## A Schiff Base Complex of Zn(II) as a Neutral Carrier for Highly Selective PVC Membrane Sensors for the Sulfate Ion

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Novel polymeric membrane (PME) and coated graphite (CGE) sulfate-selective electrodes based on a recently synthesized Schiff base complex of Zn(II) were prepared. The electrodes reveal a Nernstian behavior over wide  $SO_4{}^{2-}$  ion concentration ranges (5.0  $\times$   $10^{-5} {-} 1.0 \times 10^{-1}$ M for PME and 1.0  $\times$  10  $^{-7}\text{--}1.0$   $\times$  10  $^{-1}$  M for CGE) and very low detection limits (2.8  $\times$   $10^{-5}\,M$  for PME and 8.5  $\times$  10<sup>-8</sup> M for CGE). The potentiometric response is independent of the pH of the solution in the pH range 3.0-7.0. The electrodes manifest advantages of low resistance, very fast response, and, most importantly, good selectivities relative to a wide variety of other anions. In fact, the selectivity behavior of the proposed  $SO_4^{2-}$  ionselective electrodes shows a great improvement compared to the previously reported electrodes for sulfate ion. The electrodes can be used for at least 3 months without any appreciable divergence in potentials. The electrodes were used as an indicator electrode in the potentiometric titration of sulfate and barium ions and in the determination of iron in ferrous sulfate tablets.

The quick determination of trace quantities of anionic species by simple methods is of critical importance in chemical, clinical, and environmental analyses. Ion-selective electrodes based on solvent polymeric membranes with incorporation of ion carriers have been shown to be very useful tools for these purposes, due to their ease of preparation, simple operation, reasonable selectivity, relatively fast response, wide linear dynamic range, and low cost.<sup>1–6</sup> However, anion complexation and the design of sensing elements for anions is far less developed than the field of cation receptors.<sup>7,8</sup>

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Anion-selective electrodes based on conventional ion exchangers, such as quaternary ammonium salts, respond to anions in the order  $ClO_4^- > SCN^- > salicylate^- > NO_3^- > Br^- > NO_2^- \simeq$  $Cl^- > HCO_3^- > H_2PO_4^- \simeq F^- \simeq SO_4^{2-}$ , and this behavior reflects the order of decreasing hydrophobicity (Hofmeister selectivity).9,10 Nevertheless, the search for anion carriers with a selectivity sequence different from the Hofmeister pattern has been the subject of a series of recent investigations.<sup>5,6,11</sup> Among different anion carriers investigated for this purpose,5,6 the use of metalloporphyrins<sup>12–18</sup> and Schiff base complexes of the transition metal ions<sup>19-25</sup> as ionophores in solvent polymeric membrane electrodes is well known to induce potentiometric anion selectivity sequences that differ significantly from the classical Hofmeister pattern. The observed selectivity has been ascribed to the selective axial ligation between the metal centers coordinated to given porphyrins and Schiff bases and certain anions.

Due to its very low lipophilic character, sulfate ion recognition by potentiometric methods was found to be quite difficult.<sup>3,5</sup> Thus, despite the urgent need for selective potentiometric determination of trace amounts of the  $SO_4^{2-}$  ion in many chemical, pharmaceuti-

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Analytical Chemistry, Vol. 73, No. 13, July 1, 2001 2869

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<sup>10.1021/</sup>ac001449d CCC: \$20.00 © 2001 American Chemical Society Published on Web 05/24/2001

cal, environmental, and industrial samples, only a few reports dealing with sulfate ion-selective electrodes are available in the literature.<sup>26–29</sup> None of the solid-state and ionophore-free ion-exchange sulfate electrodes that have been reported are satisfactory, due to the lack of adequate selectivities.<sup>26</sup> Recently, new sulfate ion-selective electrodes based on a bis(thiourea) ionophore,<sup>27</sup> a derivative of imodazole,<sup>28</sup> and a zwitterionic bis(guanidinum) ionophore carrier<sup>29</sup> with a Nernstian behavior over a relatively wide concentration range have been reported. Compared to ionophore-free anion-exchange electrodes, <sup>26</sup> the interference effect of anions such as  $Cl^-$ ,  $HSO_3^-$ ,  $SO_3^{2-}$ ,  $HCO_3^-$ ,  $CH_3COO^-$ , and  $H_2PO_4^-$  for these new electrodes is significantly reduced. However, other anions, such as  $NO_3^-$ ,  $Br^-$ ,  $I^-$ ,  $NO_2^-$ ,  $CIO_4^-$ , and SCN<sup>-</sup>, show considerable interference to the potential response of the electrodes.<sup>27–29</sup>

