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Short communication

Potentiometric measurement of ascorbate by using a solvent polymeric membrane electrode

Huimin Guo [a,b], Tanji Yin [a], Qingmei Su [a], Wei Qin [a,*]

[a] *Laboratory of Environmental Chemistry, Yantai Institute of Coastal Zone Research for Sustainable Development, Chinese Academy of Sciences, P.O. Box 1488, Yantai 264003, PR China*
[b] *Department of Chemistry, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China*

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Abstract

A novel potentiometric method for the determination of ascorbate is described in this communication. It is based on ascorbate oxidation with permanganate which is continuously released from the inner reference solution of a ligand-free tridodecylmethylammonium chloride (TDMAC)-based polymeric membrane ion selective electrode (ISE). The ISE potential determined by the activity of permanganate ions released at the sample–membrane phase boundary is increased with the consumption of permanganate. The proposed membrane electrode is useful for continuous and reversible detection of ascorbate at concentrations in 0.1 M NaCl ranging from 1.0×10^{-6} to 1.0×10^{-3} M with a detection limit of 2.2×10^{-7} M.
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1. Introduction

In recent years, many efforts were made in understanding the principles that dictate the lower detection limits of solvent polymeric membrane-based ion selective electrodes (ISEs) [1–4]. It has been realized that a transmembrane concentration gradient of primary ions will occur whenever the compositions of the sample and the inner solution are not the same [3]. Either fluxes of primary ions from the inner aqueous solution towards the sample solution or fluxes in the opposite direction may perturb the primary ion concentrations at the sample–membrane phase boundary and hence deteriorate the lower detection limit of ISEs [3,4]. Numerous strategies have been developed to fabricate ISE membranes that suffer much less from ion flux effects for large improvement of lower detection limits [5–7]. However, ion fluxes across the ISE membrane have been found also analytically useful, and most of current applications are based on the ion fluxes of primary ions in the direction of inner solution. Such examples include polyion sensors [8,9], pulstrodes [10], steptrodes [11], ion-channel biosenors [12,13], electrodes sensitive to total ion concentrations [14] and ISE indicators for complexometric titrations [15].

Here, we introduce a novel detection system that makes use of outward ion fluxes through ISE membrane, i.e. the fluxes in the direction of sample solution, to provide controlled-release reagent for measuring reductants. It is well known that one significant limitation of reagent-based chemical sensors is the use of inherently irreversible recognition reactions such as most redox reagent systems [16] and immunochemical reactions [17]. To solve this problem, continuously sensing reservoir sensors have been developed for reagent renewal, and polymer matrix is commonly used to incorporate the reagent which can be released slowly upon contact with aqueous solution. However, most of such polymeric delivery systems are used for optical sensors [18–21]. The conventional membrane ISEs have been found to show the fluxes of primary ions from the inner aqueous solution towards the sample solution, which may provide an alternative way for controlled release of analytical reagents. But, so far, ISEs based on such outward ion fluxes are rather rare, only an anion electrode based on precipitate equilibrium at the sample–membrane phase boundary with the released silver ions from the sensing membrane was reported [22]. In this paper, the outward ion fluxes of ISE membrane are first used for irreversible sensing chemistries. It will be shown that the ISE membrane not

* Corresponding author. Tel.: +86 535 6910580; fax: +86 535 6910566.
E-mail address: wqin@yic.ac.cn (W. Qin).

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only can serve as a polymer matrix for reagent release as used in the polymeric delivery systems for optical sensors, but also can work as a transducer for sensitive potentiometric detection in irreversible redox systems.

2. Experimental

2.1. Reagents

Tridodecylmethylammonium chloride (TDMAC), 2-nitrophenyl octyl ether (*o*-NPOE), bis(2-ethylhexyl) sebacate (DOS), and high molecular weight poly(vinyl chloride) (PVC) were purchased from Fluka AG (Buchs, Switzerland). All chemicals and reagents were of Selectophore or analytical reagent grade. Aqueous solutions were prepared with freshly deionized water (18.2 MΩ cm specific resistance) obtained with a Pall Cascada laboratory water system.

