PERCHLORATE-SELECTIVE LIQUID MEMBRANE ELECTRODES BASED ON CRYSTAL VIOLET AND BRILLIANT GREEN AND THEIR ANALYTICAL APPLICATIONS

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ABSTRACT. Crystal Violet- and Brilliant Green-perchlorate in nitrobenzene, with poly(vinyl chloride) support, were used as liquid membranes in ion-selective electrodes. Both electrodes were found to respond to perchlorate (10^{-6} - 10^{-1} M), periodate (10^{-6} - 10^{-2} M), iodide (10^{-4} - 10^{-1} M), saccharin (10^{-4} - 10^{-1} M), and hydrogen phthalate (10^{-5} - 10^{-1} M) ions with Nernstian or sub-Nernstian slopes. The potential responses were fast (< 1 min) and independent of pH over wide ranges. The selectivity order of the Crystal Violet-perchlorate electrode to several anions showed strong correlation with hydration energy and ionic radii. The Crystal Violet-perchlorate electrode was applied to the direct determination of perchlorate and periodate, and to the indirect determinations of glucose, mannitol, ephedrine, serine, and threonine with reasonable precision (2% standard deviations) and accuracy ($> 98\%$ recoveries).

INTRODUCTION

Several perchlorate-sensitive liquid membrane electrodes, based on ion-association salts of cationic metal chelates [1-3], long-chain quaternary ammonium ions [3,4], organic bases [5], alkaloids [6], and organic dyes [7,8] have been reported. These ion-selective electrodes (ISE's) also respond to a number of anions including periodate, permanganate, and thiocyanate [9,10]. An Orion perchlorate electrode, for example, has been employed in an automatic potentiometric kinetic method for the determination of vicinal glycols via periodate oxidation (Malaprade reaction) [11]. Hassan and Elsaied used a nitron periodate electrode for indirect determination of carbohydrates, α-diols, and hydrazine after oxidations by periodate [12].

Basic dyes such as Crystal Violet and Brilliant Green are commonly found in analytical laboratories and used as extractants and spectrophotometric reagents for anion and anionic metal complex determinations, as well as acid-base indicators [13]. The availability of these dyes has widened their applicability to polymer supported anion-selective electrodes [7, 14-16]. Recently these dyes have been used for the preparation of tetrathiocyanatozincate(II) [17], saccharin [18], tetrachloroferrate(III) [19], and hexafluorotantalate(V) [20] ion-selective electrodes.

This paper deals with the preparation and evaluation of the analytical parameters of Crystal Violet- and Brilliant Green-perchlorate liquid membrane electrodes. The electrodes were found to respond to perchlorate, periodate, iodide, saccharin, and hydrogen phthalate. Selectivity for the Crystal Violet-perchlorate electrode has been studied in more detail and

the responsible factors for selectivity, i.e., hydration energy and ionic radius, have been correlated.

The Crystal Violet-perchlorate liquid membrane electrode has been used successfully for the direct determination of low concentrations of perchlorate and periodate and for the indirect determination of glucose, mannitol, ephedrine, and two amino acids (serine and threonine) via periodate oxidation.

EXPERIMENTAL

Reagents and chemicals. Twice-distilled water and analytical reagent grade chemicals were used unless stated otherwise. 1.0×10^{-1} M stock solutions of sodium perchlorate, potassium iodide and potassium hydrogen phthalate, and pharmaceutical grade saccharin as well as 1.0×10^{-2} M potassium periodate were prepared by dissolving known amounts of the salts in water. Sodium hydroxide and hydrochloric acid (0.1 M each), and 0.25 M acetic acid were used to prepare buffered solutions and for pH adjustment. For interference studies, 1.0×10^{-2} M solutions of sodium, potassium or ammonium salts of different anions were prepared in water. 1.0×10^{-3} M aqueous solution of Crystal Violet and Brilliant Green (Hopkins and Williams) were used to prepare the perchlorate ion-associates. 2.5×10^{-2} M stock aqueous solutions of glucose, mannitol, ephedrine hydrochloride, serine, and threonine were prepared. Working solutions were prepared as needed by dilution of the stock solutions. Nitrobenzene, chlorobenzene, 1,2-dichlorobenzene, and chloroform were used as received.

