

Article

Coated-Carbon Rod Ion-Selective Electrode for the Determination of Nickel(II) in Iminobis(2-Ethylamine) Medium

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Descreve-se a construção e a avaliação de um eletrodo seletivo a Ni(II) constituído por grafite recoberto com o par-iônico formado entre o cátion $[\text{Ni}(\text{dien})_2]^{2+}$ (dien=iminobis(2-etilamina)) e o ânion $[\text{BPh}_4]^-$ (tetrafenilborato) incorporado em uma matriz de PVC (cloreto de polivinila). Uma membrana fina foi preparada pela incorporação deste par-iônico, ftalato de dibutila (DBPh) em PVC e aplicados diretamente à superfície de grafite. Investigou-se o efeito da composição da membrana (par-iônico, DBPh e PVC), dien, pH e alguns cátions e ânions sobre a resposta do eletrodo. O eletrodo apresentou uma resposta linear no intervalo de concentração de níquel(II) de 5.6×10^{-5} a 10^{-1} mol/L e uma inclinação de $29,5 \pm 0,3$ mV/década, em pH 12. Variações no potencial de 2-4 mV foram registrados durante um dia de trabalho (8-9 h). O tempo de resposta do eletrodo foi menor que 5 s para o intervalo útil de resposta e o tempo de vida superior a um ano (acima de 1500 determinações/membrana polimérica), com limite de detecção prático de $3,7 \times 10^{-5}$ mol/L. Descreve-se a aplicação deste eletrodo na determinação de níquel(II) em duas ligas metálicas (Ni-Cr e Ni-Ge) e uma de aço inoxidável (AISI 316L).

The construction and evaluation of a coated-carbon rod nickel(II) ion selective electrode based on the ion pair between the $[\text{Ni}(\text{dien})_2]^{2+}$ (dien=iminobis(2-ethylamine)) cation and the BPh_4^- (tetraphenylborate) anion incorporated on to a poly(vinylchloride) (PVC) matrix are described. A thin membrane film was prepared by the incorporation of this ion pair, dibutylphthalate (DBPh) in PVC, and applying it directly to a carbon rod. The effects of membrane composition (ion pair, DBPh and PVC), dien, pH and some cations and anions on the electrode response was investigated. The electrode shows a linear response in the nickel concentration range of 5.6×10^{-5} - 10^{-1} mol/L, and a slope of 29.5 ± 0.3 mV/dec, at pH 12. Variations in the potential of about $\pm 2-4$ mV were registered during a working day (8-9 h). The response time was less than 5 seconds for the useful response range, and the lifetime of this electrode was superior to one year (over 1500 determinations for each polymeric membrane), with a practical detection limit of 3.7×10^{-5} mol/L. Application of this electrode for nickel(II) determination to two metallic alloys (Ni-Cr and Ni-Ge) and one stainless steel(AISI 316L) sample is described.

Keywords: nickel determination, nickel ion-selective electrode, iminobis(2-ethylamine), coated-carbon rod

Introduction

Since the development by Ross¹ of the first liquid membrane electrode sensitive to the calcium cation, much progress has been made. Moody and Thomas^{2,3} replaced the thick layer of liquid exchanger material supported by a dialysis membrane (cellulose acetate) with a thin polymeric film of poly(vinylchloride) (PVC), thus significantly de-

creasing the high resistance and relatively long response time of that electrode, while increasing the lifetime performance. Several electrodes were constructed for various cations, anions and organic compounds.

Tricaprylylmethylammonium salts (Aliquat 336) were introduced by Freiser *et al.*⁴⁻⁸ as anionic exchangers in several electrodes which are selective for anions. In the course of a study of a series of liquid membrane ion

selective electrodes, Cattrall and Freiser⁸ constructed the first coated-wire ion selective electrode (CWISE). This kind of electrode was prepared by dipping the tip of a platinum wire in a solution of PVC in cyclohexanone or THF also containing a suitable electroactive material, and allowing the resulting thin film to air dry overnight. The main advantages of this electrode are the elimination of the inner reference solution, the decrease in the time and cost of fabrication as well as allowing miniaturization and making intercellular or other *in vivo* electrochemical measurements possible.

Many selective electrodes based on anionic metallic complexes have been described in the literature⁹⁻¹⁷. In spite of this large number of electrodes, the majority were constructed by the incorporation of an ionic pair between an anionic cation complex and Aliquat 336 in PVC.