2.2. Membranes and electrode preparation

The ionophore-free permanganate selective membranes contained 10 wt% lipophilic anion exchanger TDMAC, 65 wt% plasticizer *o*-NPOE and 25 wt% PVC. Membranes of ~130 (65) μm thickness were obtained by casting a solution of ~240 (160) mg of the membrane components dissolved in 2.5 mL of tetrahydrofuran (THF) into a glass ring of 36 mm diameter fixed on a glass plate and letting the solvent evaporate overnight. Membrane thicknesses were visually measured with a CX31-32C02 Olympus microscope (Tokyo, Japan).

For each ISE, a disk of 7 mm diameter was punched from the membranes and glued to a plasticized PVC tube (i.d. 6 mm, o.d. 9 mm) with a THF/PVC slurry. Experimental selectivity coefficients for permanganate selective TDMAC-based membrane electrodes were measured by using 0.01 M NaCl as the internal filling and conditioning medium. For ascorbate detection, a 0.08 M potassium permanganate solution containing 0.02 M NaCl was added to each electrode as the inner filling solution, while 0.1 M NaCl was used as the conditioning solution. Before measurements, the electrodes were conditioned overnight for selectivity coefficient measurements and 3 days for ascorbate detection, respectively.

2.3. EMF measurements

All measurements of EMF were performed at 25 °C using a CHI-660 workstation (Shanghai, China) with a saturated calomel electrode (SCE) as reference electrode in the galvanic cell: SCE//sample solution/ISE membrane/inner filling solution/AgCl/Ag. For selectivity coefficient measurements, all the EMF values were corrected for the liquid-junction potential according to the Henderson equation and activity coefficients were calculated by the Debye–Hückel approximation. For reductant determination, the sample solutions were prepared with 0.1 M NaCl and adjusted with NaOH and HCl to pH 7.0 measured by a PXSJ-216 pH meter (Shanghai, China). In this case, most of the reductants exist in the anionic forms and can be completely dissolved in the whole concentration range for interference study.

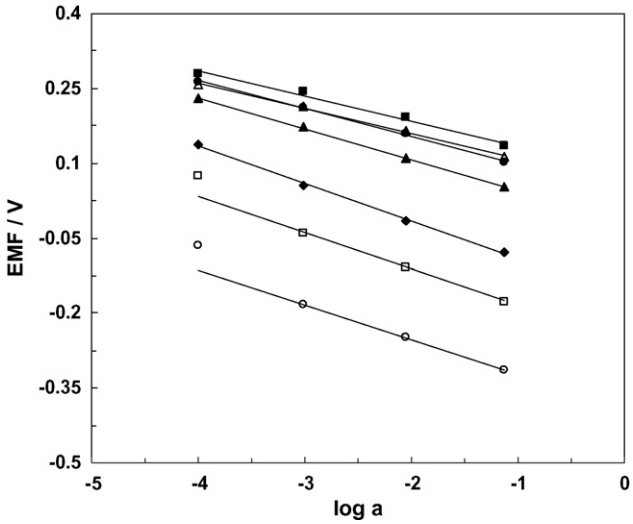

Fig. 1. EMF responses obtained according to Bakker's method toward the anions: (◯) permanganate, (□) thiocyanate, (♦) nitrate, (▲) chloride, (●) ascorbate, (△) hydrogen carbonate and (■) acetate. Membrane A as shown in Table 2.

2.4. Diffusion measurement of permanganate anion through ionophore-free TDMAC-based polymeric membrane

A 7-mm diameter disk was cut from the parent membrane and glued to a PVC tube (i.d. 6 mm, o.d. 9 mm). This tube was connected with a pipette tip containing 1.0 mL of 0.08 M potassium permanganate solution with 0.02 M NaCl, and immersed into 5.0 mL of deionized water in a glass vial. With continual stirring of the water solution in the glass vial, the amount of permanganate released per day in the recipient solution was assayed by an AA-7001 flame/graphite stove atom absorption spectrophotometer (Beijing East & West Analytical Instruments, China).