Potentiometric sensors prepared by coating polymeric films containing electroactive species on metallic or graphite conductors,<sup>30,31</sup> with no internal electrolyte solution, are known to be very effective for a variety of cations and anions.<sup>24,32–35</sup> Electrodes of this type are advantageous in terms of simplicity, durability, high mechanical durability, and low cost, and they are capable of reliable response over a wide concentration range.

We have recently introduced some PVC-based membrane sensors for SCN<sup>-,18</sup> I<sup>-,25</sup> I<sub>3</sub><sup>-,36</sup> and Br<sup>-</sup> ions<sup>37</sup> using (octabromotetraphenylporphyrinato)manganese(III) chloride, a recently synthesized salen-Mn(II) complex, a charge-transfer complex of iodine with 2,4,6,8-tetraphenyl-2,4,6,8-tetraazabicyclo[3.3.0]octane, and a benzo derivative of xanthenium bromide as suitable ion carriers, respectively. Due to the vital importance of sulfate determination in chemical, pharmaceutical, environmental, and industrial analyses, we became interested in preparing a new PVCbased membrane sensor for the selective monitoring of the sulfate ion in solution. In this paper, we report highly selective solvent polymeric membrane (PME) and membrane-coated graphite electrodes (CGE) for the SO42- ion based on the Zn(II)-2,2'-[4,4'diphenylmethane bis(nitrilomethylidyne)]-bis(phenol) complex (ZnL) recently synthesized in our laboratories<sup>38</sup> that manifests the properties of an excellent neutral sulfate ion carrier.



ZnL

## **EXPERIMENTAL SECTION**

**Reagents.** Reagent grade dibutyl phthalate (DBP), acetophenone (AP), benzyl acetate (BA), tetrahydrofuran (THF), and

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high relative molecular weight PVC were purchased from Merck and used as received. Reagent grade sodium salts of all anions used (all from Aldrich) were of the highest purity available, and they were used without any further purification except for vacuumdrying over  $P_2O_5$ . All reagents needed were purchased from Merck and used as received.

Synthesis of Schiff Base L. A solution of 0.01 mol of diamine NH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub> dissolved in 10 mL of methanol was added to a stirring solution of salicylaldehyde (0.02 mol in 10 mL of methanol). The reaction mixture was refluxed with stirring for 3 h. The resulting precipitate was filtered off and washed with cold methanol. The product was finally recrystallized from methanol to get a yellow solid with a yield of 98%, mp = 123-124 °C: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz)  $\delta$ H (ppm) 4.04 (s, 2H), 6.98 (q, 4H, J = 7.57 Hz), 7.24 (d, 8H, J = 3.78 Hz), 7.36 (dt, 4H, J, = 13.22 Hz,  $J_2$ = 4.82 Hz), 8.62 (s, 2H), 13.31 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 62.9 MHz)  $\delta_{\rm C}$  (ppm) 40.98, 96.11, 117.24, 119.05, 121.23, 129.73, 135.14, 141.19, 148.24, 161.37, 163.22; IR (KBr)  $\nu$  (cm<sup>-1</sup>) 638 (s), 710 (w), 735 (w), 750 (vs), 758 (s), 775 (m), 790 (s), 820 (s), 845 (s), 865 (m), 910 (s), 980 (w), 1030 (m), 1115 (m), 1148 (s), 1158 (s), 1185 (br, s) 1282 (vs), 1368 (s), 1410 (m), 1455 (br, m), 1495 (s), 1505 (s), 1568 (vs), 159 5 (s), 1615 (vs), 2920 (s) 294 (w) 3020 (s) 3050 (s), 3445 (br, s); UV (CHCl<sub>3</sub>)  $\lambda_{max}$  (nm) 245, 271, 323, 348.

