Selenite-Selective Membrane Electrodes Based on Ion Exchangers and Application to Anodic Slime

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A new membrane selenite selective electrode has been developed. The electrode consisted of 4% ion exchanger, QAD 86 PI (dialkyldimethylammonium chloride), as the active material, and 96% SR as the membrane matrix. An analytically useful potential change occurs from 10^{-6} – 10^{-1} M selenite ion. The slope of the linear portion is 19 mV/10 fold change in selenite concentration. No interference was observed for SO_4^{2-} , SO_3^{2-} , S^{2-} , HPO_4^{2-} , Cl^- , Br^- and I^- ions. The lifetime of the electrode was about three months. This electrode has been used for the determination of selenium in anodic slime at pH 8 (ammonia buffer) using standard addition method.

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Introduction

Increasing number of investigations about ion selective electrodes have been done in the last decade because of their ease in use and their selectivity characteristics. Many of these selective electrodes are prepared with organic ion exchangers having large-sized molecules and with neutral carriers. These membranes are sensitive to a larger number of ions than the glass and solid state membranes. Among these Ca^{2+} , K^+ and NO_3^- ion electrodes are commercially available.^{1–3} The first liquid ion exchanger membrane electrode was prepared by Ross in 1967⁴ using phosphate esters as the active material. This electrode was used for the determination of calcium in blood serum. The liquid membrane electrodes show long response times and low selectivity; thus more recently solid membrane electrodes have been prepared using various polymer matrix materials. For Ca ion-selective electrodes, vinylacetate or vinylchloride (PVC) matrix materials are used with organic phosphate ion exchanger.⁵ The electrodes prepared with quaterner ammonium salts are being used for the determination of nitrate ions in various water samples.^{6–8} The response times reported by Davies *et al.*⁶ for the PVC nitrate electrode ranged from approximately 2.5 to 5 min in the range 10^{-1} – 10^{-4} M nitrate, but were extended to 30 min at 10^{-5} M. However, response times measured by a rapid standard addition procedure for small concentration increases in the 10^{-2} – 10^{-5} M range were much smaller. It was claimed that the response time was also dependent on the rate of stirring, changing from 15 s to 6 min. There is no selenite selective electrode found in the literature in which ion exchangers have been used. Picrate-selective electrode was used indirectly for the determination of selenite; this method is based on the catalytic effect of selenium on the reaction between picrate and sulfide.^{9,10} In another study, a liquid membrane was prepared with the solution of 3,3-diaminobenzidine in hexane, and selenite could be determined.¹¹ However, the detection limit of this electrode was larger than

10^{-4} M for Se and the lifetime was shorter than one day. With a membrane electrode composed of 1,2-phenylenediamine-Se complex as the active membrane constituent and silicon rubber as membrane matrix, a linear response was observed for selenite in 10^{-1} – 10^{-5} M concentration range with a slope of 20.7 mV.¹² The lifetime of this electrode was found to be about two months. A solid state selenite selective electrode was also prepared¹³ by using silver selenite and copper(I) sulfide; the change of potential with concentration was linear in the range of 10^{-1} – 10^{-5} M with a slope of 28 mV.

Since there are no investigations about electrodes prepared using ion exchangers, the aim of this study was to make and use some of them. In the present study, solid membrane electrodes were prepared using ion exchangers such as QAD 86 PI, TOAB, TDMAI, MTOACl as the active material, PVC and SR as inert matrix and DBF as plasticizer. Their optimum working conditions for the determination of selenium were investigated. Interference studies have been made and this electrode has been used for the determination of selenium in anodic slime using a standard addition procedure.

Experimental

Apparatus and reagents

For the potentiometric measurements, a JENWAY 3030 Ion Analyser was used. A double junction Ag/AgCl electrode 924036 was used as the outer reference electrode. As the inner reference a home-made Ag/AgCl electrode¹⁴ was prepared. For the pH measurements, the Ion Analyser with 924005 combined pH electrode was used. All measurements were done in a 10 ml glass cell prepared for this purpose. A magnetic stirrer was used throughout the experiments.

All reagents used were of analytical reagent grade (Merck). Triply distilled water was used for the preparation of solutions. The stock solution of 0.1 M Se^{IV} was prepared by dissolving 2.63 g $\text{Na}_2\text{SeO}_3 \cdot 5\text{H}_2\text{O}$ in 100 ml water.