3. Results and discussion

Potassium permanganate, $KMnO_4$, is a commonly used chemical oxidizing agent and has been widely used for titrations of reductants by irreversible redox reactions. Interestingly, permanganate was found very lipophilic and showed a high anion response compared to other tested anions such as thiocyanate, nitrate, chloride, ascorbate, hydrogen carbonate and acetate when using a ligand-free ISE membrane based on anion exchanger TDMAC. The selectivity of such TDMAC-based polymeric membrane electrodes was characterized by using Bakker's method to eliminate the influence of the inherent sensitivity limit on the response toward discriminated ions [23]. The results are shown in Fig. 1. The apparent super-Nernstian response which occurs at a relatively high concentration of 10^{-4} M for permanganate and thiocyanate is induced by the high concentration of ion-exchanger in the membrane [24]. The

Table 1
Potentiometric selectivity coefficients for a permanganate-selective membrane electrode[a]

Ion J	log $K^{pot}_{MnO_4J}$ [b]	Ion J	log $K^{pot}_{MnO_4J}$ [b]
SCN^-	−2.36 ± 0.05	$AscH^-$ [c]	−6.86 ± 0.17
NO_3^-	−3.97 ± 0.03	HCO_3^-	−7.07 ± 0.17
Cl^-	−6.08 ± 0.10	OAc^- [d]	−7.50 ± 0.08

[a] Membrane A as shown in Table 2.
[b] Mean value obtained from three corresponding pairs of concentrations of permanganate and the respective interfering anion in the measuring range of 10^{-1} to 10^{-3} M ± standard deviation.
[c] Ascorbate anion.
[d] Acetate anion.

logarithmic Nikolskii coefficients for permanganate ($K^{pot}_{MnO_4J}$) over other anions are summarized in Table 1. The high discrimination against these anions allows the permanganate membrane ISE to be used in the presence of physiological saline medium (e.g. 0.1 M NaCl). Fig. 1 also illustrates that TDMAC-based membrane ISE shows much less response toward ascorbate with a low logarithmic selectivity coefficient of −6.86. This indicates that it is impossible to directly measure low concentrations of ascorbate in the presence of interfering anions by using the conventional ion-exchanger-based ISE.

The constant release of primary ions under zero-current conditions from inner solution into sample solution which dictates the detection limit of the potentiometric sensor at low sample concentrations has been extensively studied in recent years [3]. In the case of the present permanganate selective membrane electrode, the release of permanganate may be accompanied by a simultaneous release of the ion-exchanger TDMAC [25], which shows less lipophilicity compared with other tetraalkylammonium salts [24]. The diffusion of permanganate ions across the polymeric membrane was monitored by atom absorption spectroscopy in the recipient solution as a function of time. The results are shown in Fig. 2. It can be seen that a constant release of permanganate ions could be available after conditioning the electrode for 3 days.

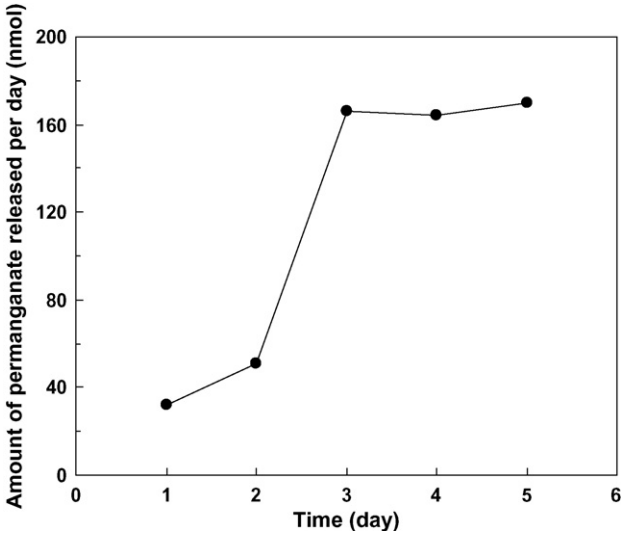

Fig. 2. Dependence of the amount of permanganate ions released per day in the receiving phase as a function of time. The average of five measurements. Membrane C as shown in Table 2.