**Synthesis of a Zn–L Complex.** A solution of 0.1 mol of Schiff base L dissolved in 20 mL of methanol was added to a stirring solution of zinc acetate (0.1 mol in 20 mL of methanol). The mixture was heated to  $\sim$ 50 °C for 5 h under a nitrogen atmosphere. The reaction mixture was then cooled, and the resulting dark yellow precipitate was filtered off and washed with cold methanol. The precipitate was recrystallized from dichloromethane (yield, 91%). The structure of the pure complex Zn–L was confirmed by elemental analysis.

**Apparatus.** NMR spectra were recorded on a Bruaker Advance DPX-250 spectrometer. All chemical shifts are reported as ppm downfield from the TMS. The IR spectra were obtained on a Perkin-Elmer 781 spectrometer. The UV spectra were recorded on a Philips PU 8750 spectrophotometer. A Corning ion analyzer 250 pH/mV meter was used for the potential measurements at  $25.0 \pm 0.1$  °C.

**Preparation of Electrodes.** Membrane solutions were prepared by thoroughly dissolving 2 mg of the Zn–L ionophore, 37 mg of powdered PVC, and 61 mg of plasticizer BA in 3 mL of THF. The resulting clear mixture was evaporated slowly until an oily concentrated mixture was obtained. A Pyrex tube (5-mm o.d.) was dipped into the mixture for ~10 s so that a nontransparent membrane 0.3 mm thick was formed. The tube was then pulled out from the mixture and kept at room temperature for ~1 h. The tube was then filled with an internal solution ( $1.0 \times 10^{-3}$  M Na<sub>2</sub>SO<sub>4</sub>). The electrode was finally conditioned for 48 h by soaking in a  $1.0 \times 10^{-2}$  M sodium sulfate solution. A silver/silver chloride

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electrode or a silver/silver chloride-coated wire was used as the internal reference electrode.

To prepare the coated graphite electrodes, spectroscopic grade graphite rods 10 mm long and 3 mm in diameter were used. A shielded copper wire was glued to one end of the graphite rod, and the electrode was sealed into the end of a PVC tube of about the same diameter with epoxy resin. The working surface of the electrode was polished with fine alumina slurries on a polishing cloth, sonicated in distilled water, and dried in air. The polished graphite electrode was dipped into the membrane solution mentioned above, and the solvent was evaporated. A membrane was formed on the graphite surface, and the electrode was allowed to stabilize overnight. The electrode was finally conditioned by soaking in a  $1.0 \times 10^{-3}$  M solution Na<sub>2</sub>SO<sub>4</sub>.

**EMF Measurements.** The EMF measurements with the polymeric membrane electrodes and the coated graphite electrodes were carried out with the following cell assemblies:

Hg<sub>2</sub>Cl<sub>2</sub>, KCl (satd) | sample solution |

membrane | graphite surface (CGE)

The EMF observations were made relative to a double-junction saturated calomel electrode (SCE, Philips) with the chamber filled with an ammonium nitrate solution. A double-junction silver/silver chloride electrode (Metrohm) containing a 3 M solution of KCl was used as the internal reference electrode. It should be noted that a silver/silver chloride-coated wire electrode, in conjunction with an internal filling solution containing 3 M solutions of both Na<sub>2</sub>SO<sub>4</sub> and NaCl, can also be used as a proper reference electrode. Activities were calculated according to the Debye–Hückel procedure.<sup>39</sup>

## **RESULTS AND DISCUSSION**

In preliminary experiments, we found that the plasicized PVCbased membranes containing Zn-L as a neutral ionophore, generated stable potentials in solutions containing the sulfate ion, after proper conditioning in a  $1.0 \times 10^{-2}$  M solution of Na<sub>2</sub>SO<sub>4</sub>. The membranes revealed remarkable selectivity for SO<sub>4</sub><sup>2-</sup> relative to most common inorganic and organic anions. Such anti-Hofmeister selectivity is believed to originate from the selective axial ligation between the metal ion centers and certain anions.<sup>12–14</sup> With the aid of UV-visible spectra, as illustrated in Figure 1, it was possible to distinguish the specific interaction between the central metal and sulfate ion. That is, the neutral Zn–L (1.0  $\times$ 10<sup>-4</sup> M) shows two maximums at 254.5 and 287.3 nm, but in the presence of an equimolar concentration of the sulfate ion, the two spectral maximums are shifted to 247.2 and 296.0 nm, respectively. The observed spectral shifts, together with the substantial increase in absorbance, after contact of the carrier solution with the SO42ion-containing phase, suggests that the absorbing species had increased in size, and axial coordination was thought to take place.





