

# Selectivity properties of corrin-doped polypyrrole film

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**Abstract** We report the synthesis of a new pyrrole-substituted vitamin B<sub>12</sub> derivative functioning as a corrin monomer, its electrochemical copolymerization with pyrrole, and the potentiometric behavior of the resultant electrodes based on the corrin-doped polypyrrole film. Electropolymerization of the corrin monomer on a glassy carbon electrode and its redox properties were evaluated by cyclic voltammetry in acetonitrile in the presence of tetrabutylammonium perchlorate. We investigated the effect of various parameters that control the film properties, such as the concentration of the monomer, potential range, scan rate, and number of scans. The optimal conditions for potentiometric measurements were also determined. We found that the electropolymerized corrin film-based electrode exhibited an anion selectivity pattern that favors thiocyanate and deviates from the Hofmeister series. The obtained electrode demonstrates near-Nernstian behavior for a period of at least 6 months. The detection limit of the

electrode along with selectivity coefficients toward various anions was also determined.

**Keywords** Electropolymerization · Vitamin B<sub>12</sub> derivative · Cobalt corrin · Thiocyanate-selective electrode · Conducting polymers

## Introduction

Doping polymers with ions or molecules has become popular in the preparation of functional polymeric materials. These polymeric materials can selectively bind various chemical species through coordination with recognition sites within the polymer [1, 2]. Conductive polymers constitute a special class of doped polymer that have high electrical conductivity. Such conducting polymers doped with molecules/ions have drawn considerable attention because of their mechanical/chemical stability, low cost, and ease of preparation. Electrochemical sensors based on conducting polymers maintain chemical stability and allow for control of selectivity that is determined by the nature of both the monomer and doping ions/molecules [3, 4]. Accordingly, ion-selective electrodes (ISEs) have been constructed using conductive polymers, such as poly(*o*-phenylenediamine) [5], polyphenol [6], polyaniline [7], and polypyrrole [2, 8–11].

The demand for the development of sensitive and selective ISEs with sufficient stability has been an area of recent interest. Numerous attempts have been made to produce electrodes with good response properties and long lifetimes. Electrochemical polymerization of a suitable monomer onto an electroactive substrate has proven to be a powerful way to achieve ISEs with enhanced selectivity and longer stabilities [12]. The successful implementation

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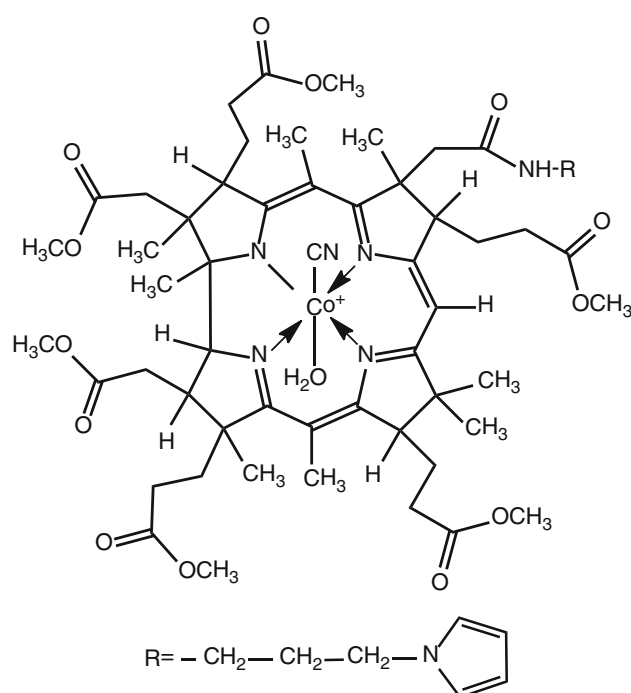
of electropolymerized membranes in potentiometric sensors has been recently reviewed [3, 4]. Electropolymerized membranes offer advantages over electrodes prepared with conventional polymers such as plasticized poly(vinyl chloride) (PVC); PVC membrane electrodes can have shorter lifetimes that have been attributed to the leaching of the ionophore and other membrane components from the sensor matrix to the sample solution [13, 14] and occasionally to crystallization of ionophore in the membrane [15]. The lack of solubility of electropolymerized films in organic solvents is another advantage that enables the use of such electrodes in potentiometric analysis in non-aqueous media.

From the chemical recognition point of view, the design and synthesis of new ionophores, such as organometallic compounds, hydrogen-bonding molecules, metallomacrocycles including corrin, porphyrin, and phthalocyanine derivatives that can selectively coordinate anions has been the focus of much activity [16–18]. Despite the significant number of publications on electropolymerized phthalocyanine and porphyrin derivatives coordinated with different metals, only limited attention has been paid to the electropolymerization of corrins [19, 20], although hydrophobic derivatives of vitamin B<sub>12</sub> have been successfully employed in the development of thiocyanate-, nitrite-, iodide-, and salicylate-selective PVC membrane electrodes [21–23].

Considering the ability to electropolymerize metalloporphyrin and metallophthalocyanine derivatives bearing pyrrole substituents as well as the anion coordination characteristics of corrins, we aimed to synthesize a new pyrrole-substituted corrin, *a,b,d,e,f,g*-hexamethyl-*c*-[3-(1*H*-pyrrol-1-yl)propyl]-*Co* $\alpha$ ,*Co* $\beta$ -di(cyano- $\kappa$ C)cob(III)yrinate (III) to demonstrate the feasibility of combining the chemical recognition properties of corrins and the controlled pore organization in the design of novel electrochemical sensors. The resulting electropolymerized corrin film-coated electrode displayed good selectivity toward thiocyanate over other anions with a fast response time and a long lifetime.

