

## SHORT PAPERS

## Periodate-selective Liquid Membrane Electrode

Ajay K. Jain, Muzayan Jahan and Vipendra Tyagi

Department of Chemistry, University of Roorkee, Roorkee-247 667, India

A liquid membrane electrode that responds to periodate ion is described. It incorporates a berberine - periodate ion-pair complex, dissolved in *o*-nitrotoluene, as the ion-exchange material. The electrode exhibits a near-Nernstian response for  $10^{-1}$ – $5.0 \times 10^{-5}$  M periodate with a slope of 62 mV per activity decade. The static response time is 5–10 s, the working pH 1.5–7.5 and the limit of detection  $2.5 \times 10^{-5}$  M periodate. The selectivity towards the periodate ion relative to other common inorganic and organic anions is reasonably high. However, perchlorate and permanganate ions cause significant interference. The electrode was used successfully for the direct potentiometric determination of periodate in the presence of iodate and bromate.

**Keywords:** Berberine; liquid membrane; ion-selective electrode; periodate electrode; periodate determination

Perchlorate ion-selective electrodes have been used as periodate sensors for the potentiometric determination of  $\alpha$ -diols,<sup>1–3</sup>  $\alpha$ -amino alcohols<sup>4</sup> and carbohydrates,<sup>5–7</sup> and the catalytic determination of a number of metal ions.<sup>4,8–10</sup> Prior to 1980, there was no electrode available that responded to periodate as the primary ion. Since then, efforts have been made to develop periodate-selective electrodes, both of the PVC matrix<sup>11,12</sup> and liquid membrane<sup>13,14</sup> types.

The determination of periodate in the presence of iodate and bromate is difficult with the conventional gravimetric method<sup>15</sup> as all three ions are determined under similar conditions after their reduction to silver halides. The electrodes available<sup>11–14</sup> to date could not be used for this purpose. Therefore, it seemed worthwhile to develop a periodate-selective electrode that could be used for the determination of periodate in the presence of iodate and bromate. This paper describes a periodate-selective liquid membrane electrode incorporating berberine - periodate as the ion-exchange material. The electrode responds to a wide concentration range of periodate, having a fast response, wide pH range and good selectivity. It was used successfully for the determination of periodate in the presence of iodate and bromate.

## Experimental

## Apparatus

All potential measurements were carried out at  $30 \pm 1^\circ\text{C}$  with a pH 5652 digital pH meter - millivoltmeter (Electronics Corporation of India, Hyderabad, India). Saturated calomel electrodes (SCEs) were used as reference electrodes.

## Reagents and Materials

All reagents used were of analytical reagent grade. Berberine hydrochloride ( $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}^+\text{Cl}^-$ ), an alkaloid, was obtained from Sheeba Laboratories (Saharanpur, India) and purified further by repeated crystallisation from doubly distilled water.

Preparation of Berberine - Periodate ( $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}^+\text{IO}_4^-$ ) Liquid Ion-exchange Membrane

Berberine - periodate was precipitated by the addition of equimolar solutions ( $10^{-3}$  M) of  $\text{NaIO}_4$  and berberine hydrochloride at  $70^\circ\text{C}$ . The washed and dried complex was found to be highly soluble in nitrobenzene and *o*-nitrotoluene, but only sparingly soluble in water. A stock solution ( $5.0 \times 10^{-3}$  M) of the exchanger in *o*-nitrotoluene was prepared and used as the liquid ion exchanger.

## Potential Measurements

Potential measurements were carried out with the cell assembly described by Ishibashi *et al.*<sup>16</sup>

SCE	Internal solution, 0.1 M $\text{NaIO}_4$	1.0 mM $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}^+ \text{IO}_4^-$ in <i>o</i> -nitrotoluene	Test solutions	SCE
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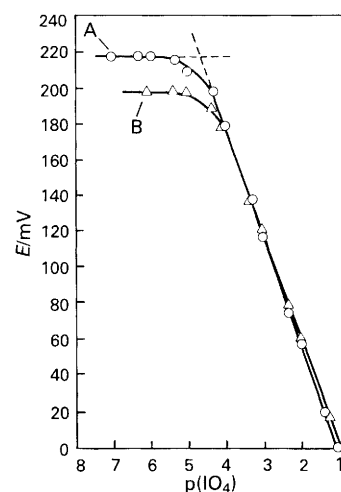
## Results and Discussion

## Selection of Solvent and Ion-exchanger Concentration

The berberine - periodate complex was only sparingly soluble in benzyl alcohol and chloroform, but was appreciably soluble in nitrobenzene and *o*-nitrotoluene. Of the two solvents, a  $10^{-3}$  M concentration of the ion exchanger in *o*-nitrotoluene was considered to be the best in that it gave a linear potential response over a wide concentration range of periodate, a faster response and reproducibility of potentials.