**Figure 1.** Absorption spectra of  $1.0 \times 10^{-4}$  M Zn–L in acetonitrile in the absence (1) and presence of an equimolar concentration of the sulfate ion (2).

Meanwhile, the influences of other anions on the spectrum of Zn–L were also investigated, and almost no detectable spectral change was observed. Thus, the results obtained clearly revealed the specific interaction of the sulfate ion with Zn–L.

It is well understood that the sensitivity, linearity, and selectivity obtained for a given ionophore depend significantly on the membrane composition and nature of plasticizer used.<sup>6,24,25,39,40</sup> Thus, several membranes of varying plasticizer/PVC/carrier ratios were tested. The optimum membrane ingredient showing the most sensitive, reproducible, and stable results was obtained with a plasticizer/PVC ratio of  $\sim$ 1.6 together with 2% of the ionophore. A study of the influence of the plasticizer on the potentiometric response characteristics was conducted by using BA, AP, and DBP, and the results are given in Figure 2. That is, while BA as plasticizer implies the Nernstian behavior of the electrode over a wide concentration range, the use of AP and DBP resulted in the pronounced reduction in both sensitivity and linear dynamic range of the electrode. Thus, a membrane with the optimized ingredient composition of BA/PVC/Zn-L, in the ratio of 61:37:2, was selected to prepare both the polymeric membrane and the coated graphite electrodes for the sulfate ion. It has been shown that the presence of lipophilic ionic additives in the ion-selective membrane sensors is necessary to introduce permselectivity.<sup>40</sup> However, the selective and Nernstian response of the proposed electrodes in the absence of an additional lipophilic anion exchanger may be caused by possible ionic impurities within the used PVC.

The influence of the concentration of the internal solution on the potential response of the polymeric membrane electrode was also studied. The Na<sub>2</sub>SO<sub>4</sub> concentration was changed from 1.0 ×  $10^{-4}$  to  $1.0 \times 10^{-1}$  M and the EMF–pSO<sub>4</sub><sup>2–</sup> plots were obtained (Figure 3). As is obvious from Figure 3, the concentration of the internal solution has a negligible effect on the potential response

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Figure 2. Effect of plasticizer on potential response of the CGE.



Figure 3. Effect of internal filling solution on the potential response of the PME: 1,  $1.0 \times 10^{-1}$  M; 2,  $1.0 \times 10^{-2}$  M; 3,  $1.0 \times 10^{-3}$  M; 4,  $1.0 \times 10^{-4}$  M.

of the electrode, except for an expected change in the intercept of the resulting plots. Obviously, a  $1.0 \times 10^{-3}$  M concentration of the reference solution is quite appropriate for a smooth Nernstian function of the polymeric membrane system.

The critical response characteristics of the proposed electrodes were assessed according to IUPAC recommendations.<sup>41</sup> The EMF response of the polymeric membrane and coated graphite elec-



Figure 4. Calibration graphs for the CGE and PME at pH 5.5.

trodes (Figure 4) indicates their Nernstian behavior over a wide concentration range. The slopes and linear ranges of the resulting EMF–pSO<sub>4</sub><sup>2–</sup> graphs are given in Table 1. The limits of detection, defined as the concentration of sulfate obtained when the linear regions of the calibration graphs are extrapolated to the baseline potentials, are also included in Table 1. The improved performance characteristics of the CGE over those of the PME presumably originate from the coated graphite technology, where an internal  $1.0 \times 10^{-3}$  M Na<sub>2</sub>SO<sub>4</sub> solution, in the case of PME, has been replaced by a copper wire of much higher electrical conductivity, in the case of CGE.

The average time required for the electrodes to reach a potential response within  $\pm 1~\text{mV}$  of the final equilibrium value after successive immersion in a series of  $\text{SO}_4{}^{2-}$  solutions, each having a 10-fold difference in concentration, was investigated. Thus, the static response time of the electrodes obtained for concentrations of  $\leq 1.0~\times~10^{-3}$  M are also listed in Table 1.