## Results and discussion

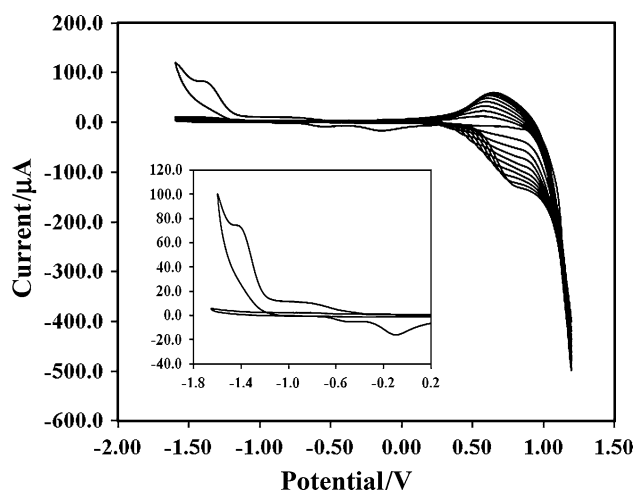
Corrins, in which a cyano group occupies one of the axial ligands and the second ligand is water, have been shown previously to behave as charged carriers in ISE membranes [23, 24]. Conversely, after the removal of one of the axial  $-\text{CN}$  ligands from the dicyano derivative, the corresponding corrin should behave as a positively charged carrier in the electropolymerized film on the glassy carbon electrode. This acetic acid treated compound IV (Fig. 1), referred to as the corrin monomer throughout this manuscript,



**Fig. 1** Structure of new pyrrole-substituted vitamin B<sub>12</sub> derivative

is expected to respond to various anions via the replacement of water molecule by anions.

The electrochemical behavior of the new corrin monomer (corrin monomer concentration,  $C_M$ , 10.0 mM) in 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile solution on a glassy carbon (GC) electrode surface was investigated by cyclic voltammetry at a scan rate of  $0.1 \text{ V s}^{-1}$ . The cyclic voltammogram illustrated two cathodic peaks upon reductive scanning from 0.2 to  $-1.6 \text{ V}$  (Fig. 2). The first cathodic peak can be attributed to  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  ( $E_p^c -0.79 \text{ V}$ ); at more negative potentials the current increased as a result of further conversion of  $\text{Co}(\text{II})$  to  $\text{Co}(\text{I})$  ( $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$   $E_p^c -1.42 \text{ V}$ ). The peaks observed are in good agreement with those discussed by other authors studying cobalt redox couples [19, 20, 25]. On the reverse potential scan, two oxidation peaks occurred at  $E_p^a -0.56 \text{ V}$  and  $E_p^a -0.14 \text{ V}$ , which can be assigned to the oxidation of products formed during the reduction of the corrin monomer. The broad peak observed at  $E_p^a 0.74 \text{ V}$  was due to the oxidation of pyrrole. In the subsequent scan, a broad peak appeared at  $E_p^c \sim 0.60 \text{ V}$ , which demonstrates the electrochemical response of the polymerized pyrrole in the film. Figure 2 is a representative cyclic voltammogram typically observed in this study for a low number of scans with a corrin monomer concentration of 10.0 mM. When the concentration of the corrin monomer was decreased to 1.0 mM, similar voltammograms were observed with lower peak currents. Hence, 1.0 mM was deemed to be a sufficient concentration to electropolymerize compound IV on



**Fig. 2** Cyclic voltammogram of corrin monomer in acetonitrile containing 0.1 M TBAP on GC electrode at a scan rate of  $0.10 \text{ V s}^{-1}$  (vs. Ag/AgCl, 12 scans). *Inset* is the overlaid voltammogram of corrin monomer in 0.1 M TBAP/acetonitrile

the GC electrode. As it can be seen in Fig. 2, after continuous potential cycling the currents assigned to  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  decreased dramatically owing to surface modification via PPy film formation, while the peak current for polymerized pyrrole increased indicating that the film deposited on the electrode surface was conductive. The decrease in the  $\text{Co}^{\text{III}}/\text{Co}^{\text{II}}$  and  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  peak currents also revealed that access of the corrin monomer from the solution to the GC electrode surface was being hindered by steric effects.

In order to improve the electropolymerization capacity of the pyrrole-substituted corrin monomer, copolymerization with pyrrole was performed in solutions containing a mixture of different concentrations of pyrrole with a fixed concentration of the corrin monomer at 1.0 mM. Each time, uniform, insoluble, adherent, and reproducible films were obtained on the surface of the electrode.

The polymer film-coated electrode was immersed in a 0.1 M TBAP/acetonitrile solution to obtain evidence of the successful copolymerization of the pyrrole-substituted corrin. In the voltammogram, a small peak at more negative potential than the PPy reduction was observed. To ensure that the additional peak was not due to the reduction of polypyrrole, cyclic voltammetry of a PPy film-coated GC electrode was conducted in the absence of the corrin monomer in the same electrolyte solution. Because the cyclic voltammogram of this electrode showed no peak other than the reduction of PPy, the smaller peak in the cyclic voltammogram of the original electrode can be attributed to the doping of corrin units and the reduction process for their cobalt center. The peak currents for this reduction were measured to determine the amount of corrin

in the film according to the following equation reported for a Nernstian adsorbate layer [26]:

$$\Gamma_0^* = \frac{i_p}{(9.30 \times 10^5)n^2\nu A}$$

where  $\Gamma_0^*$  is the number of moles of corrin per unit area,  $i_p$  is the peak current with respect to the baseline (average of three peak currents,  $i_p = 1.4 \times 10^{-5} \text{ A}$ ) obtained during cyclic voltammetry,  $n$  is the number of electrons involved in the oxidation/reduction ( $n = 1$ ),  $\nu$  is the scan rate ( $\nu = 0.1 \text{ V s}^{-1}$ ), and  $A$  represents the surface area of the electrode ( $A = 0.07 \text{ cm}^2$ ). It was found that  $\Gamma_0^* = 2.2 \times 10^{-9} \text{ mol/cm}^2$ , and the total number of moles of corrin on the surface of the electrode was  $1.5 \times 10^{-10} \text{ mol}$ . The surface coverage achieved in this study was found to be comparable to values reported in previous studies involving various porphyrin and vitamin B<sub>12</sub> derivatives [27–29].

#### *Effect of electropolymerization conditions on potentiometric response*

It is well known that the morphology of the polymer film can change the ion-exchange properties of electropolymerized film-based ISEs; these ion-exchange properties can be controlled by the electropolymerization conditions [30, 31]. It has been previously demonstrated that these conditions not only affect the detection limit and slope of the calibration plots of ISEs, but also other response characteristics such as selectivity and response time. Therefore, the conditions used for the copolymerization of pyrrole with the corrin monomer were varied to determine their effect on the potentiometric response of the corresponding electrodes.

The polymerization rate of the new pyrrole-substituted corrin was expected to be significantly lower than that of unsubstituted pyrrole because of steric effects. Numerous studies in the literature have shown that pyrrole and substituted pyrrole monomers are readily polymerized from dilute solutions (e.g., 1.0 mM) [32]. Tables 1, 2, and 3 show the conditions used for the preparation of electrodes that provided promising response characteristics as thiocyanate-selective electrodes with regard to the slope of the calibration plot and linear working range.