Preparation of basic dye salts. 100 mL of 1.0×10^{-3} M solution of the basic dye was mixed with 20 mL of 1.0×10^{-3} M perchlorate and shaken for 10 min. The resulting mixture was saturated with sodium chloride to promote precipitation of the perchlorate salt of the basic dye and allowed to stand overnight. The product was separated by centrifugation, washed twice with water and dried at 50 - 60° for 5 - 6 h. A 1.0×10^{-3} M stock solution of the perchlorate salt of the basic dye was prepared in nitrobenzene or 1,2-dichlorobenzene for the desired investigation as a liquid ion-exchange membrane.

Preparation of liquid membrane electrodes. The electrode body was prepared from two concentric Pyrex glass tubes (of length 138 mm and diameters of 11 and 6 mm, respectively) joined to a common ground glass joint at one end. The other ends were drawn narrower to give internal diameters of about 8 and 4 mm, respectively. The electrode is represented in Figure 1.

100 mg of PVC was dissolved in about 3 mL of tetrahydrofuran (THF) and 0.25 mL of 1-chloronaphthalene was added to this solution as plasticizer. The tips of the electrode body were dipped into the PVC solution every two minutes to allow partial evaporation of the THF. This was continued until the glass tips were covered with a PVC film of 1.5 - 2.0 mm thickness. The electrode body was then kept upright in a hood for 24 h to allow evaporation of the THF.

About 3 mL of 3×10^{-4} - 6×10^{-4} M solution of the dye perchlorate in nitrobenzene or 1,2-dichlorobenzene was introduced into the outer tube using the port on the outer glass tube, and the dye solution was allowed to permeate into the PVC film for at least 24 h. The inner tube was filled with a solution containing 0.1 M sodium perchlorate and sodium chloride into which a Ag/AgCl reference electrode was immersed. The sensing tip of the electrode was then kept in 1.0×10^{-2} M aqueous sodium perchlorate for 2 h, and at this

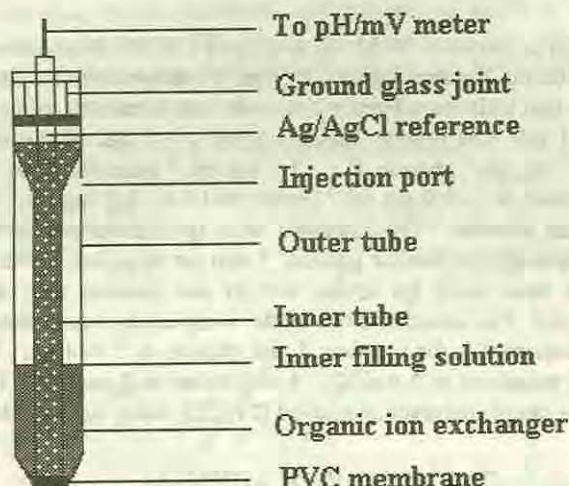stage, the electrode was ready for use. The electrode was stored in this solution when not in use.

To pH/mV meter
Ground glass joint
Ag/AgCl reference
Injection port
Outer tube
Inner tube
Inner filling solution
Organic ion exchanger
PVC membrane

Figure 1. Crystal Violet-perchlorate liquid membrane electrode. Inner filling solution: 0.1 M $NaClO_4$ + 0.1 M NaCl, organic ion exchanger: 4×10^{-4} M $CVClO_4$ solution in nitrobenzene.

Instrumentation. Potential measurements of the solutions were made with the liquid membrane electrode against external saturated calomel reference electrode (SCE) using a Phillips PW 9409 pH/mV meter at room temperature ($22 \pm 2°$). Measurements were made after continuous stirring with a Teflon stirring bar. The complete cell is represented by the scheme:

Ag/AgCl | 0.1 M Cl⁻, 0.1 M ClO_4^- | Liquid membrane | Test solution | SCE
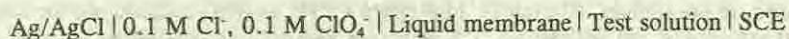
pH measurements of solutions were made with a Beckman Chem Mate pH meter.

Procedures

Electrode calibration. Calibrations of electrode responses to the anions were made with the standard solutions of the anions.