Dialkyldimethylammonium chloride (KO Cooperation S.A) which is commonly called "QAD 86 PI in composition 5% C_{14} , 32% C_{11} , 63% C_{18} ", TOAB (tetraoctylammonium bromide,

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Table 1 The slopes for electrodes in different compositions

% Composition							Slope ($10^{-5} - 10^{-2}$)/mV
TOAB	TDMAI	MTOACI	QAD86PI	DBF	PVC	SR	
20	—	—	—	40	40	—	9.8
—	20	—	—	40	40	—	4.9
—	—	20	—	40	40	—	3.3
		—	10	40	50	—	4.9
			20	40	40	—	11.7
			30	40	30	—	2.2
			8	—	—	92	5.6
			4	—	—	96	19.2
			2	—	—	98	11.8

Fig. 1 Calibration curves for QAD 86 PI-SR electrodes prepared with varying amounts of ion exchanger. ♦, 8% IE; ■, 4% IE; △, 2% IE.

Sigma), TDMAI (tridodesylmethylammonium iodide, Aldrich), MTOACI (Methyltrioctylammonium chloride, Aldrich) were used as the ion exchangers for the preparation of electrodes.

Preparation of the electrode

PVC membrane electrodes. In a 50 ml beaker with a diameter of 4.2 cm, 100–200 mg PVC dissolved in 5 ml THF (tetrahydrofuran), 200–300 mg ion exchangers dissolved in 5 ml THF, and 0.2–0.3 ml of DBF (dibutylphthalate) are mixed and stirred. The solvent is then allowed to evaporate at room temperature for about 24 h. The membrane formed as a film in the bottom is taken out carefully using a Teflon forceps. This film membrane is cemented to the flat end of a PVC tube (1 cm diameter) with an adhesive of PVC dissolved in THF. One day after, the excess membrane is cut and the tube is filled with 0.1 M Na_2SeO_3 and 0.1 M NaCl solution. Ag/AgCl electrode is immersed as the inner reference. The membrane electrode is immersed into a 10^{-5} M Na_2SeO_3 solution for about 2 days in order to condition the electrode.

Silicon rubber membrane electrode. For this purpose, 10 ml beakers with flat and 2 cm diameter bottoms are used. First 4–16 mg of ion exchanger and 250–300 mg Siloprene K-1000 are mixed until the ion exchanger was homogeneously dispersed. Then 50–60 mg of cross-linking agent, Silopren K-11, is added. The solvent is allowed to evaporate for about 3 h at room temperature. The membrane is taken out carefully as a film from the beaker and is mounted on the end of a glass tube

with a silicon rubber sealant. After about half an hour, the excess membrane is cut from the edges of tubing and after about 1–2 h it is filled with 0.1 M Na_2SeO_3 and 0.1 M NaCl solution and the Ag/AgCl electrode is immersed as a inner reference electrode. The electrode has to wait for about 24 h in 10^{-5} M Na_2SeO_3 solution so that steady potentials can be obtained.

Results and Discussion

Various ion exchangers, whose compositions are given in the experimental section were used for the preparation of selective electrodes. For this purpose, either PVC or SR (silicon rubber) were used as membrane matrix and DBF as plasticizer.

Effect of composition and thickness

TOAB, TDMAI, MTOACI, QAD 86 PI ion exchangers all in different compositions were used to prepare electrodes, with PVC as supporter and DBF as plasticizer. Their responses were measured at different selenite concentrations between 10^{-1} – 10^{-6} M. The ionic strength was held constant with 0.1 M NaNO_3 solution. Among the electrodes prepared with PVC and different ion exchangers, the one with QAD 86 PI had the largest slope. The slope of the electrode depends both on the membrane matrix and on the percentage of the ion exchanger. While the largest slope was 11.7 mV for PVC electrodes, the slope increased to 19.2 mV for silicon rubber (SR) electrodes. As can be seen from Fig. 1, the electrode prepared with SR as the membrane matrix and various amounts of QAD 86 PI as ion exchanger, had the highest slope when the ion exchanger was 4%. An analytically useful potential change occurs from 10^{-1} – 10^{-6} M selenite ion; the slope of the linear portion is 19.2 mV/10 fold change in selenite concentration. This non-ideal Nernstian slope may be caused by many as yet-unidentified sources. The slopes for electrodes in different compositions are summarised in Table 1.

It was also found that with increasing quantities of plasticizer (DBF) and ion exchanger, the membrane became too soft to handle. On the other hand, at lower quantities the membrane was hard and breakable. There were also sealing and splitting problems with PVC electrodes. Thus SR electrodes were preferred and used throughout this work. Thanks to the hydrophobic character of SR, there was also no problems of swelling.