## Potential Response and Response Time

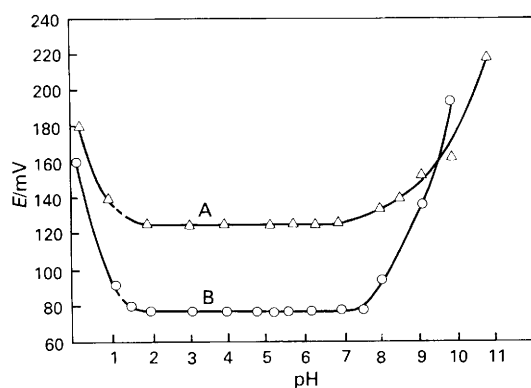
From a graph of potential *versus* periodate activity (Fig. 1) it can be seen that the electrode shows a linear potential



**Fig. 1.** Potential response of the electrode as a function of periodate. A, Activity, slope = 62 mV decade<sup>-1</sup>; and B, concentration (fixed ionic strength, 1.0 M NaCl), slope = 60 mV decade<sup>-1</sup>

**Table 1.** Selectivity coefficients for the periodate ion-selective electrode. Concentrations of interfering ions: separate solution method,  $10^{-3}$  M; fixed interference method,  $10^{-2}$  M

Interfering ion (B)	Selectivity coefficient ( $k_{\text{IO}_4^-}^{\text{pot}}, \text{B}$ )	
	Separate solution method	Fixed interference method
$\text{F}^-$	$1.4 \times 10^{-4}$	$1.1 \times 10^{-4}$
$\text{Cl}^-$	$1.6 \times 10^{-4}$	$1.4 \times 10^{-4}$
$\text{Br}^-$	$2.7 \times 10^{-3}$	—
$\text{I}^-$	$3.9 \times 10^{-2}$	—
$\text{NO}_2^-$	$5.2 \times 10^{-3}$	—
$\text{NO}_3^-$	$2.6 \times 10^{-2}$	$1.4 \times 10^{-2}$
$\text{ClO}_3^-$	$3.3 \times 10^{-2}$	$1.5 \times 10^{-2}$
$\text{ClO}_4^-$	1.8	1.2
$\text{SCN}^-$	$2.9 \times 10^{-1}$	$1.8 \times 10^{-1}$
$\text{IO}_3^-$	$7.3 \times 10^{-3}$	$7.3 \times 10^{-3}$
$\text{BrO}_3^-$	$8.6 \times 10^{-3}$	$8.7 \times 10^{-4}$
$\text{MnO}_4^-$	112.5	109.2
$\text{CrO}_4^{2-}$	$6.6 \times 10^{-3}$	$3.4 \times 10^{-3}$
$\text{SO}_4^{2-}$	$3.5 \times 10^{-3}$	$3.9 \times 10^{-3}$
$\text{CO}_3^{2-}$	$6.6 \times 10^{-4}$	$3.2 \times 10^{-4}$
$\text{S}_2\text{O}_8^{2-}$	$2.5 \times 10^{-4}$	$1.5 \times 10^{-4}$
$\text{MoO}_4^{2-}$	$3.7 \times 10^{-3}$	$2.2 \times 10^{-4}$
$\text{Cr}_2\text{O}_7^{2-}$	$2.4 \times 10^{-3}$	$7.9 \times 10^{-4}$
$\text{Fe}(\text{CN})_6^{3-}$	$1.0 \times 10^{-3}$	$2.3 \times 10^{-3}$
$\text{Fe}(\text{CN})_6^{4-}$	$5.2 \times 10^{-4}$	—
Acetate	$7.6 \times 10^{-3}$	$6.3 \times 10^{-3}$
Oxalate	$4.6 \times 10^{-3}$	$6.3 \times 10^{-4}$
Salicylate	$2.5 \times 10^{-2}$	$1.9 \times 10^{-2}$



**Fig. 2.** Effect of pH on the potential response of the electrode.  $[\text{IO}_4^-]$ : A,  $10^{-3}$ ; and B,  $10^{-2}$  M

response to periodate over the range  $10^{-1}$ – $5.0 \times 10^{-5}$  M with an anionic slope of 62 mV per activity decade. The limit of detection of the electrode is  $2.5 \times 10^{-5}$  M (see Fig. 1). On repeated use, no change in the slope was observed and the drift in the potential was less than +1 mV. The standard deviation of a single measurement was 0.4 mV.