The nickel(II) ion selective electrode has been less investigated. It includes a membrane electrode made of a solution with the chemical composition $[(C_2H_5)_4N]_2 [Ni(5,6\text{-dithiobenzo-7,8-phenazine})_2]$ added to nitrobenzene on a support of graphite¹⁸, and a solid membrane electrode using $Ag_2[Ni(SCN)_4](s)$ dispersed together dibutylphthalate or dioctylphthalate with a vinyl plastic repair cement (Lepage no. 330)¹⁹ on one end of a glass tube (5 mm id) or a medicine dropper. The latter offers low selectivity and sensitivity, and the former has a short life time and selectivity and poor reproducibility, due to the high leaching of the ion pair and especially the "water immiscible mediator".

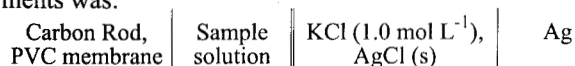
This paper describes the construction and analytical application of a coated carbon rod ion-selective electrode for the determination of nickel (II). The nickel (II) electrode was constructed by a prior complexation of Ni (II) with dien, followed by precipitation with sodium tetraphenylborate (NaBPh₄) to form an ionic pair $[Ni(dien)_2][BPh_4]_2$. After filtration, this solid compound was dried and incorporated in a PVC matrix onto a carbon rod. This electrode, which needs no internal reference solution or internal reference electrode, is easier and cheaper to make than the conventional PVC^{2,3} and/or solid membranes¹⁹. In addition, the proposed electrode has been successfully used for the determination of nickel in three alloy samples.

Experimental

Apparatus

All potentiometric measurements were obtained at 25 ± 0.2 °C with the nickel (II) ion selective electrode and a R684 model Analion Ag/AgCl double junction reference electrode (Brazil), either attached to a EA 940 model Orion pH/ion meter(USA) with ± 0.1 mV precision.

The electrochemical cell used for potential measurements was:



The salt bridge was a 3 mol/L KNO₃ solution.

All pH measurements were made with the same pH meter and a 10/402/3092 model Ingold glass membrane electrode(USA). Calibration curves were obtained by the addition of nickel(II) in iminobis(2-ethylamine) (dien) standard solution, at a controlled pH, using a E274 model Metrohm microburette, to a dien solution at same pH and ionic strength. In the studies of response time, electrode stability, and lifetime, the signals were recorded on a two-channel strip-chart recorder (Cole Parmer, model 12020000-USA).

Reagents and Solutions

All solutions were prepared using distilled deionized water. Analytical-reagent grade chemicals were used without further purification, unless stated otherwise. The nickel(II) acetate (Riedel-de Haën) stock solution was first prepared in water and standardized conveniently²⁰. After that, reference solutions of Ni(II) in a dien medium were obtained by the suitable dilution of the stock solution with the appropriate amount of the complexant at several pHs. The pH of the solutions was adjusted by the addition of concentrated nitric acid solution.

Metallic cation solutions in the same medium and pH used in the potentiometric selectivity coefficient determinations were prepared in the same fashion.

The sodium tetraphenylborate (NaBPh₄) (Aldrich) solution was prepared by dissolving 0.6055 g of this solid in 25 mL of water.

High molecular weight poly(vinylchloride) (PVC, pure grade, available from Fluka), tetrahydrofuran (reagent grade, Aldrich), dibutylphthalate (DBPh, Aldrich), and 5 mm diameter spectroscopically pure carbon rod, were used as received.

Preparation of the ionic pair

First, 25 mL of 0.1 mol/L Ni (II) in 1.0 mol/L dien solution was shaken with a saturated solution of sodium tetraphenylborate for 5 min. The ionic pair obtained was filtered in a 10-15 μ (medium porosity) sintered glass Gooch filter, washed with distilled water and dried in a desiccator for 2-3 days before being used. The coating solutions were prepared by dissolving PVC in 10 mL of tetrahydrofuran (THF) following the addition of DBPh: a) 1% (w/w) ion pair, 69% (w/w) DBPh and 30% (w/w) PVC; b) 2% (w/w) ion pair, 68% (w/w) DBPh and 30% (w/w) PVC; c) 5% (w/w) ion pair, 65% (w/w) DBPh and 30% (w/w) PVC; and d) 10% (w/w) ion pair, 60% (w/w) DBPh and 30% (w/w) PVC.