When the anodic potential was less than 0.55 V, no polymer film was obtained on the electrode surface. In order to identify the positive potential limit of the working potential range, the anodic switching potentials were changed in the range of 0.75–1.2 V. As the potential became more positive, the slope of the calibration plots of the corresponding ISEs were closer to Nernstian, and the detection limit observed was better. However, when the anodic switching potential exceeded 1.3 V, the potential

**Table 1** Effect of the potential scan range on the response behavior of the thiocyanate-selective electrode

Starting potential/V	Negative switching potential/V	Positive switching potential/V	Slope/mV/pSCN $\pm tS/\sqrt{N}$ ( $N = 4$ )	Detection limit/M
0.2	-1.6	1.1	$56.5 \pm 1.0$	$4.0 \times 10^{-5}$
0.2	-1.6	1.2	$58.7 \pm 0.9$	$1.5 \times 10^{-5}$
0.2	-1.6	1.3	$49.3 \pm 1.0$	$3.1 \times 10^{-4}$
0.2	-1.4	1.2	$42.8 \pm 2.9$	$4.6 \times 10^{-4}$
0.2	-1.5	1.2	$51.2 \pm 2.6$	$1.0 \times 10^{-4}$
0	-1.6	1.1	$54.2 \pm 2.2$	$8.0 \times 10^{-5}$
0	-1.6	1.2	$55.3 \pm 2.0$	$1.0 \times 10^{-4}$

Electropolymerization conditions: scan rate,  $0.1 \text{ V s}^{-1}$ ; number of scans, 100;  $C_M$ , 1.0 mM;  $C_P$ , 0.5 M in 0.1 M TBAP/acetonitrile. Given data are for the same electrode; however, at least three replicates of each scan range were employed for the reproducibility of the electrode preparation

**Table 2** Effect of electropolymerization conditions on the potentiometric response behavior of the thiocyanate-selective electrode

Scan rate/ $\text{V s}^{-1}$	Number of scans	Slope/mV/pSCN $\pm tS/\sqrt{N}$	Response time/s
0.2	100	$53.8 \pm 1.4$ ( $N = 3$ )	>15
0.15	100	$55.7 \pm 0.4$ ( $N = 6$ )	10–15
0.1	100	$56.9 \pm 0.6$ ( $N = 42$ )	10–25
0.05	100	$43.6 \pm 1.8$ ( $N = 5$ )	10
0.1	50	$52.8 \pm 1.5$ ( $N = 3$ )	5–10
0.1	200	No stable potentiometric response	–

Starting potential, 0.2 V; negative switching potential, -1.6 V; positive switching potential, 1.2 V;  $C_M$ , 1.0 mM;  $C_P$ , 0.5 M in 0.1 M TBAP/acetonitrile; scan rate,  $0.1 \text{ V s}^{-1}$ ;  $\pm tS/\sqrt{N}$  is the confidence interval for the mean slope of  $N$  replicate measurements calculated from the standard deviation  $S$ ; the statistical parameter  $t$  corresponded to a probability level of 95 %. Given data are for the same electrode; however, at least three replicates of each scan range were employed for the reproducibility of the electrode preparation

readings of the resulting electrodes were unstable. This could be attributed to alteration of the film due to overoxidation of pyrrole. Altering the starting potential to more positive values did not significantly change the potential response of the ISEs.

In order to obtain electrode surfaces with good polymer coverage, the effect of the negative potential limit of the working range was investigated. Potentials that were more negative than the potential at which the  $\text{Co}^{\text{II}}/\text{Co}^{\text{I}}$  reduction takes place were applied as the negative switching potential up to -1.7 V. ISEs obtained by potential cycling using different negative switching potentials between -1.45 and -1.7 V showed important differences in the potentiometric response. The slopes of the electrodes were between 42.8 and 58.7 mV/pSCN, while the detection limits were in

**Table 3** Effect of electropolymerization conditions on the potentiometric response behavior of the thiocyanate-selective electrode

$C_{\text{TBAP}}$ or $C_{\text{TBAC}}/\text{M}$	$C_P/\text{M}$	Slope/mV/pSCN $\pm tS/\sqrt{N}$	Response time/s
$C_{\text{TBAP}}$ 0.1	1.0	$52.7 \pm 2.2$ ( $N = 3$ )	>25
	0.5	$56.9 \pm 0.6$ ( $N = 42$ )	10–25
	0.1	$51.1 \pm 1.2$ ( $N = 3$ )	15
	0.01	$47.7 \pm 1.5$ ( $N = 3$ )	10
$C_{\text{TBAC}}$ 0.1	0.5	$48.9 \pm 0.8$ ( $N = 3$ )	10–15
$C_{\text{TBAP}}$ 0.5	0.5	$54.1 \pm 1.2$ ( $N = 3$ )	30–35

Starting potential, 0.2 V; negative switching potential, -1.6 V; positive switching potential, 1.2 V;  $C_M$ , 1.0 mM;  $\pm tS/\sqrt{N}$  is the confidence interval for the mean slope of  $N$  replicate measurements calculated from the standard deviation  $S$ ; the statistical parameter  $t$  corresponded to a probability level of 95 %. Given data are for the same electrode; however, at least three replicates of each scan range were employed for the reproducibility of the electrode preparation

the range of  $4.6 \times 10^{-4}$ – $1.5 \times 10^{-5}$  M. Moreover, when the electrodes were prepared with potentials more negative than -1.6 V, sub-Nernstian slopes and narrower working ranges were observed. This can be attributed to the different surface modification of the electrodes.

According to the literature, the potentiometric anion response of electrodes could be affected depending on whether the electrodes are poised at a reduced or an oxidized state [33, 34] after electropolymerization. Therefore, the electrodes were kept under constant final potentials of either -1.6 or 1.2 V for a period of 2 min. In our study, a selective response to thiocyanate was obtained in both cases; however, the electrodes that were prepared at -1.6 V showed a better anion selectivity pattern with the slope of the calibration plot being closer to Nernstian.