The static response time (the time required to attain a potential within 1 mV of the equilibrium value) of the electrode was short (fast response), and was found to vary from 5–10 s at concentrations  $\geq 10^{-4}$  M to 2–5 min for  $\leq 5 \times 10^{-4}$  M periodate.

### Effect of pH

The effect of pH on the potential response of the electrode was investigated at different concentrations of periodate ( $10^{-2}$  and  $10^{-3}$  M). Potentials were recorded at various pH values (1.0–11.0), keeping the ionic strength constant at 1.0 M (NaCl). The desired pH was obtained by the addition of HCl or NaOH solution. It can be seen from Fig. 2 that the useful pH range for the electrode is 1.5–7.5 at  $10^{-2}$  M periodate and 2.0–7.0 at  $10^{-3}$  M periodate.

**Table 2.** Determination of periodate in the presence of iodate and bromate. Ionic strength of the mixture, 1.0 M (NaCl)

Concentration of $\text{IO}_3^-$ and $\text{BrO}_3^-$ ions added to periodate solution/M	Periodate concentration/M	$\text{IO}_4^-$ concentration/mg l $^{-1}$		
		Taken	Determined*	Error, %
$5 \times 10^{-2}$	$10^{-2}$	1908.9	1962.0	+2.8
$1 \times 10^{-3}$	$10^{-2}$	1908.9	1926.0	+0.9
$1 \times 10^{-4}$	$10^{-2}$	1908.9	1897.0	−0.6
$5 \times 10^{-2}$	$10^{-3}$	190.9	197.1	+3.2
$1 \times 10^{-3}$	$10^{-3}$	190.9	186.5	−2.3
$1 \times 10^{-4}$	$10^{-3}$	190.9	193.0	+1.1
$5 \times 10^{-2}$	$10^{-4}$	19.1	16.4	−14.1
$1 \times 10^{-3}$	$10^{-4}$	19.1	19.9	+4.2
$1 \times 10^{-4}$	$10^{-4}$	19.1	18.6	−2.6

\* Average of three measurements.

### Selectivity

The selectivity coefficient ( $k_{\text{IO}_4^-}^{\text{pot}}, \text{B}$ ) for various anions were evaluated using both the separate solution and fixed interference methods.<sup>17</sup> Ionic concentrations were converted into activities ( $f$ ) by using the extended form of the Debye - Hückel equation

$$-\log f = \frac{0.51 z_i^2 \mu^{1/2}}{1 + \mu^{1/2}}$$

where  $z_i$  is the charge on the ion and  $\mu$  the ionic strength. The results are summarised in Table 1 and it can be seen that only perchlorate and permanganate ions cause significant interference. Bromide,  $\text{I}^-$ ,  $\text{NO}_2^-$  and  $\text{Fe}(\text{CN})_6^{4-}$  are oxidised by periodate; therefore, the selectivity coefficient data for these ions were evaluated using the separate solution method only.

### Determination of Periodate in the Presence of Iodate and Bromate

In order to determine periodate in the presence of iodate and bromate with this electrode, a calibration graph was constructed at an ionic strength of 1.0 M (NaCl). Sample solutions having different concentrations of periodate, iodate and bromate were prepared while maintaining the ionic strength of the mixtures at 1.0 M (NaCl). The potentials were recorded for the sample solutions and the corresponding concentrations of periodate were read from the calibration graph (Fig. 1). The results are summarised in Table 2, which shows that the electrode can tolerate a 500-fold excess of iodate and bromate with an error of 14.1%. When equal amounts of periodate, iodate and bromate were present, the error was almost negligible (2.3–2.6%).

The performance of the electrode described here is comparable to that of existing electrodes<sup>11–14</sup> with respect to selectivity and concentration range. However, it is superior to these electrodes in that it operates over a wider pH range and shows a faster response at higher concentrations. The proposed electrode was used successfully for the determination of periodate in the presence of iodate and bromate.

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