Aliquots (20 mL) of 1×10^{-7} - 1×10^{-1} M solutions of the anions (ClO_4^-, IO_4^-, I⁻, Sacc⁻, and HP⁻) were transferred into 100-mL beakers and the liquid membrane electrode, in conjunction with the reference electrode, was immersed in the solution. The solutions were stirred with a Teflon coated stirring bar and the potential (within $\pm$ 1 mV) was recorded after stabilization (within $\pm$ 1 min).

Selectivity coefficient (k_{ij}^{pot}) determinations. In the separate solution method, potentials of 1.0 x 10^{-2} M solutions of perchlorate, i, and the interfering ion, j, were measured separately and the k_{ij}^{pot} values evaluated [21, 22]. In the mixed solution method, potentials of 1 x 10^{-7} - 1 x 10^{-1} M perchlorate, in presence of 1 x 10^{-2} M of the interfering anion, were measured and the k_{ij}^{pot} values evaluated [21, 22].

Indirect determination of samples. A 20 mL aliquot of 1 x 10^{-2} M periodate solution was transferred into a 100-mL beaker and the Crystal Violet-perchlorate liquid membrane electrode, in conjunction with the reference electrode, was immersed in the solution. The potential within ± 1 mV was initially measured and 1 - 5 mL of the sample solution (containing 0.1 - 3.0 mg mL^{-1} glucose, 0.1 - 2.0 mg mL^{-1} mannitol, 0.04 - 5.0 mg mL^{-1} ephedrine hydrochloride, 0.1 - 4.0 mg mL^{-1} serine, and 0.4 - 4.0 mg mL^{-1} threonine) was added to the periodate solution. The potentials were again measured after the complete oxidation of the compounds (20 min for glucose, 5 min for mannitol, 5 min for ephedrine, 5 min (heating over water bath) for serine, and 30 min (heating over water bath) for threonine, respectively). The concentrations of the compounds were calculated from the moles of periodate consumed in the reaction: 1 mol glucose ≡ 5 mol IO_4^-, 1 mol mannitol ≡ 5 mol IO_4^-, 1 mol ephedrine ≡ 1 mol IO_4^-, 1 mol serine ≡ 2 mol IO_4^-, 1 mol threonine ≡ 2 mol IO_4^-, by the sample subtraction method [21, 22], using the equation

$$C_X = \frac{C_S [V_S - V_T \times 10^{\Delta E/S}]}{V_X \times n}$$

where C_X is the concentration of the sample solution, V_X is the volume of the sample solution, C_S is the concentration of periodate, V_S is the volume of periodate solution, V_T is the total volume of the solution, ΔE is the change in potential, S is the slope, and n is the number of moles of periodate consumed by one mole of the compound in the reaction.

RESULTS AND DISCUSSIONS

The liquid membrane electrodes. PVC adheres to glass and can easily be used as a support to organic ion-exchangers when an all-glass electrode body is used. This property was earlier used, in the authors' laboratory, to prepare a PVC membrane electrode for saccharin [18]. Nitrobenzene, chlorobenzene, 1,2-dichlorobenzene, and chloroform were tested as membrane solvents. The solvents with low dielectric constants, namely, chlorobenzene and chloroform, did not appreciably dissolve the dye-perchlorates and could not be employed as membrane solvents. The salts showed appreciable solubility in the other two solvents. Hence nitrobenzene and 1,2-dichlorobenzene were used as membrane solvents.

Various concentrations (1 x 10^{-5} - 1 x 10^{-3} M) of the Crystal Violet and Brilliant Green perchlorates in nitrobenzene were examined as liquid membranes. At concentrations below 3 x 10^{-4} M of the dye salts, the measured electrode potentials were unstable owing to high resistance of the membranes, and at concentrations greater than 6 x 10^{-4} M, the potentials decreased gradually, probably due to elution of the membrane solute into the adjacent aqueous phases. Hence 3 x 10^{-4} - 6 x 10^{-4} M of the basic dye salts in nitrobenzene were employed as the optimum organic ion-exchanger concentrations. The same concentration range was applied for the Crystal Violet-based electrode in 1,2-dichlorobenzene.