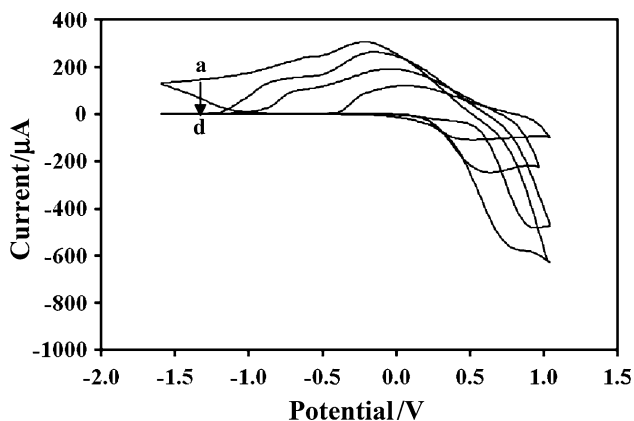
Employing a different number of scans and scan rates during electropolymerization may also influence the potentiometric response of the ISEs. To determine the optimum film thickness, electrodes were prepared with a different number of scans, and their potentiometric response was compared by means of slopes and detection limits. When the number of scans was raised to 100, the sensitivity of the electrodes increased as evidenced by the value of the slope of the calibration plots. Electrodes prepared with 100 scans also gave the longest lifetimes. Thicker films obtained with 200 scans gave unstable potentiometric responses, and the films peeled off after a few measurements because of weak adherence to the electrode surface. Increasing the scan rate from 0.05 to  $0.2 \text{ V s}^{-1}$  resulted in electrodes with good response characteristics. However, no further improvement was obtained when the scan rate was greater than  $0.1 \text{ V s}^{-1}$ . Consequently, the optimum potential scan rate and number of scans were determined to be  $0.1 \text{ V s}^{-1}$  and 100, respectively (Table 2).

### Effect of monomer concentration

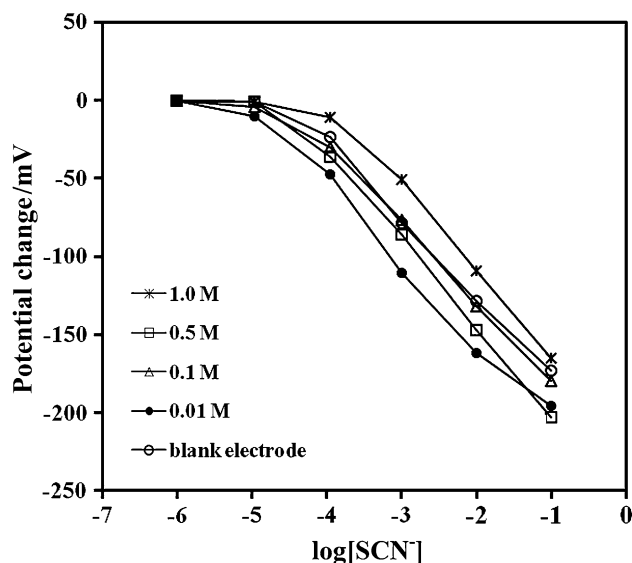
After establishing the optimum working potential range, we investigated the effect of various concentrations of pyrrole. A solution containing 0.01 M pyrrole was employed in the initial experiments. The potential response was poor resulting in narrow working ranges between  $1.0 \times 10^{-2}$  and  $1.0 \times 10^{-4}$  M. Therefore, films were grown in solutions containing a constant corrin monomer concentration of 1 mM and pyrrole concentration varying from 0.1 to 1.0 M to achieve better functioning sensor responses. The results are given in Table 3. The data in Fig. 3 suggested that different pyrrole to corrin ratios formed different arrangements in the polymer film by means of the amount of corrin doped and the polymer surrounding the corrin ring. Lower slopes in the presence of 0.01 and 0.1 M pyrrole can be attributed to the control of the selectivity provided by the variation of film properties which resulted in different possible potentiometric response mechanisms. Figure 4 shows the calibration plots of the polymer film-coated electrodes for comparison purposes. ISEs with slopes close to the Nernstian value for thiocyanate were obtained upon increasing pyrrole concentration to 0.5 M. Further increase in pyrrole concentration led to worse detection limits and slopes of the calibration plots. In conclusion, employing a 0.5 M pyrrole concentration while maintaining 1 mM corrin resulted in ISEs with slopes that were closer to Nernstian in the linear range of  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-4}$  M and a detection limit of  $1.5 \times 10^{-5}$  M.

### Effect of electrolyte and its concentration

During the oxidative and reductive processes, anions from the electrolyte diffuse into or out of the polymer to ensure



**Fig. 3** Cyclic voltammograms of corrin-doped polypyrrole prepared in a 1.0 M, b 0.5 M, c 0.1 M, d 0.01 M pyrrole containing 0.1 M TBAP/acetonitrile on GC electrode at a scan rate of  $0.10 \text{ V s}^{-1}$  ( $C_M$  1.0 mM, vs. Ag/AgCl)



**Fig. 4** Effect of pyrrole concentration on the potentiometric response of the electrodes in 0.1 M 2-(N-morpholino)ethanesulfonic acid (MES)-NaOH, pH 5.5 (electropolymerization conditions:  $v$   $0.1 \text{ V s}^{-1}$ ; 100 scans in 0.1 M TBAP/acetonitrile;  $C_P$  1.0, 0.5, 0.1, 0.01 M as indicated in the figure). The open circle is the potentiometric response of the blank electrode prepared in the absence of corrin with a pyrrole concentration  $C_P$  of 0.5 M

the electroneutrality of the films [35]. Therefore, the size, shape, and polarity of these anions may influence the electrical conductivity and the mechanical properties of the polymer films [36]. We maintained a constant optimum working potential range, scan rate, number of scans, and pyrrole concentration to investigate the effect of different electrolyte solutions and their concentration (0.01–0.5 M, Table 3). Polymer films were deposited in the presence of perchlorate and chloride ions as templates. When the concentration of TBAP was 0.01 M, the electrodes gave worse slopes, and the response disappeared after a week. Electrodes prepared by using 0.5 M TBAP showed unstable responses, and the slope could not be determined. However, when the electropolymerization was performed in 0.1 M TBAP in acetonitrile, a good stable near-Nernstian response and an improved detection limit were observed. When using 0.1 M tetrabutylammonium chloride (TBAC) as the electrolyte, electrodes with worse slopes and selectivity for thiocyanate over chloride were obtained. The reason for this phenomenon may be the difference in efficiency of the electrodeposition, which can be attributed to using a different electrolyte anion during electrodeposition.