In the absence of reductant, the flux of permanganate ions released from the inner solution into the membrane surface layer equals to the flux diffusing further into the sample bulk, thus generating a stead-state process with a constant concentration of permanganate ions released at the sample–membrane phase boundary [21]. The potential response of the electrode is determined by the activity of those permanganate ions, assuming the influence of the background anion activities is negligible:

$$E_{min} = E^0 - \frac{RT}{F}\ln \alpha_{MnO_4^-} \quad (1)$$

When a reductant is added into the sample solution, an efficient redox reaction occurs and the permanganate activity at the phase boundary is decreased, thus increasing the measured potential. A steady-state response can be obtained when the difference between the fluxes into and out of the membrane surface layer of permanganate ions equals to the consumption rate of permanganate ions in the redox reaction with the reductant. Such consumption rate depends not only on the concentration of reductant in sample solution but also on the reducing power of the tested reductant (see below). The maximum potential will reach if all the permanganate ions at the interface are consumed by the reductant, and the sample activity of the interfering anion governs the sensor response:

$$E_{max} = E^0 - \frac{RT}{F}\ln\left(K^{pot}_{MnO_4J}(\alpha_{J^{z-}})^{\frac{1}{z_J}}\right) \quad (2)$$

The total potential change can be expressed as:

$$\Delta E_{total} = \frac{RT}{F}\ln\left(\frac{\alpha_{MnO_4^-}}{K^{pot}_{MnO_4J}(\alpha_{J^{z-}})^{\frac{1}{z_J}}}\right) \quad (3)$$

Apparently, higher potential response for reductants will be obtained with higher activities of permanganate ions released at the sample–membrane interface, with higher selectivities over the sample interfering anions, and with lower interfering ion activities. In our experiments, 0.1 M NaCl was used as the sample medium. Fig. 3 illustrates a typical response curve of the ISE showing changes in EMF with successive addition of ascorbate. It can be seen that a total voltage change of ca. 160 mV could be obtained using 0.08 M potassium permanganate with 0.02 M NaCl as inner filling solution of the permanganate selective membrane electrode. The released permanganate activity at the sample–membrane phase boundary was 2.7×10^{-5} M, measured by calibrating with a series of permanganate solutions at higher concentrations of 10^{-3}, 10^{-2}, and 10^{-1} M [26]. Factors influencing the potential response such as membrane compositions and thicknesses were studied. The results are summarized in Table 2. It was found that higher EMF values could be induced by higher concentrations of ion-exchangers, thinner membranes and higher contents of polar plasticizers, all of which could promote the ion fluxes from the inner filling solution into the sample solution and therefore cause higher permanganate activities at the sample–membrane interface. These results are con-

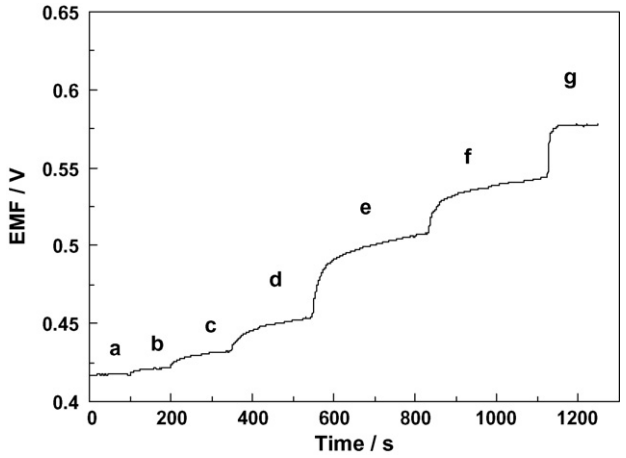

Fig. 3. Time history of ISE response to successive additions of ascorbate: (a) 0 (the blank), (b) 1.0×10^{-6} M, (c) 5.0×10^{-6} M, (d) 1.0×10^{-5} M, (e) 5.0×10^{-5} M, (f) 1.0×10^{-4} M, and (g) 1.0×10^{-3} M. Membrane C as shown in Table 2.

sistent with those for ion fluxes of primary ions in the direction of inner solution which result in a super-Nernstian response [4].