Construction of the coated-carbon rod electrode

The coated-carbon rod electrodes were constructed as described elsewhere^{16,17}. The carbon rod was coated by

immersion in the previously prepared solutions (a, b, c, d), and then removed and dried for 30-60 min. This operation was repeated 3-4 times, taking care to form a well-distributed thick membrane on the electrode tip. Then, the other end of the electrode was connected to a coaxial cable (which prevents external noise) and the remainder of the carbon rod was covered with an insulating PVC membrane.

Before use, the electrode was conditioned for 2-3 h by immersion in a 0.1 mol/L Ni(II) in 1.0 mol/L dien solution, pH 12, and finally rinsed with deionized water.

Sample Preparation

For potentiometric determination of Ni(II) in two special alloys (1: Ni-Cr and 2: Ni-Ge, available from the Departamento de Engenharia de Materiais, UFSCar) and one stainless steel (AISI 316L, available from Aços Vileares, São Paulo, SP), an accurately weighed amount (0.050 - 0.150 g) of each of the solid samples was first dissolved in concentrated nitric acid and heated until dryness. Then, the samples were dissolved in 1.0 mol/L dien solution and filtered in a Gooch crucible to eliminate the hydroxide of trivalent cations. The filtrate was transferred to a 100 mL volumetric flask, and this volume was completed with the same dien solution. The percentage of the mass content of nickel in these samples was determined by the standard addition method (potentiometry), and by atomic absorption spectrophotometry at a wavelength of 232.0 nm.

Results and Discussion

Several parameters were investigated in order to evaluate the performance of the nickel(II) electrode in terms of membrane composition, reproducibility, response time, calibration curve slopes, selectivity, and sample analysis.

The effect of membrane composition over the response (slope (mV/dec)) of the nickel(II) ion selective electrode was initially evaluated in triplicate, at pH 12. The best response (29.5 mV/dec) was reached for the 5% (w/w) ion pair, 65% (w/w) DBPh and 30% (w/w) PVC (electrode c), indicating that the electrode preferentially responds to the cationic Ni(dien)₂²⁺ species at this pH.

The effect of pH on the response of the nickel(II) electrode was determined in solutions with 5×10^{-4} , 5×10^{-3} and 5×10^{-2} mol/L of nickel (II) in 1.0 mol/L dien solution.

The diagrams (Fig. 1) show that there are no significant variations in the values of the potential when the pH of the solution varies between 6.0 and 10.0 units. For pH values less than 6 there is a decrease in the potential of the electrode due to the protonation of the H₂dien⁺⁺ and/or Ni(dien)₂⁺⁺ species by the formation of H₃dien³⁺, which reaches a maximum ($\alpha_3 = 1$) at pH 1-1.5 (Fig. 2). At this pH, the ion-selective electrode does not respond to the Ni(II) concentration, since the difference in the electrode potential is almost zero (Fig. 1). In the pH range of 2-6,

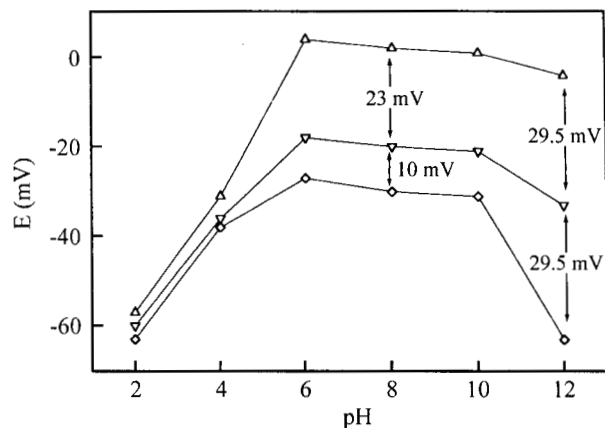


Figure 1. Effect of pH on the response of the nickel (II) ion-selective electrode for a nickel(II) concentration of: $\diamond\diamond\diamond$: 5×10^{-4} , $\nabla\nabla\nabla$: 5×10^{-3} , and $\Delta\Delta\Delta$: 5×10^{-2} mol/L, and 1.0 mol/L dien, at 25.0 °C.

