one-oxygen and three donating nitrogen atoms in its structure was expected to act as a

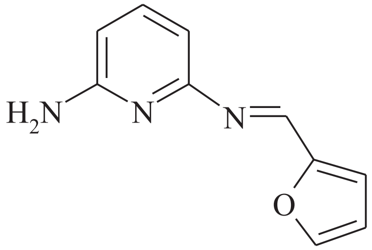

Figure 1. Structure of ionophore FPD.

suitable ion carrier for special transition and heavy metal ions (due to their higher charge density), in the PVC membranes. Thus, at first, FPD was used as a neutral carrier to prepare PVC-based membrane electrodes for a variety of trivalent transition metal ions, including lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, and ytterbium ions. The potential responses of the most sensitive ion-selective membrane electrodes based on FPD are shown in Figure 2. It is obvious that, among the nine lanthanide ions tested, Nd(III), with the most near-to-Nerstian response, can be suitably determined with the PVC membrane sensor based on FPD. This is probably due to both the selective behavior of the ionophore against neodymium (with relatively low charge density and hydration energy), in comparison to other metal ions and the rapid exchange kinetics of the resulting FPD-neodymium complex.

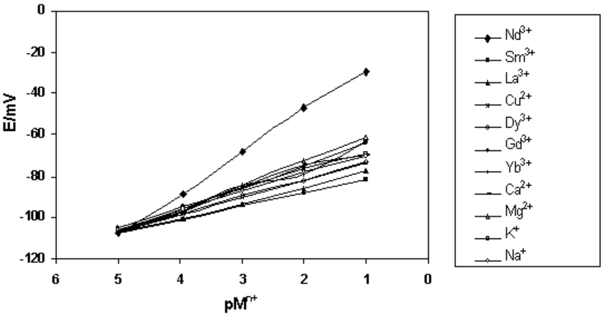

Figure 2. Potential responses of various metal ion-selective electrodes based on FPD (membrane No. 6).

Effect of membrane composition

It is well known that some important features of the PVC-based membranes, such as the nature and amount of ion-carrier, the properties of the plasticizer, the plasticizer/ PVC ratio and, especially, the nature of additives used, significantly influence the sensitivity and selectivity of the ion-selective electrodes.[26,27] To study the effects of these parameters, different aspects of preparing a membrane based on FPD, were optimized (Table 1).

The results show that the quantity of FPD affects the sensitivity of the membrane electrode (No. 1-4). The sensitivity of the electrode response increases with increasing ion-carrier content until a value of 6% is reached.

The solvent mediator/PVC ratio in solvent polymeric membrane ion-selective electrodes is usually found to be about 2, because polymeric films with such a plasticizer/ PVC ratio will result in optimum physical properties and high enough mobility of their constituents. In this study, the same plasticizer/PVC ratio (about 2) was found to be the most suitable, for the construction of the membrane sensors.

The selectivity and working concentration range of membrane sensors are also affected by the nature and amount of the plasticizers used. This is due to the influence of the plasticizer on the dielectric constant of the membrane phase, the mobility of the ion-carrier molecules, and on the state of complex. The results of Table 1 shows that among the four different plasticizers used, NB (No. 6) having a higher polarity than the other three, namely DBP, AP and BA, is a more effective solvent mediator in preparing the neodymium membrane sensor.

The optimum perm-selectivity of membrane sensors is known to be highly dependent on the incorporation of additional membrane compounds.[28] It is has been accepted that, the presence of suitable negatively charged lipophilic additives, improves the potentiometric behavior of certain cation-selective electrodes. The data given in Table 1

Table 1. Optimization of membrane ingredients

Membrane No.	Composition / (%)				Slope / (mV decade^{-1})
	PVC	Plasticizer	Additive	Ionophore	
1	33	NB[a], 64	——	3	10.9±0.2
2	33	NB, 62	——	5	11.4±0.4
3	33	NB, 60	——	7	12.6±0.2
4	33	NB, 61	——	6	13.1±0.3
5	33	NB, 60	1	6	17.7±0.2
6	33	NB, 59	2	6	19.6±0.3
7	33	AP[b], 59	2	6	15.3±0.2
8	33	DBP[c], 59	2	6	14.7±0.4
9	33	NB, 63	2	6	3.7±0.4

[a]NB=Nitrobenzene; [b]AP= Acetophenon; [c]DBP=Dibutyl phthalate.