In the corrin-doped polypyrrole film, the corrin provides coordination sites for selective anion binding, whereas pyrrole, which is in excess, determines the morphology of the polymer around the corrin monomer. During electropolymerization, the electrolyte anions enter and leave the film to maintain electroneutrality, which in turn results in

films of different characteristics. Of the two electrolyte anions, perchlorate is larger leading to an electropolymerized film in which enough space around the cobalt center is provided for thiocyanate to diffuse to and coordinate with the metal center. In the presence of a smaller anion like chloride, thiocyanate was still the most preferable anion; however, the slope of the corresponding electrodes was worse, and the working range was narrower than those obtained when perchlorate was used as the electrolyte anion. In short, the proposed mechanism for the observed selectivity depends on cobalt coordination with the anion of interest as the axial ligand of the corrin, and this selectivity can be modified by changing the nature of the chemical environment that surrounds the corrin ring [37, 38]. Additionally, anions like nitrate and perchlorate, which are known to be weak coordination ligands, do not interact with the cobalt center [39]. In the case of thiocyanate, it is easier for this linear anion to coordinate to the cobalt center, whereas other strong ligand anions like nitrite are bulkier and may be sterically hindered from coordinating directly to the cobalt center.

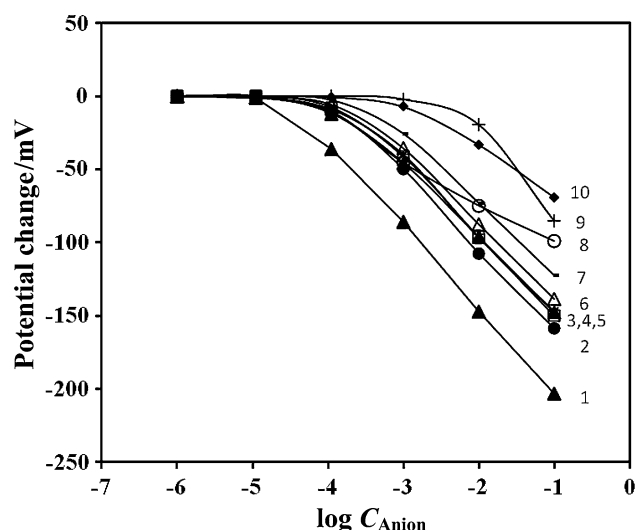
As shown in Table 4, the electropolymerized corrin film-coated GC electrode gave the best selectivity toward thiocyanate when the copolymerization was performed in 0.1 M TBAP/acetonitrile solution containing 1.0 mM corrin monomer and 0.5 M pyrrole by cycling in an optimum potential range starting at 0.2 V, going cathodically to  $-1.6$  V, and then scanning anodically to 1.2 V with a scan rate of  $0.1 \text{ V s}^{-1}$ . Figure 5 shows the anion selectivity pattern of this electrode.

#### Effect of conditioning time and pH on potentiometric response

The potentiometric response of the electrodes was tested after 2, 12, and 24 h of conditioning in  $1.0 \times 10^{-2}$  and

**Table 4** Selectivity coefficients,  $\log K_{\text{SCN}^-}^{\text{pot}}$ , of the thiocyanate-selective electrode in comparison with the polypyrrole-coated electrode calculated by the separate solution method

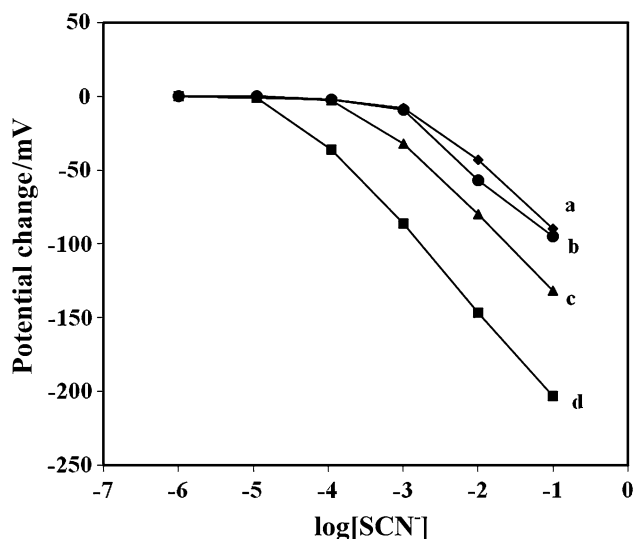
Anion	Corrin film-coated electrode $\log K_{\text{SCN}^-}^{\text{pot}}$	PPy-coated electrode $\log K_{\text{SCN}^-}^{\text{pot}}$
$\text{ClO}_4^-$	-1.08	-0.70
$\text{I}^-$	-1.00	-0.66
Salicylate	-2.09	-1.77
$\text{NO}_3^-$	-1.06	-0.22
$\text{CH}_3\text{COO}^-$	-2.65	-2.35
$\text{Br}^-$	-1.25	-0.83
$\text{Cl}^-$	-1.63	-1.26
$\text{NO}_2^-$	-0.78	-0.49
$\text{HCO}_3^-$	-2.31	-1.98



**Fig. 5** Potentiometric response curves of electrodes assembled under the optimized electropolymerization conditions ( $C_M$  1.0 mM,  $C_P$  0.5 M,  $v$   $0.1 \text{ V s}^{-1}$ , 100 scans) in 0.1 M MES–NaOH, pH 5.5; 1  $\text{SCN}^-$ , 2  $\text{NO}_2^-$ , 3  $\text{ClO}_4^-$ , 4  $\text{I}^-$ , 5  $\text{NO}_3^-$ , 6  $\text{Br}^-$ , 7  $\text{Cl}^-$ , 8 salicylate, 9  $\text{HCO}_3^-$ , 10  $\text{CH}_3\text{COO}^-$

$1.0 \times 10^{-3}$  M NaSCN. Better slopes and working ranges were obtained when the electrodes were conditioned in  $1.0 \times 10^{-2}$  M NaSCN for at least 12 h. The electrode showed no further improvement in response after 12 h of conditioning. Consequently, the thiocyanate-selective electrodes were conditioned for at least 12 h before experiments.