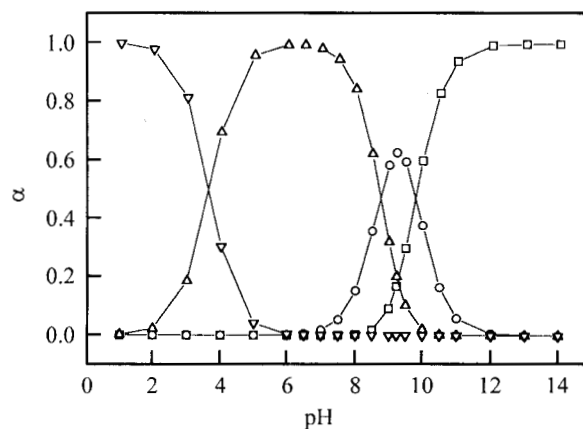


Figure 2. Distribution of dien species as a function of pH: $\square\square\square$: α_0 ([dien]), $\circ\circ\circ$: α_1 ([Hdien]⁺), $\Delta\Delta\Delta$: α_2 ([H₂dien]²⁺), and $\nabla\nabla\nabla$: α_3 ([H₃dien]³⁺).

H₃O⁺ strongly competes with Ni(II) for dien. Also, at pH values equal to and/or less than 4 there is decomposition of BPh₄⁻. On the other hand, at pH 12 there is a predominance of the Ni(dien)₂²⁺ species, since α_0 is equal to unity (Fig. 2). The distribution of the dien species as a function of pH shown in this figure was calculated using the values of the dien protonation constants from the literature²², at an ionic strength (0.1 mol/L) very close to that used in this work. As can be seen from the diagrams presented in Fig. 1, the difference in potential is 29.5 mV/dec between the three Ni(II) solutions, indicating that at this pH the electrode has a Nernstian response to nickel(II) concentration, and the main equilibrium in the formation of Ni(dien)₂²⁺ complex is not influenced by side-reactions²² with H₃O⁺. Table 1 shows the mean values (three determinations each) of the response characteristics of the electrode at several pH values (2, 4, 6, 8, 10 and 12). As can be seen from this table,

Table 1. Effect of pH on the response characteristics of the nickel(II) ion-selective electrode in 1.0 mol/L dien, at 25 °C.

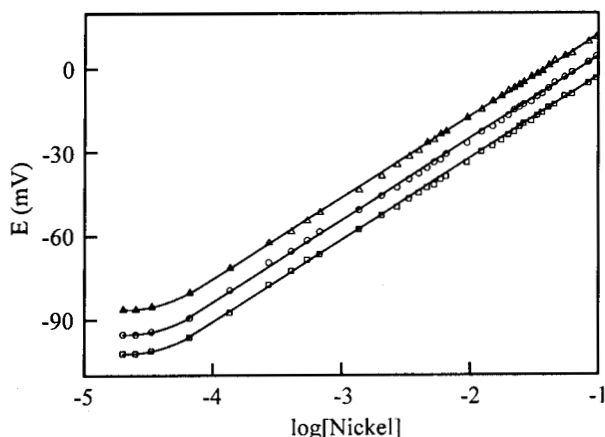
pH	Slope (mV/dec)	Linear range (mol/L)
2	2.1 ± 0.1	3.9 × 10 ⁻² - 1 × 10 ⁻¹
4	6.5 ± 0.2	1.9 × 10 ⁻² - 1 × 10 ⁻¹
6	22.1 ± 0.5	9.5 × 10 ⁻³ - 1 × 10 ⁻¹
8	22.8 ± 0.5	9.1 × 10 ⁻³ - 1 × 10 ⁻¹
10	23.2 ± 0.3	6.3 × 10 ⁻³ - 1 × 10 ⁻¹
12	29.5 ± 0.3	5.6 × 10 ⁻⁵ - 1 × 10 ⁻¹

the best performance of this electrode was obtained at pH 12. Consequently, all studies were carried out at this pH.

Figure 3 shows the potential response of the electrode at pH 12 in three dien concentrations (0.5, 1.0, and 1.5 mol/L) as a function of log[Nickel (II)]. The response was Nernstian (29.5 ± 0.3 mV/dec) in the nickel concentration range from 5.6 × 10⁻⁵ to 1.0 × 10⁻¹ mol/L, showing that dien concentrations in the 0.5-1.5 mol/L range shift the E⁰ to higher values with an increase in dien concentration, but do not modify the slope, linearity or detection limit of this electrode.

Stable potentials were achieved within a few seconds (less than 5 s within the useful response range), and the variations in the potential of 2-4 mV were observed during a working day (8-9 h). No memory effect occurred for seven potential measurements in solutions containing 10⁻³ and 10⁻² mol/L Ni(dien)₂⁺⁺, alternatively.