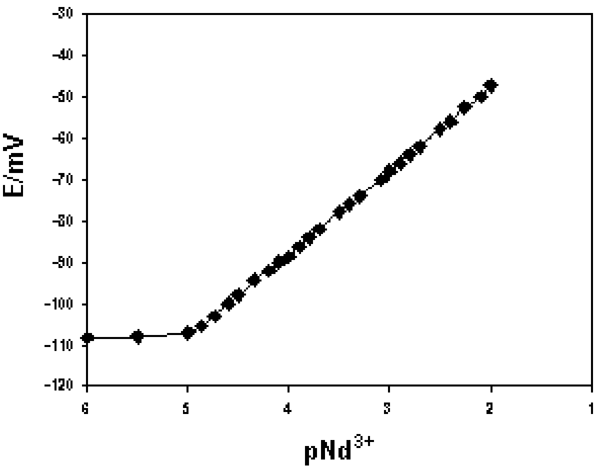

Figure 3. Calibration curve of the Nd^{3+} membrane sensor based on FPD (membrane No. 6) in pH=4.5.

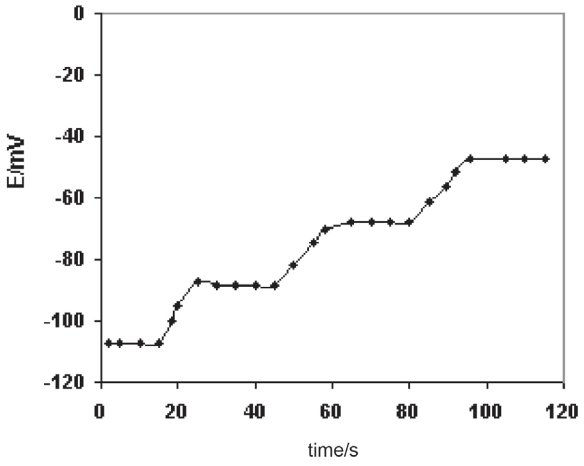

Figure 4. Dynamic response time of the Nd^{3+} membrane sensor (membrane No. 6) over a 1.0 × 10^{-5} to 1.0 × 10^{-2} mol L^{-1} solution of neodymium ions.

revealed that the absence of a proper additive causes the sensitivity of the FPD based membrane to be relatively low (No. 4 with a slope of 13.1 mV *per* decade) while, the addition of about 2% of KTpClPB, as a suitable additive, in the membrane will improve the sensitivity of the neodymium membrane electrode considerably (no. 6 with slope 19.6 mV *per* decade).

Calibration curve

The optimum equilibration time for the neodymium membrane sensor in the presence of 1.0 × 10^{-2} mol L^{-1} neodymium nitrate was 24 h, after which it would generates stable potentials in contact with the neodymium solutions. The proposed sensor displays a linear response to the activity of the neodymium ion in the range 1.0 × 10^{-5} to 1.0 × 10^{-2} mol L^{-1} (Figure 2). The slope of the calibration curve was 19.6 ± 0.3 mV *per* decade. The limit of detection, as determined from the intersection of the two extrapolated segments of the calibration curve, was 7.0 × 10^{-6} mol L^{-1}.

For stability and lifetime evaluation, three sensors were chosen and using 1 h *per* day, and their slopes and detection limits were monitored. This experiment revealed that after six weeks, only a very slight decrease in the slopes and detection limits were observed (from 19.6 ± 0.3 and 7.0 × 10^{-6} to 18.7 ± 0.4 mV *per* decade and 1.0 × 10^{-5} mol L^{-1}, respectively).

Dynamic response time

Dynamic response time is one of the most important factors for the evaluation of any ion-selective electrode. In this report, the practical response times of the sensor were recorded by changing the neodymium ion concentration in solution, over a 1.0 × 10^{-2} to 1.0 × 10^{-5} mol L^{-1}. The actual potentials *versus* time traces are shown in Figure 4. As it is seen, in whole concentration range the electrode reaches its equilibrium response very fast (<15 s).

To evaluate the reversibility of the electrode, a similar procedure in the opposite direction was adopted. The measurements were performed in the sequence of high-to-low (from 1.0 × 10^{-2} to 1.0 × 10^{-3} mol L^{-1}) sample concentrations and the results showed that, the potentiometric responses of the electrode was reversible; although the time needed to reach equilibrium value (35 s) was longer than that of low-to-high sample concentrations (1).