Response characteristics. The response characteristics of the three electrodes, namely, Crystal Violet-perchlorate (nitrobenzene as membrane solvent), Brilliant Green-perchlorate (nitrobenzene as membrane solvent), and Crystal Violet-perchlorate (1,2-dichlorobenzene as membrane solvent), were investigated. All the three electrodes were found to respond to perchlorate, periodate, iodide, saccharin, and hydrogen phthalate in wide concentration ranges with sub-Nernstian slopes (Figure 2 and Table 1-3). The sub-Nernstian anionic slopes, linear concentration ranges and detection limits are typical of liquid membrane electrodes.
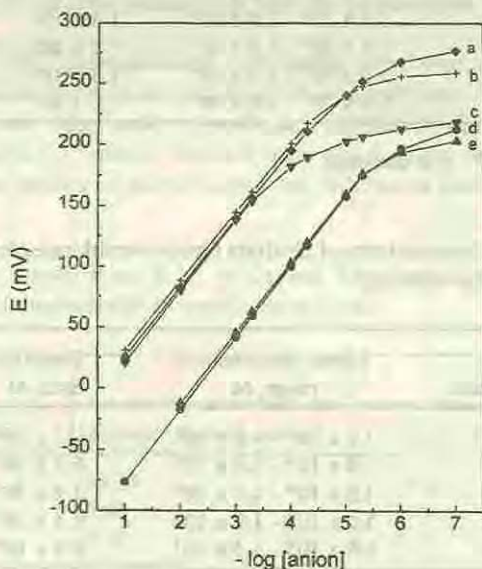

Figure 2.   Response curve of Crystal Violet-perchlorate
liquid membrane electrode for, (a) I^-, (b) HP^-,
(c) $Sacc^-$, (d) ClO_4^-, and (e) IO_4^-.

Table 1 and 2 show that the response characteristics of the Crystal Violet-perchlorate and the Brilliant Green-perchlorate (both with nitrobenzene as membrane solvent) electrodes are similar to each other. However the Crystal Violet-perchlorate electrode gave responses with better slopes than the Brilliant Green-perchlorate electrode for all the anions except saccharin. Hence the response behavior of the Crystal Violet-perchlorate electrode was also studied in 1,2-dichlorobenzene as membrane solvent. Comparison of the response parameters for the electrode with nitrobenzene as membrane solvent (Table 1) against the electrode with 1,2-dichlorbenzene as membrane solvent (Table 3) suggests better performance of the former over the latter in terms of sensitivity (slopes) particularly to iodide, saccharin, and hydrogen phthalate. Hence the Crystal Violet-perchlorate electrode with nitrobenzene as membrane solvent was used for further studies.

The dynamic response time [23] (the time required to reach a potential to within ± 1 mV) of the electrodes was 15-20 s for concentrations $\geq 1 \times 10^{-3}$ M, and up to 60 s for concentrations $< 1 \times 10^{-3}$ M of the anions. The electrodes had average life-times of 7-8

weeks, when used every day (more than 4 h per day), with no significant changes in electrode parameters. The day-to-day potential reproducibility was within ± 2 mV.

Table 1. Response characteristics of Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent).

Anion	Slope mV/decade	Linear concentration range, M	Detection limit, M	pH range
ClO_4^-	59.0	$3.5 \times 10^{-6} - 1.0 \times 10^{-1}$	9.6×10^{-7}	3.0 - 11.0
IO_4^-	57.5	$5.0 \times 10^{-6} - 1.0 \times 10^{-2}$	1.4×10^{-6}	3.5 - 7.5
I^-	57.0	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$	7.5×10^{-6}	3.5 - 7.0
Sacc⁻	58.7	$5.0 \times 10^{-4} - 1.0 \times 10^{-1}$	1.3×10^{-5}	3.0 - 10.0
HP⁻	56.6	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	1.0×10^{-5}	3.0 - 4.0

Sacc⁻ = saccharin, HP⁻ = H-phthalate.

Table 2. Response characteristics of Brilliant Green-perchlorate electrode (nitrobenzene as membrane solvent).