A comparison of the data given in Table 1 revealed that, while both electrodes show a nice Nernstian behavior with fast response, the linear range and limit of detection of the coated graphite electrode are greatly improved relative to those of the polymeric membrane electrode. Furthermore, the membrane electrodes prepared could be used for at least 3 months without any measurable divergence, the lifetime of the CGE being longer than that of the PME.

The potentiometric response of the Zn–L-based electrodes was found to be sensitive to pH changes. Thus, the pH dependence of the electrodes was tested by measuring the potential response of solutions containing  $1.0 \times 10^{-3}$  M of the sulfate ion in the pH range 1.0-9.5, and the results are shown in Figure 5. A similar pH dependence has been reported before,<sup>36,42,43</sup> although the

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Table 2. Selectivity Coefficients of Various Interfering Anions

	selectivity coefficient											
ref	SCN-	$F^-$	Cl-	$Br^{-}$	I-	CN-	$NO_2^-$	$NO_3^-$	$ClO_4^-$	CH <sub>3</sub> COO <sup>-</sup>	$SO_3^{2-}$	CO32-
CGE PME 27 28 29	$\begin{array}{c} 1.0\times 10^{-2} \\ 7.9\times 10^{-2} \\ 7.9\times 10^{3} \end{array}$	$\begin{array}{c} 9.5 \times 10^{-3} \\ 1.5 \times 10^{-3} \\ - \end{array}$	$\begin{array}{l} 9.1\times10^{-3}\\ 4.0\times10^{-3}\\ 7.9\times10^{-1}\\ 1.1\times10^{-1}\\ 6.3\times10^{-1} \end{array}$	$\begin{array}{c} 8.5 \times 10^{-3} \\ 3.2 \times 10^{-3} \\ 1.3 \times 10^{1} \\ 7.9 \\ 2.5 \times 10^{2} \end{array}$	$\begin{array}{l} 3.2 \times 10^{-3} \\ 1.6 \times 10^{-2} \end{array}$ $2.5 \times 10^{7} \end{array}$	$\begin{array}{l} 8.3\times 10^{-3}\\ 1.5\times 10^{-2} \end{array}$	$\begin{array}{c} 1.3\times 10^{-3}\\ 1.0\times 10^{-2}\\ 4.0\\ 2.0\end{array}$	$\begin{array}{c} 1.7\times10^{-3}\\ 6.2\times10^{-3}\\ 4.0\times10^{1}\\ 1.2\times10^{2}\\ 2.0\times10^{4} \end{array}$	$\begin{array}{c} 6.2 \times 10^{-3} \\ 3.1 \times 10^{-2} \\ \\ \\ . \\ 2.5 \times 10^{10} \end{array}$	$\begin{array}{c} 1.6\times10^{-3}\\ 6.3\times10^{-3}\\ 3.2\times10^{-2}\\ 1.0\times10^{-3}\\ 2.0\times10^{-2} \end{array}$	$\begin{array}{l} 5.1\times 10^{-3}\\ 1.2\times 10^{-3}\\ 5.0\times 10^{-1} \end{array}$	$1.8 \times 10^{-3}$ $6.3 \times 10^{-3}$ 7.9



Figure 5. Effect of pH of the test solution on the potential response of the CGE and PME, at a sulfate concentration of 1.0  $\times$  10<sup>-3</sup> M.

doping and sensing anions are different. That is, for both electrodes, the potential response remains almost constant over the pH range 3.0–7.0 in a  $1.0 \times 10^{-3}$  M SO<sub>4</sub><sup>2–</sup> solution. The significant change in potential response observed at a pH below 3.0 can be reasonably related to the simultaneous response of the electrode to the oppositely charged H<sub>3</sub>O<sup>+</sup> and SO<sub>4</sub><sup>2–</sup> ions; the contribution of H<sub>3</sub>O<sup>+</sup> to potential response counteracts that of SO<sub>4</sub><sup>2–</sup> ion. On the other hand, the observed potential drift at high pH values could be due to competition of OH<sup>-</sup> ion with SO<sub>4</sub><sup>2–</sup> ion for the sensing species. Therefore, the best performance for the sulfate ion electrodes based on Zn–L should be achieved in the pH range 3.0–7.0.