The effect of the pH

The effect of the pH of the test solution (1.0 ×10^{-3} mol L^{-1} neodymium ions) on the potential response of the sensor was investigated in the pH range 2.0–10.0 (the pH of solutions was adjusted by the 0.1 mol L^{-1} HNO_3 or KOH) and the results are illustrated in Figure 5. As can be seen from Figure 5, the potential response of the sensor is independent on pH in the range 4.0–8.0, beyond which the potential changes considerably. The observed drift at higher alkali media could be due to the formation of insoluble $Nd(OH)_3$ in solution. The observed increase in the potential at the acidic solutions indicates that the membrane responds to the proton (protonation of nitrogen atoms of ion carrier in the membrane).

Selectivity

Potentiometric selectivity coefficients of the proposed sensor were evaluated by the matched potential method

(MPM).[29] According to MPM, the specified activity (concentration) of the primary ion (Nd^{3+}) is added to a reference solution, and the potential is measured. In a separation experiment interfering ions (*B*) are successively added to an identical reference solution until the measured potential matched that obtained before by adding the primary ions. The matched potential method selectivity coefficient, K^{MPM}, is then given by the resulting primary ion to interfering ion activity (concentration) ratio, $K_{Nd^{3+},B} = a_{Nd^{3+}}/a_B$. The experimental conditions employed and the resulted values for the neodymium membrane sensor are given in Table 2. As can be seen, for the lanthanide ions with close properties to neodymium ions (gadolinum, lanthanum, and samarium ions), the selectivity coefficients are smaller than 2.7×10^{-2} and for other ions tested (smaller ionic radius), selectivity coefficients are smaller than 8.9×10^{-3}.

Table 2. The selectivity coefficients of various interfering cations for Nd^{3+}membrane sensor

Ion	log K^{MPM}	log K^{SSM}
Na^+	-2.6	-2.9
K^+	-2.6	-2.7
Mg^{2+}	-2.5	-2.8
Ca^{2+}	-2.4	-2.6
Cu^{2+}	-2.0	-2.1
La^{3+}	-1.6	-1.7
Gd^{3+}	-1.8	-1.9
Sm^{3+}	-1.5	-1.7
Dy^{3+}	-2.1	-2.3
Yb^{3+}	-2.2	-2.3

Stability and lifetime

The lifetime of the Nd(III) membrane sensor were tested over a period of 70 days. During this period, the electrodes were in daily use over an extended period of time (one hour *per* day), and the results are given in Table 3. As can be seen from Table 3, after 49 days a very slight gradual decrease and increase in the slopes and detection limit was observed respectively. This is due to the leaking of membrane ingredients from membrane to the solution. This kind of behavior has been already seen for the most of introduced liquid membrane sensors.

Table 3. The lifetime of the Nd^{3+} membrane sensor

Week	Slope / (mV *per* decade)	Detection Limit
First	19.6 ± 0.3	7.0×10^{-6} mol L^{-1}
Second	19.5 ± 0.6	8.0×10^{-6} mol L^{-1}
Third	19.3 ± 0.2	8.5×10^{-6} mol L^{-1}
Fourth	19.0 ± 0.3	9.3×10^{-6} mol L^{-1}
Fifth	18.8 ± 0.5	9.5×10^{-6} mol L^{-1}
Sixth	18.6 ± 0.3	9.9×10^{-6} mol L^{-1}
Seventh	18.1 ± 0.4	1.0×10^{-5} mol L^{-1}
Eighth	17.5 ± 0.2	4.0×10^{-5} mol L^{-1}
Ninth	17.0 ± 0.5	7.2×10^{-5} mol L^{-1}
Tenth	16.2 ± 0.7	8.7×10^{-5} mol L^{-1}

Table 4. Determination of Nd(III) ions in various binary mixtures

Nd^{3+} / (mol L^{-1})	Added cation / (mol L^{-1})	Recovery / (%)
5.0×10^{-5}	Na^+ (5.0×10^{-3})	102.2±0.2
5.0×10^{-5}	K^+ (5.0×10^{-3})	102.3±0.3
5.0×10^{-5}	Ca^{2+} (5.0×10^{-3})	103.5±0.2
5.0×10^{-5}	Mg^{2+} (5.0×10^{-3})	102.6±0.4
5.0×10^{-5}	Cu^{2+} (2.5×10^{-3})	99.7±0.2
5.0×10^{-5}	La^{3+} (1.2×10^{-3})	104.4±0.4
5.0×10^{-5}	Sm^{3+} (2.5×10^{-3})	103.6±0.3
5.0×10^{-5}	Gd^{3+} (2.5×10^{-3})	103.5±0.2
5.0×10^{-5}	Dy^{3+} (2.5×10^{-3})	103.3±0.4
5.0×10^{-5}	Yb^{3+} (2.5×10^{-3})	102.2±0.4