The polymer film properties are strongly affected by solution acidity because of the possible protonation and deprotonation of the polymer. Changes in the potential response of polypyrrole film-based electrodes were observed when the pH was below 3.5 and above 7.5 as a result of simultaneous response of the electrodes to  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$ , respectively [40]. Thus, to identify the best buffer system, calibration plots of the thiocyanate-selective electrode were obtained by using different buffers (0.01 M) in the pH range of 4.0–7.0. The starting potentials of the electrodes shifted to more negative values when the pH was increased in this range. As a result, significant changes were observed in the detection limit and slope of the electrodes. The electrodes presented better response and linearity at pH 5.0 for the 0.01 M MES–NaOH buffer solution. An additional study was undertaken by using the same buffer system to investigate the effect of its concentration on the provision of higher buffer capacity. The electrode had better detection limits with a negligible change in the slope of the calibration plot in 0.1 M MES–NaOH. The pH for this buffer was changed in the range of 5.5–7.0 to optimize the buffer pH. Our findings suggest that a pH 5.0–5.5 can be used for optimum response characteristics for thiocyanate. As Fig. 6 shows, the detection



**Fig. 6** Effect of pH on the potentiometric response of electrodes assembled under the optimized electropolymerization conditions ( $C_M$  1.0 mM,  $C_P$  0.5 M,  $v$  0.1 V s<sup>-1</sup>, 100 scans) in 0.1 M MES–NaOH buffer at pH *a* 7.0, *b* 6.5, *c* 6.0, *d* 5.5

limit of the electrodes shifted toward a higher concentration as the pH of the solution increased up to 7.0. As a result of these studies, all experiments were performed in 0.1 M MES–NaOH buffer at an optimum pH of 5.5.

#### Selectivity coefficients

Selectivity is one of the most important characteristics of any sensor and demonstrates the relative response for the primary ion over other ions present in solution. The selectivity coefficients were determined by the separate solution method, and the electropolymerized corrin electrode demonstrated a selectivity pattern as follows:  $\text{SCN}^- > \text{NO}_2^- > \text{I}^- > \text{ClO}_4^- \approx \text{NO}_3^- > \text{Br}^- > \text{Cl}^- > \text{salicylate} > \text{HCO}_3^- > \text{CH}_3\text{COO}^-$ , which clearly indicates deviation from the Hofmeister series (Table 4).

The selectivity of a polypyrrole film-coated electrode (no corrin present) was established for comparison purposes. It showed a selectivity pattern of  $\text{SCN}^- > \text{NO}_3^- > \text{NO}_2^- > \text{I}^- \approx \text{ClO}_4^- > \text{Br}^- > \text{Cl}^- > \text{salicylate} > \text{HCO}_3^- > \text{CH}_3\text{COO}^-$ , which was different from the electropolymerized corrin electrode while also exhibiting a lower slope of the calibration plots than the latter. Although the selectivity coefficients of the polypyrrole electrode were worse than the corrin electrode, both electrode types showed preference toward the thiocyanate ion. Therefore, it may be concluded that the polypyrrole in the copolymerized corrin electrode may also play a role in determining its anion selectivity because of the possibility of interaction between the charged poly(cationic) sites on

the organic backbone of polypyrrole film with anions. The corrin-based thiocyanate-selective electrode showed improved selectivity coefficients compared to the PPy film-coated electrode as a result of additional anion coordination to the cobalt center.

#### Response time and lifetime

The response time of an ISE is an important factor in determining its analytical utility, and it was evaluated by measuring the time required to achieve a steady-state potential (within  $\pm 1$  mV). The electrode responded rapidly after additions of thiocyanate to the sample solution, with response times ranging from 10 s at concentrations above  $1.0 \times 10^{-4}$  M to 25 s at lower concentrations.

The effect of light on the lifetime of the corrin film-coated thiocyanate-selective electrode was also evaluated. The electrode demonstrated a lifetime of a few weeks when it was exposed to light between measurements because of the light sensitivity of the film. In contrast, the electrode, when stored in the dark at 4 °C, presented a potentiometric response that remained almost the same for at least 6 months.

In order to compare the lifetimes and response times of the thiocyanate-selective corrin film-coated GC electrode with those of conventional PVC membrane electrodes, different compositions of PVC membrane electrodes were prepared. A composition of 2 % (w/w) corrin monomer, 64.7 % PVC, 32.5 % 2-nitrophenyl octyl ether (NPOE), and 0.8 % tridodecylmethylammonium chloride (TDMACl) was found to be the optimum membrane composition. This PVC membrane electrode showed a different anion selectivity pattern than the electropolymerized corrin film-coated electrode because of the different nature of the membrane. Deviation from the Hofmeister series was observed in the order of  $\text{I}^- \approx \text{salicylate} > \text{ClO}_4^- > \text{SCN}^- > \text{Br}^- > \text{NO}_3^- \approx \text{NO}_2^- > \text{Cl}^- > \text{HCO}_3^- \approx \text{CH}_3\text{COO}^-$ . Among several anions, the PVC membrane electrode gave the best response to iodide with an initial near-Nernstian slope of  $56.3 \pm 1.2$  mV/pI within the concentration range  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-6}$  M. Its response time was close to that of the electropolymerized film-coated thiocyanate-selective GC electrode, which was 20–30 s. However, because membrane components can leach out of the membrane during conditioning and potentiometric measurement periods, the iodide-selective PVC membrane electrodes lost their response after 2 weeks. This fact demonstrates the stability advantage of the developed thiocyanate-selective polymer film-coated GC electrode.

On the basis of the results in this study, the proposed thiocyanate-selective polymer film-coated GC electrode and iodide-selective PVC membrane electrode have comparable Nernstian slopes, selectivities, and response times.

They have a narrower working range and higher detection limit when compared to other thiocyanate-selective electrodes based on similar organometallic compounds and polymer films reported in the literature. However, the corrin-doped polypyrrole film-coated GC electrode has an improved lifetime over most of the previously reported thiocyanate-selective polymer film-coated electrodes and PVC membrane electrodes [14, 15, 33, 41].

## Conclusions

This work demonstrates that electropolymerized corrin film-coated anion-selective electrodes can be obtained by using a new pyrrole-substituted vitamin B<sub>12</sub> derivative. The response characteristics of the new thiocyanate-selective electrode were controlled by changing the electropolymerization conditions, pH of the solution, and conditioning time. This electrode exhibits a selectivity pattern that deviates from the Hofmeister series. The majority of the selectivity coefficients against the anions tested were in the order of  $1.0 \times 10^{-2}$ . The electrodes exhibited a near-Nernstian slope of  $56.9 \pm 0.6$  mV/pSCN<sup>-</sup> within the range  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-4}$  M, a detection limit of  $1.5 \times 10^{-5}$  M, and rapid response time of 10–25 s. An advantage of this electrode is the extended lifetime of at least 6 months with no significant deterioration in the slopes during this period.