Potentiometric selectivity coefficients, describing the preference of the Zn-L-based membrane for an interfering ion, B, relative to sulfate ion, A, were determined by the matched potential method (MPM), which is recommended by IUPAC44 to overcome the difficulties associated with the methods based on the Nicolsky-Eisenman equation.44,45 According to this method, the specified activity (concentration) of the primary ion (A) is added to a reference solution, and the potential is measured. In a separate 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,  $K_{A,B}^{MPM}$ , is then given by the resulting primary ion to interfering ion activity (concentration) ratio,  $K_{A,B}^{MPM} = a_A / a_B$ . The resulting values for both sulfate ionselective electrodes are listed in Table 2. The selectivity coefficients for the previously reported sulfate ion-selective electrodes based on a bis(thiourea) ionophore,<sup>27</sup> a derivative of imidazole,<sup>28</sup> and a zwitterionic bis(guadinium) ionophore,<sup>29</sup> are also included in Table 2 for comparison.

From the data given in Table 2, it is immediately obvious that the proposed sulfate sensors are highly selective with respect to other common anions. The selectivity coefficients are on the order



<sup>(44)</sup> Umezawa, Y.; Umezawa, K.; Sato, H. Pure Appl. Chem. 1995, 67, 507.



**Figure 6.** Potentiometric titration curves of  $1.0 \times 10^{-3}$  M solutions of SO<sub>4</sub><sup>2-</sup> (1) and Ba<sup>2+</sup> (2) with  $1.0 \times 10^{-1}$  M solutions of Ba<sup>2+</sup> (1) and SO<sub>4</sub><sup>2-</sup> (2), using the CGE as an indicator electrode.

of  $10^{-3}$ , which seems to indicate that these anions have negligible impact on the functionality of the  $SO_4^{2-}$  sensors. Meanwhile, the data given in Table 2 revealed that, in most cases, the selectivity coefficients obtained for the coated graphite electrode are lower than those for the polymeric membrane electrode, emphasizing the superiority of the former electrode in this respect as well.<sup>32–35</sup>

It is interesting to note that a comparison of the selectivity coefficients obtained with the proposed sensors along with those reported before<sup>27–29</sup> clearly indicated a tremendous enhancement in the selectivity behavior of the proposed electrodes for the  $SO_4^{2-}$  ion. That is, despite the fact that the previously reported electrodes for the  $SO_4^{2-}$  ion<sup>27–29</sup> show a close Nernstian EMF–concentration behavior, they could actually be considered good selective electrodes for thiocyanate,<sup>27</sup> nitrate,<sup>28</sup> and perchlorate<sup>29</sup> ions (rather than for sulfate ion), as is quite obvious from the selectivity coefficient data given in Table 2. Therefore, on the basis of these data, we may conclude that the membrane sensors proposed in this work are the most selective sulfate electrodes prepared to date.

The proposed membrane electrodes were found to work well under laboratory conditions. The coated graphite electrode was used as an indicator electrode in the successful titration of a sulfate ion solution  $(1.0 \times 10^{-3} \text{ M})$  with the Ba<sup>2+</sup> ion  $(1.0 \times 10^{-1} \text{ M})$  and vice versa. The results of both titrations are shown in Figure 6,

<sup>(45)</sup> Bakker, E. Electroanalysis 1997, 9, 7.

indicating that the amount of  $\mathrm{SO}_4{}^{2-}$  or  $\mathrm{Ba}{}^{2+}$  ions can be accurately determined with the electrode.

The CGE was also used for the determination of iron in a ferrous sulfate tablet (from Rose Daru Pharmaceutical Co., Tehran, Iran). Each tablet was dissolved in water in a 50-mL volumetric flask, and 0.5 mL of 3 M nitric acid was added and diluted to the mark with water. The resulting solution was then titrated with a  $1.0 \times 10^{-1}$  M standard BaCl<sub>2</sub> solution, using the proposed sensor

as an indicator electrode. The iron content of the drug calculated from four replicate measurements (50.4  $\pm$  1.0 mg/tablet) was found to be in satisfactory agreement with the declared amount of 50 mg/tablet.

Received for review December 8, 2000. Accepted March 1, 2001.

AC001449D