Membrane mixtures of 0.2, 0.3, 0.4 and 0.5 g quantities were used in the same size beakers and membranes of different thickness were obtained. In the concentration range of 10^{-5} – 10^{-1} M selenite, the slopes for 0.2, 0.3, 0.4 and 0.5 g of electrodes were 8.4, 18.5, 14.2 and 7.5 mV respectively. It was therefore decided to prepare electrodes with 0.3 g of quantity in

Fig. 2 The change of potential with selenite concentration at various pH values (electrode: 4% QAD 86 PI-96% SR). $\diamond$, 1×10^{-3} M SeO_3^{2-} ; $\blacksquare$, 1×10^{-4} M; $\blacktriangle$, 1×10^{-5} M.

a beaker with a 2 cm diameter bottom. An electrode prepared in 4% QAD 86 PI and 96% SR composition (0.3 g) was used throughout this work.

Effect of pH

The effect of pH on the potential readings at various selenite concentrations are also investigated. For this purpose 10^{-3} , 10^{-4} and 10^{-5} M selenite solutions are prepared and the pH was adjusted to certain values by the addition of HCl or NaOH (the pH is controlled with a pH meter). For each selenite concentration, measured potentials at each pH values are plotted against pH. As can be seen from Fig. 2, the potential readings remained nearly unchanged within the pH range of about 3–9 for 10^{-4} and 10^{-5} M selenite concentrations; there is a slight change at lower and higher pH values. However, since standard addition procedure was applied for the concentration determinations the small dependence on pH will not affect the results. For 10^{-3} M selenite solution, the potential was steady between pH ranges of 6–9 and 2–5.

Conditioning of the electrode, and lifetime

The electrodes prepared with PVC and SR can not be used immediately after they are prepared. In order to obtain steady potentials, the electrodes have to be immersed into selenite solution for a certain time after the inner filling solution is added. When they were left to wait in 10^{-5} , 10^{-4} and 10^{-3} M selenite solutions, the slopes of 18.1 mV, 17.6 mV and 15.2 mV were observed. Electrodes in 4% QAD 86 PI and 96% SR composition were left in 10^{-5} M selenite solution for 2 h, one, two and three days. As can be seen from Fig. 3, while the slope after one day was 5 mV, it was 18.5 mV after 2 and 3 days. It was therefore decided to leave the freshly prepared electrode for 2 days in 10^{-5} M selenite solution. It is known that the membrane loses its sensitivity because of the effect of interfering ions or some other surface-ruining effects such as mechanical rubbing. Therefore, after some time the membrane surfaces have to be cleaned by washing with distilled water and leaving the membrane in 10^{-5} M selenite solution for about 24 h. The lifetime of the electrode is found to be three months when it was immersed into a 10^{-5} M selenite solution, for 30 min after each set of measurements.

The response time of the electrodes

The response times of the electrode in 4% QAD 86 PI and

Fig. 3 The dependence of conditioning period of 4% QAD 86 PI-96% SR electrodes. $\diamond$, 2 h; $\blacksquare$, 1 d; $\triangle$, 2 d; $\times$, 3 d.

Fig. 4 The dependence of response time on the change of selenite concentration (electrode: 4% QAD 86PI-96% SR).

96% SR composition were measured for different selenite concentrations. When the selenite concentration was increased from 10^{-5} to 10^{-4} M by the addition of concentrated selenite solution, the response time was 5 min 20 s, when it changed from 10^{-4} to 10^{-3} it was 5 min, for a change from 10^{-3} to 10^{-2} it was 4 min 30 s. The larger the change in concentration, the larger is the response time, e.g. for a change from 10^{-5} to 10^{-2} it is 8 min 20 s. The response times are given for 100% responses. 90% response was achieved in much less time. The changes of potential with time by the selenite additions at different concentrations are given in Fig. 4. As the stirring rate or temperature is increased, the response time will be shorter (this work is done at $20 \pm 2^\circ\text{C}$).

Table 2 Selectivity coefficients ($k_{A,B}^{pot}$) for the selenite electrode in mixed solutions (in the presence of 10^{-5} M SeO_3^{2-})

B	SO_4^{2-}	SO_3^{2-}	S^{2-}	HPO_4^{2-}	I^-	Cl^-	Br^-
$k_{A,B}^{pot}$	8.31×10^{-5}	2.86×10^{-3}	2.47×10^{-4}	2.94×10^{-3}	1.81×10^{-3}	7.77×10^{-3}	4.88×10^{-3}

A = selenite ion in pH=8–9. B = interfering ion.

Fig. 5 The response of electrode against some anions in pH=8–9 and the presence of 10^{-5} M SeO_3^{2-} (electrode: 4% QAD 86PI-96% SR).