## Experimental

*Cox*, *Cob*-di(cyano-κC)cobyrinic acid *a,b,d,e,f,g*-hexamethyl ester [42], 1-(3-aminopropyl)pyrrole [43], and *a,b,d,e,f,g*-hexamethyl-*c*-[3-(1*H*-pyrrol-1-yl)propyl]-*Cox*, *Cob*-di(cyano-κC)cob(III)yrinate [44] were synthesized as described earlier with minor modifications. TLC plates with a 250-μm layer thickness and 60 Å pore size, silica gel (70–230 mesh, 60 Å for column chromatography), the sodium salts of the anions tested, Amberlite IRA-400(Cl) ion-exchange resin, tetrabutylammonium perchlorate (TBAP), TBAC, tetrabutylammonium hydrogen sulfate (TBAS), 2,2,2-trichloro-1,1-dimethylethyl chloroformate, triethylamine, anhydrous acetonitrile, and ferrocene (Fc) were purchased from Sigma-Aldrich (St. Louis, MO). *N*-(2-Hydroxyethyl)piperazine-*N*-(2-ethanesulfonic acid) (HEPES), 2-amino-2-(hydroxymethyl)propane-1,3-diol hydrochloride (Tris-HCl), and 2-(*N*-morpholino)ethanesulfonic acid (MES) for buffer solutions were also obtained from Sigma-Aldrich. The solvents for all chemical reactions and chromatography were obtained from Acros Organics (Geel, Belgium) and EMD

Chemicals (Gibbstown, NJ) in high purity, and they were used without any further purification.

Pyrrole, obtained from Acros Organics, was stored under nitrogen atmosphere at  $-20$  °C, protected from light and was distilled prior to use. The solutions were prepared in anhydrous acetonitrile, which was stored over 3 Å molecular sieves. Sodium bicarbonate, sodium phosphate dibasic, sodium acetate, sodium hydroxide, citric acid, and glacial acetic acid were obtained from EMD Chemicals. Selectophore-grade 2-nitrophenyl octyl ether (NPOE), poly(vinyl chloride) (PVC), and tridodecylmethylammonium chloride (TDMACl) were purchased from Fluka (Ronkonkoma, NY). For all aqueous media experiments, deionized water of 18 MΩ (Mili-Q water purification system; Milipore, Bedford, MA) was used to prepare working solutions.

## Instrumentation

Electropolymerization studies were carried out with a Bioanalytical Systems (BAS) (Bioanalytical Systems, West Lafayette, IN) BASi CV-50 W voltammetric analyzer and BAS 100B C3 electrode cell stand. A conventional three-electrode cell was employed with a glassy carbon electrode (GC, BAS MF-2012) as the working electrode, while a platinum wire (BAS MW-1032) and Ag/AgCl (BAS MF-2052) were used as the counter and reference electrodes, respectively. The redox potentials were determined using the ferrocenium/ferrocene redox couple, Fc<sup>+</sup>/Fc, a standard reference material for nonaqueous media.

For potentiometric measurements, potential differences between the electropolymerized film-coated GC electrodes and a double junction Ag/AgCl electrode (Orion, model 900200, Beverly, MA) were obtained using an eight-channel SC-2345 interface (SCC-LP01, National Instruments, Austin, TX). A PCI-6036E multifunction I/O data acquisition device was used to connect the interface to a computer running LabVIEW 7.0 (National Instruments) software with a custom-designed program for data acquisition and analysis. The pH studies and buffer preparations were performed with the aid of a Fisher Scientific Accumet 915 pH/ion meter, which was equipped with an Orion pH glass electrode.

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectroscopy was carried out with Varian 200 MHz and Varian 400 MHz (Agilent Technologies, Santa Clara, CA) spectrometers. High-resolution mass spectroscopy analysis was performed with a Bruker microTOF-Q (Bruker Daltonics, Billerica, MA).

## *Cox*, *Cob*-di(cyano-κC)cobyrinic acid *a,b,d,e,f,g*-hexamethyl ester (**I**)

Compound **I** was prepared according to a published procedure [42] in 68 % yield. *R*<sub>f</sub> = 0.44 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH



10:1 with 0.1 % KCN); spectroscopic results closely matched the previously reported results [42, 45–49]. The product was stored in the dark at 4 °C.

#### *1-(3-Aminopropyl)pyrrole (II)*

The synthesis of compound **II** was performed according to Pablo et al. [43]. Briefly, to a solution containing 4.0 g of freshly distilled pyrrole (0.06 mol) in 33.0 cm<sup>3</sup> of acetonitrile, 9.4 g of powdered sodium hydroxide (0.23 mol) and 0.80 g of TBAS (2.4 mmol) were added, and the mixture was stirred at room temperature for 30 min. Then, 10.0 g of 3-chloropropylamine hydrochloride (0.07 mol) was added, and the reaction mixture was refluxed for 24 h in an oil bath. The inorganic solid was filtered off, and the solvent was removed under reduced pressure to yield a brown liquid product, 1-(3-aminopropyl)pyrrole. The product was purified with silica gel column chromatography using 1:1 ethyl acetate/MeOH containing 0.1 % NH<sub>4</sub>OH (7.40 g, 92 %).  $R_f = 0.23$  (ethyl acetate/MeOH 1:1 + 0.1 % NH<sub>4</sub>OH); <sup>1</sup>H NMR spectroscopic results closely matched the previously reported results [50].

#### *a,b,d,e,f,g-Hexamethyl-c-[3-(1H-pyrrole-1-yl)propyl]-Co $\alpha$ ,Co $\beta$ -di(cyano- $\kappa$ C)cob(III)yrinate (III, C<sub>60</sub>H<sub>81</sub>CoN<sub>8</sub>O<sub>13</sub>)*

The cobester **I** (142 mg, 132  $\mu$ mol) was dissolved in 10 cm<sup>3</sup> dry CH<sub>2</sub>Cl<sub>2</sub> under Ar, and the solution was cooled externally with ice/H<sub>2</sub>O/NaCl to –10 °C. Then, 36 mg 2,2,2-trichloro-1,1-dimethylethyl chloroformate (150  $\mu$ mol) and 117 mm<sup>3</sup> triethylamine (833  $\mu$ mol) were added to the cooled solution. The solution was stirred magnetically for 15 min and warmed to room temperature. Then, 579 mg of 1-(3-aminopropyl)pyrrole (4.7 mmol) was added, and the mixture was heated under reflux for 18 h. The product was purified by column chromatography using 96:4 CH<sub>2</sub>Cl<sub>2</sub>/MeOH (0.1 % KCN) as the mobile phase. The product fraction was shaken with aq. NaHCO<sub>3</sub> (containing KCN), and the organic phase was subsequently dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed by evaporation at ambient temperature to give the violet-red product (125.9 mg, 81 %).  $R_f = 0.70$  (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 96:4 + 0.1 % KCN). Compound **III** was co-purified with 0.4 mol ratio of the starting material, 1-(3-aminopropyl)pyrrole (**II**). ESI-TOF HRMS found 1,154.5229 (M<sup>+</sup> – CN), calculated for C<sub>60</sub>H<sub>81</sub>CoN<sub>8</sub>O<sub>13</sub> 1,180.5255.