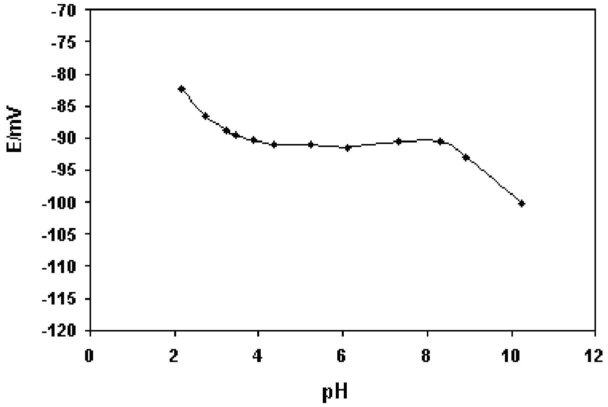

Figure 5. Effect of the pH of the test solution of 1.0×10^{-3} mol L^{-1} neodymium ions on the potential response of the Nd^{3+} ion-selective electrode based on FPD (membrane no. 6).

Analytical applications

The proposed sensor was used as an indicator electrode in the titration of 25.0 mL neodymium solution (1.0×10^{-3} mol L^{-1}) with a standard EDTA solution (1.0×10^{-1} mol L^{-1}) with the pH of 10.0, and the resulted titration curve is given in Figure 6, that has a very sharp end point. As can be seen, the amount of Nd^{3+} ions in solution can be determined with the electrode accurately ($1.0 \pm 0.1 \times 10^{-3}$ mol L^{-1}).

The sensor was applied to direct monitoring of Nd^{3+} in various binary mixtures, and the results are summarized in Table 4. As it is obvious, the recovery of Nd^{3+} ions is very good (97.7-104.4%). This is due to the relatively good selectivity of the proposed sensor.

Comparison

Table 5 compares the selectivity coefficients, Detection limit, and dynamic linearity range of the proposed Nd(III)

Table 5. Comparison of the characteristics of the proposed sensor and the best reported Nd(III) sensors

Sensor	Linear Dynamic Range	Limit of Detection	Slope / (mV)	log K^{SSM} / (transition metal)	log K^{SSM} / (alkali and alkali metal ion)
Ref. 25	1.0×10^{-6} to 1.0×10^{-2} mol L^{-1}	7.9×10^{-7} mol L^{-1}	20.1±0.2	La^{3+}(-1.4); Gd^{3+}(-1.4); Sm^{3+}(-1.6); Yb^{3+}(-1.2); Cu^{2+}(-1.5)	Na^+(-2.9); K^+(-2.8); Mg^{2+}(-2.8); Ca^{2+}(-2.5)
This work	1.0×10^{-5} to 1.0×10^{-2} mol L^{-1}	7.0×10^{-6} mol L^{-1}	19.6±0.3	La^{3+}(-1.7); Gd^{3+}(-1.9); Sm^{3+}(-1.7); Yb^{3+}(-2.3); Dy^{3+}(-2.3); Cu^{2+}(-2.1)	Na^+(-2.9); K^+(-2.7); Mg^{2+}(-2.8); Ca^{2+}(-2.6)

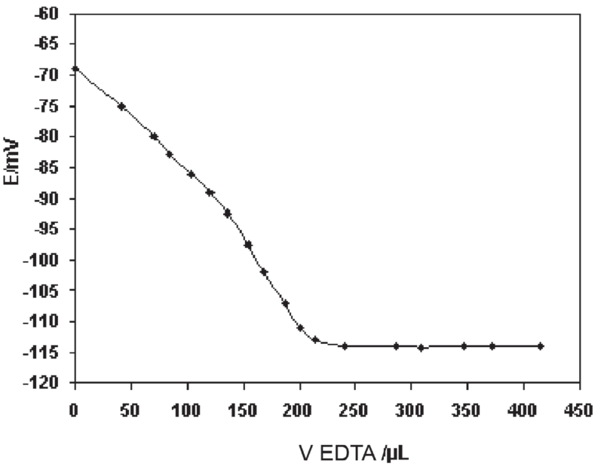

Figure 6. Potentiometric titration curve of 25.0 mL Nd^{3+} (1.0×10^{-3} mol L^{-1}) with 10^{-1} mol L^{-1} EDTA using the membrane no. 6 as an indicator electrode in pH=10.0.

sensor, with previously Nd(III) electrode reported in the literature[25]. As can be seen from Table 5, the proposed Nd(III) sensor in the terms of selectivity coefficient, specially for transition metals, is better than the previously reported sensor.

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