Reversibility of the sensor was evaluated by measuring the alternating responses to ascorbate at a high concentration (1.0×10^{-3} M) and a low concentration (3.0×10^{-6} M). The results are shown in Fig. 4. It can be seen that the signal changes are fully reversible in both cases. For the high concentration measurement, the time to achieve 95% of the full-scale response is very fast (0.5 min), whereas recovery to 95% of the initial value takes ca. 30 min. In contrast, response toward low concentrations of ascorbate is a bit longer (1.5 min), but the recovery time is considerably shorter (2 min). It should be noted that the response time for medium concentrations of ascorbate ranging from 5.0×10^{-5} to 1.0×10^{-4} M is much longer (ca. 4 min) as compared to those for high and low concentrations (Fig. 3). This is probably due to the fact that the permanganate ions released at the sample–membrane interface may be largely consumed by the efficient reduction with ascorbate at medium concentrations so that chloride ions in the sample solution are able to partially ion exchange with the permanganate ions in the interfacial layer of the membrane phase, which renders the response processes longer. Indeed, faster potential response was observed when no NaCl was added in the sample solution (data not shown).

Table 2
Total potentiometric response for ascorbate in the presence of 0.1 M NaCl obtained by using TDMAC-based PVC membrane ion selective electrodes with various membrane compositions and thicknesses

Membrane	ΔE_{total} [a] (mV)	TDMAC (wt%)	Plasticizer (wt%)	PVC (wt%)	Thickness [a] (μm)
A	60 ± 6	5	63(NPOE)	32	107 ± 4
B	84 ± 8	10	65(NPOE)	25	131 ± 7
C	164 ± 11	10	65(NPOE)	25	65 ± 3
D	58 ± 7	10	65(DOS)	25	63 ± 3
E	9 ± 3	10	40(NPOE)	50	73 ± 3

[a] Average value of three determinations ± standard deviation.

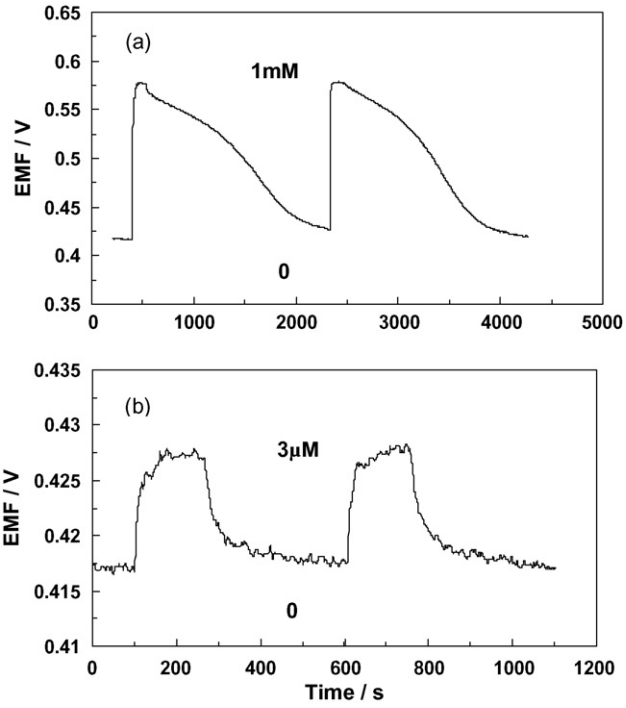

Fig. 4. Recycle response profiles for the blank and ascorbate solutions: (a) 1.0×10^{-3} and (b) 3.0×10^{-6} M. Membrane C as shown in Table 2.

A recent paper shows that using thin supported liquid membranes can establish steady-state concentration profiles across ion-selective membranes rapidly [27], which might significantly reduce both the response time and recovery time for the present sensor.