Interference studies

To check the effect of interfering ions, selectivity coefficients have to be determined. For this purpose, the mixed solution method¹⁵ is preferred, as it usually corresponds more closely to the situation in samples. In this method, solutions are prepared with a constant activity of the main ion and varying activity of interfering ion. The equation given below is used for this purpose:

$$k_{A,B}^{pot} a_B^{n_A/n_B} = a_A \{ \text{antilog}[(E_1 - E_2)/S] \} - a_A \quad (1)$$

Here, $k_{A,B}$ is the selectivity coefficient, a_A is the activity of the primary ion, a_B is the activity of the interfering ion, E_1 is the potential when only A is present, E_2 is the potential responsive to the primary ion in the presence of interfering ion, $S = 2.303 \times RT/n_A F$ (the slope of selenite electrode) and n_A and n_B are the charges of A and B. The $a_B^{n_A/n_B}$ values are plotted against the right-hand side of Eq.(1), and the slope will be equal to the selectivity coefficient of the interfering ion.

In this work, interference studies are made with the most common ions such as SO_4^{2-} , SO_3^{2-} , HPO_4^{2-} , S^{2-} , I^- , Br^- and Cl^- . For this purpose, the potential of 10^{-5} M selenite solution is first measured (E_1); then in the presence of 10^{-5} , 10^{-4} , 10^{-3} and 10^{-2} M of interfering ions, the potential values are once more recorded (E_2). The potentials obtained at different concentrations of selenite and interfering ions are plotted against concentrations, as shown in Fig. 5. The selectivity coefficients obtained for each ion are given in Table 2. As can be observed from Fig. 5 and Table 2 there is nearly no interference caused by these ions.

Determination of selenium in anodic slime

Anodic slime collects at the bottom of the anode compartment during the electrolytic purification of copper. It is the most important source for selenium. Anodic slime contains 8–20% of selenium, next to 20–40% of copper. There are also Ag, Pb

and Te in much smaller quantities, 0.3–3 %. The newly-developed membrane electrode is applied to some samples prepared from anodic slime which are digested with different acid mixtures. For this purpose, about 1.0 g of anodic slime samples are dissolved either in $\text{HCl} + \text{HNO}_3$ (1 + 3) or in HNO_3 .¹⁵ Acids are then evaporated nearly to dryness and then the sample is diluted into 50.0 ml. An aliquot of 0.05 ml is taken, 5.0 ml 0.1 M $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH=8) and 1 ml of 1 M NaNO_3 is added and the mixture is diluted into 10.0 ml. The potential of this solution is measured using the new membrane electrode against Ag/AgCl reference electrode. Then standard additions are made with standard 10^{-2} M selenite solution and the changes in potential are recorded. The same procedure is applied also to a solution of which the pH was adjusted to 6.5 by the addition of NaOH. The slope of this electrode was determined prior to these experiments and this slope is used in the equation given below for the calculation of selenite concentration in the sample.

$$C_X = \frac{C_S \cdot V_S}{(V_X + V_S) 10^{\Delta E/S} - V_X} \quad (2)$$

Here C_X is the selenite concentration of sample, C_S is the concentration of the standard, V_X and V_S are the corresponding volumes, S is the slope of the electrode, and ΔE is the change in potential.

The results obtained are given in Table 3 together with their standard deviations in 95% confidence interval. As can be seen there is a very good agreement with the results obtained for different digestion procedures and pH values. To check the validity of the results obtained with this electrode, the same anodic slime was analyzed by volumetric¹⁶ spectrophotometric^{17,18} polarographic¹⁹ and ISE electrodes,^{12,13} the results are given in Table 4.

The electrode developed enables the determination of selenium in complex matrices such as anodic slime. There is no interference coming from the most common ions. Its lifetime is quite long if compared with the electrodes reported earlier. It can be used directly, as there is no need for long and tedious separation procedures. If results are compared with those of spectrophotometric and polarographic methods given in Table 4 we see there is no need for expensive and sophisticated instruments.

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Table 3 Determination of selenium in anodic slime using standard addition method

Sample	$\Delta E_{ave}/$ mV	Calculated ave. $C_{SeO_3^{2-}}/M$	Average % Se	$S = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{N-1}}$	$CI^a = \bar{x} \pm \frac{t \cdot S}{\sqrt{N}}$
Digested in HNO_3 (NH_3-NH_4Cl pH=8)	14.1	1.36×10^{-4}	10.7	0.3	10.5 ± 0.3
Digested in HNO_3 HCl (NH_3-NH_4Cl pH=8)	14.2	1.33×10^{-4}	10.5	0.6	10.5 ± 0.7
Digested in HNO_3 (NaOH pH=8)	14.1	1.36×10^{-4}	10.7	0.3	10.5 ± 0.3

Number of samples (n) = 5. a. 95% confidence interval.

Table 4 Percentage of selenium in anodic slime determined by four different methods

Method used	Weight percentage of selenium in slime
This work	10 ± 1
ISE (membrane electrode)(12)	10 ± 1
ISE (solid electrode)(13)	10 ± 1
Volumetric (15)	10 ± 1
Spectrophotometric (16 - 17)	10 ± 1
Polarographic (18)	10 ± 1

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