This electrode presents a useful lifetime of at least one year (over 1500 determinations for each polymeric membrane), without significant loss in sensitivity and with a practical detection limit of 3.7 × 10⁻⁵ mol/L, determined from the calibration curves (Fig. 3) as the concentration value that corresponds to a 9 mV deviation from the linear response^{23,24}.

**Figure 3.** Effect of dien concentration on the calibration curves of the nickel(II) ion selective electrode: \square : 0.5, \circ : 1.0 and Δ : 1.5 mol/L, at pH 12 and 25 °C.

The effect of some common species on the potential response of the nickel electrode was tested by determining the potentiometric selectivity coefficients of the membrane by the separate and mixture solution methods, as described by Moody *et al.*² In the separate solutions method, the concentrations of Ni(II) and the interfering ion were fixed at 2.5 × 10⁻³ mol/L in 1.0 mol/L dien, while in the mixture method the interfering ion was fixed at 2.5 × 10⁻³ mol/L and the principal ranged from 10⁻⁵ to 10⁻¹ mol/L in 1.0 mol/L dien. The values of the potentiometric selectivity coefficients ($K^{pot}_{Ni,J}$) obtained (see Table 2) by the mixture method were lower than those obtained by the separate, indicating that a competitive equilibrium between the Ni(II) and the interfering ion at the interface of the electrode is favorable to the analyte. Also, these results show good selectivity for most solutions containing 2.5 × 10⁻³ mol/L of common cations and anions, and confirms that the potentiometric selectivity coefficient is related to the stability constant value(β), such that the lower the β value of the cation species, the higher the selectivity of the electrode.

The electrode shows poor selectivity for cadmium and moderate selectivity for zinc, copper and cobalt in this medium. Nevertheless, in both the alloys and the steel analyzed these ions were not detected at ppm levels by atomic absorption spectrophotometry. Trivalent cations (e.g. Fe(III), Al(III), Cr(III)) are not a problem, since they precipitate as hydrous oxide in the alkaline medium (pH 12). In addition, the low values of the selectivity coefficients obtained for chloride, thiocyanate and citrate indicate that these anions do not have any influence on the electrode potential.

Results obtained for nickel(II) determination by the potentiometric and atomic absorption spectrophotometric

Table 2. Potentiometric selectivity coefficients for the nickel(II) ion-selective electrode ($K^{pot}_{Ni,J}$) in 1.0 M dien, determined by separated and mixture solution methods².

interferent ion (J)	Methods ($K^{pot}_{Ni,J}$)	
	separation	mixture
Cu ²⁺	0.225	0.144
Zn ²⁺	0.245	0.130
Co ²⁺	0.227	0.250
Pb ²⁺	0.039	2.3 × 10 ⁻²
Cd ²⁺	0.872	0.401
Na ⁺	1.8 × 10 ⁻³	9.1 × 10 ⁻⁴
NH ₄ ⁺	3.8 × 10 ⁻³	7.0 × 10 ⁻³
Cl ⁻	1.7 × 10 ⁻³	9.0 × 10 ⁻⁴
SCN ⁻	1.8 × 10 ⁻³	1.8 × 10 ⁻³
*Cit ³⁻	1.0 × 10 ⁻³	2.4 × 10 ⁻³

*Citrate

Table 3. Determination of nickel(II) in alloys using a nickel(II) electrode compared with the atomic absorption spectrophotometric method.

Samples	Methods* (mg)		Relative Errors (%)
	spectrophotometry	potentiometry	
1	72.19 ± 0.37	72.80 ± 5.01	+0.8
2	86.75 ± 1.25	85.57 ± 3.79	-1.3
3	13.25 ± 0.35	12.85 ± 1.75	-3.1

* 3 replicates

method in two metal alloys (Ni-Cr and Ni-Ge) and one stainless steel sample are presented in Table 3. The results are in close agreement with those obtained by atomic spectrophotometry, and are within an acceptable range of error.

Conclusions

The construction and evaluation of a coated-carbon rod nickel(II) ion-selective electrode was demonstrated. This electrode presented a low fabrication cost, a long lifetime (one year, over 1500 determinations/membrane), a practical detection limit of 3.7×10^{-5} mol/L, and a fairly good selectivity that allowed the determination of nickel(II) in two alloys (Ni-Cr and Ni-Ge) and one stainless steel (AISI 316L).

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