Typical calibration curves for ascorbate and for other reductants including dopamine, urate, sulfite and oxalate are shown in Fig. 5. As indicated in the figure, the present membrane electrode is useful for measuring ascorbate in the presence of 0.1 M NaCl at concentrations ranging from 1.0×10^{-6} to 1.0×10^{-3} M with a relative standard deviation of less than 5 % for 1.0×10^{-5} M ($n = 5$). The detection limit is 2.2×10^{-7} M which gives a signal equal to the blank signal plus three times the

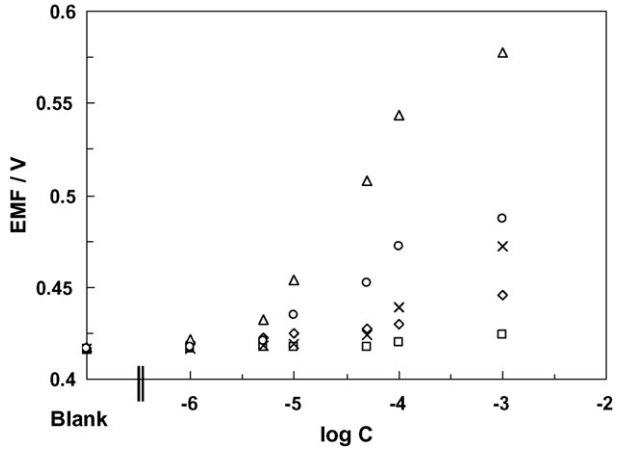

Fig. 5. ISE response curves for reductants: (△) ascorbate, (◯) dopamine, (×) urate, (◇) sulfite, and (□) oxalate. The average of five measurements. Membrane C as shown in Table 2.

Table 3
Results of ascorbate in vegetables and pharmaceutical preparations

Sample	Proposed sensor (mg/g)[a]	Iodiometry (mg/g)[a]
Tomato	0.117 ± 0.005	0.122 ± 0.002
Mung bean sprouts	0.092 ± 0.004	0.095 ± 0.002
Vitamin C tablet[b]	950 ± 5	952 ± 5
Multi-vitamin tablet[c]	35 ± 1	36 ± 1

[a] Average value of five determinations ± standard deviation.
[b] Jiangsu Jiangshan Pharmaceutical Factory, China.
[c] Jiangxi Jurentang Pharmaceutical Industries Co., China.

standard deviation of the blank measurement ($n = 11$). No significant changes were observed in the response characteristics of the polymeric membrane electrode after one week. At neutral pH, permanganate ions released at the membrane–sample interface are converted to manganese dioxide by the redox reaction with reductants. However, the formation of manganese dioxide could not poison the electrode membrane surface, which is due to the fact that manganese dioxide produced is in relatively small amounts and can be dissolved in the sample solution. Negligible response was observed up to 10^{-5} M for urate, sulfite and oxalate, while dopamine showed nearly 50% of the potential changes as compared with those for ascorbate. The order of decreasing potential response for these reductants is ascorbate > dopamine > urate > sulfite > oxalate, which corresponds directly to the order of reducing powers. Compared with other electrochemical sensors [28,29], the proposed polymeric membrane electrode offers potential advantages of simplicity, rapidity and high sensitivity for ascorbate determination.

Finally, the present sensor was applied to the determination of ascorbate in vegetables and pharmaceutical preparations. The samples were treated for analysis as described before [30]. Potentionmetric measurement was done for each sample and the concentration of ascorbate was quantified according to the calibration curve of the proposed electrode. The results are listed in Table 3 which agree well with those obtained by iodimetric analysis [31].

4. Conclusion

In summary, using permanganate–ascorbate redox system as a prototype, we have shown that the outward ion fluxes of ISE membrane can be used as a reagent controlled-release approach for irreversible sensing chemistries with submicromolar lower detection limits. The ISE membrane not only serves as a polymer matrix for reagent release as used in the polymeric delivery systems for optical sensors, but also works as a transducer for sensitive potentiometric detection. This combination makes the ISE membrane very attractive for sensor miniaturization. Further studies on the mechanism of this new detection principle and its application to other irreversible sensing chemistries are in progress in our laboratory.

Acknowledgements

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