Compound **III** was treated with 10 % (v/v) acetic acid in ethanol solution to displace one of the coordinated cyanide ligands with water, and thus generate a positively charged coordination site on the cobalt center (compound **IV**, Fig. 1). This treatment has been successfully employed in previous syntheses of vitamin B<sub>12</sub> derivatives [33]. A volume of 10.0 cm<sup>3</sup> of this solution was placed in a round-bottom flask and concentrated acetic acid (enough to

achieve a 10 % (v/v) acetic acid solution) was added. The solvent was evaporated in a rotary evaporator while heating at 45 °C. The residue was redissolved in 10 cm<sup>3</sup> of a 10 % acetic acid–ethanol solution, and the procedure described above was repeated for a total of three times. After the last treatment, the color of the compound had changed from purple to red. This method removes only one of the –CN ligands from the dicyano derivative resulting in an aquo-cyano derivative [23].

#### *Preparation of electropolymerized corrin film-coated electrode*

Before electropolymerization, the surface of the GC electrodes was polished on microcloths to a mirror finish by using successively finer grades of a slurry made from alumina powder, deionized water, and suspensions of 1-, 3-, and 15- $\mu$ m-sized diamond dust. Polished electrodes were successively sonicated in deionized water, electrolyte solution, and acetone for 5 min each. Electropolymerization of the corrin films was accomplished in anhydrous acetonitrile containing TBAC or TBAP ( $C_{\text{TBAP}}$  0.1 M and 0.5 M;  $C_{\text{TBAC}}$  0.1 M). The concentration of the corrin monomer was kept constant at 1.0 mM, and the concentration of pyrrole ( $C_P$ ) was varied between 0.01 and 1.0 M. The corrin monomer was copolymerized with pyrrole on GC electrodes by cycling repetitively between a set of starting potential (0–0.2 V), negative switching potential (–1.45 to –1.7 V), positive switching potential (0.55–1.3 V), and a constant final potential at –1.6 V for 2-min periods. The electrodes were then thoroughly washed with water. The total number of scans and scan rate were varied between 50–200 repetitions and 0.05–0.20 V s<sup>–1</sup>, respectively. All solutions were thoroughly deoxygenated directly in the electrochemical cell for 20 min by purging with pure nitrogen before electropolymerization. Electropolymerization was also performed under an inert nitrogen atmosphere. Once the film electrodes were prepared, they were rinsed thoroughly with water and stored in the dark at 4 °C.

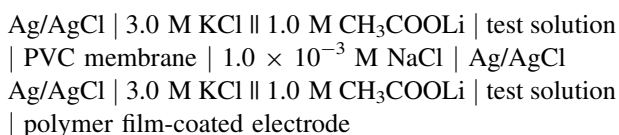
#### *Preparation of PVC membrane electrode based on new corrin compound*

A PVC membrane electrode based on the new corrin compound was prepared by using NPOE as plasticizer and TDMACl as lipophilic additive. Different membrane compositions in the range of 1–3 % ionophore, 32–33 % PVC, 67–64 % NPOE, and 60 mol % of TDMACl relative to the ionophore were used to prepare electrodes to compare with the electropolymerized corrin electrodes with respect to their lifetimes and selectivities. The PVC membrane-based ISEs were prepared by dissolving the

specific amounts of compound **IV** (the ionophore), TDMACl, PVC, and NPOE in 3 cm<sup>3</sup> of THF. After complete dissolution of all components, the membrane cocktail solution was poured into a 22-mm-i.d. glass ring located on a glass slide. The solvent was allowed to evaporate at room temperature overnight, leaving a PVC membrane with a thickness of about 150–200 µm. Small disks of each membrane were punched using a cork borer and mounted onto commercial Philips IS-561 (Gläsblaserei Möller, Zurich, Switzerland) electrode bodies. A solution of 1.0 × 10<sup>-3</sup> M NaCl was used as the internal filling solution.

### Potentiometric studies

All potentiometric measurements were performed at 21 ± 1 °C with a galvanic cell of the two following types:



The potentiometric responses of the electrodes were recorded in 1.0 × 10<sup>-1</sup>–1.0 × 10<sup>-6</sup> M working solutions of different anions (ClO<sub>4</sub><sup>-</sup>, I<sup>-</sup>, salicylate, SCN<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, CH<sub>3</sub>COO<sup>-</sup>) by adding, while stirring, known volumes of the solutions of anions to a beaker containing 50 cm<sup>3</sup> of one of the following 0.010 M buffer solutions: Tris–HCl, pH 7.0; phosphate, pH 7.0; HEPES, pH 7.0; MES, pH 6.2; citrate, pH 5.5; MES, pH 5.0; acetate, pH 4.0. The selectivity coefficients of the polymer film-coated GC electrodes and PVC membrane electrodes were determined by the separate solution method [51]. The effects of pH and conditioning time on the potentiometric response characteristics of the electropolymerized film-coated electrodes were also investigated.

In preliminary experiments for anion selectivity measurements, both types of electrodes were tested for response to various anions in deionized water without conditioning. After observing a significant thiocyanate response, we performed the potentiometric measurements in buffer solutions with the electrodes conditioned in 0.01 M NaSCN for 2–24 h. In order to minimize the effect of subsequent runs on the measured potential, between each set of measurements, the electrodes were washed with deionized water, and then equilibrated in deionized water and in buffer solution by stirring gently for 15 and 5 min, respectively.

An additional study was undertaken with an electrode on which pyrrole was electropolymerized under the same conditions described for the electrode containing the corrin film, and the differences in potentiometric behavior were compared.

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