Anion	Slope mV/decade	Linear concentration range, M	Detection limit, M	pH range
ClO_4^-	56.5	$4.0 \times 10^{-6} - 1.0 \times 10^{-1}$	1.7×10^{-6}	3.5 - 9.0
IO_4^-	57.0	$1.0 \times 10^{-6} - 1.0 \times 10^{-2}$	6.7×10^{-7}	3.5 - 7.5
I^-	53.0	$5.0 \times 10^{-4} - 1.0 \times 10^{-1}$	2.4×10^{-5}	3.5 - 7.0
Sacc⁻	60.5	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$	8.4×10^{-5}	3.5 - 9.0
HP⁻	56.4	$1.0 \times 10^{-5} - 1.5 \times 10^{-2}$	5.0×10^{-6}	3.0 - 4.0

Table 3. Response characteristics of Crystal Violet-perchlorate electrode (1,2-dichlorobenzene as membrane solvent).

Anion	Slope mV/decade	Linear concentration range, M	Detection limit, M
ClO_4^-	56.0	$7.5 \times 10^{-6} - 1.0 \times 10^{-1}$	2.0×10^{-6}
IO_4^-	57.8	$1.0 \times 10^{-5} - 1.0 \times 10^{-2}$	2.2×10^{-6}
I^-	53.6	$5.0 \times 10^{-4} - 1.0 \times 10^{-1}$	4.7×10^{-5}
Sacc⁻	53.6	$2.5 \times 10^{-4} - 1.0 \times 10^{-1}$	8.9×10^{-6}
HP⁻	53.6	$5.0 \times 10^{-4} - 1.5 \times 10^{-2}$	3.2×10^{-6}

The influence of pH. The response behavior of the Crystal Violet-perchlorate (nitrobenzene as membrane solvent) and Brilliant Green-perchlorate electrodes were tested at various pH values for different concentrations of the anions. The electrode potentials were almost

constant to within ± 2 mV over wide pH ranges for all the anions except for hydrogen phthalate (Tables 1 and 2). The narrow pH range for the hydrogen phthalate is attributed to the fact that phthalic acid is a weak dibasic acid and hence at higher acidities, i.e., pH < 3 the acid is not completely dissociated into hydrogen phthalate anion, and at lower acidities, i.e., pH > 4, the hydrogen phthalate anion begins to dissociate into the divalent phthalate anion.

Both nitrobenzene and 1,2-dichlorbenzene are aprotic solvents. Hence a pH study on the liquid membrane electrode, with 1,2-dichlorbenzene as solvent, was not made because of the expected similar pH-response relationship with the nitrobenzene-based electrodes.

Selectivity coefficient, k_{ij}^{pot}, determinations. The influence of other anions on the response of Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent) was investigated by both the separate and mixed solution methods. The results (Table 4) show that both methods give comparable k_{ij}^{pot} values. No such study was made for the other two electrodes because of the similar pattern expected despite the differences between the dyes and the solvents.

Table 4.   Selectivity coefficients, k_{ij}^{pot}, of Crystal Violet-perchlorate liquid membrane electrode (nitrobenzene as membrane solvent).

Interfering ion, j	k_{ij}^{pot}	
	Separate solution method	Mixed solution method
MnO_4^-	12.13	10.65
ClO_4^-	1.00	1.00
IO_4^-	0.78	0.98
I^-	1.62×10^{-2}	1.48×10^{-2}
Sacc	1.52×10^{-2}	1.32×10^{-2}
HP^-	1.22×10^{-2}	9.83×10^{-3}
SCN^-	6.74×10^{-2}	7.44×10^{-2}
F^-	2.14×10^{-4}	8.84×10^{-3}
Cl^-	5.04×10^{-4}	5.91×10^{-4}
Br^-	3.50×10^{-4}	8.84×10^{-3}
ClO_3^-	1.00×10^{-2}	9.93×10^{-3}
BrO_3^-	4.70×10^{-4}	4.98×10^{-4}
IO_3^-	4.03×10^{-4}	1.48×10^{-4}
NO_3^-	2.21×10^{-3}	1.76×10^{-3}
Acetate	4.03×10^{-3}	9.91×10^{-4}
Benzoate	4.32×10^{-4}	5.27×10^{-4}
Oxalate	9.97×10^{-5}	6.38×10^{-5}
SO_4^{2-}	4.97×10^{-5}	6.28×10^{-5}

Comparison of the selectivity order of the electrode for some ions shows the following pattern: $MnO_4^- > ClO_4^- \approx IO_4^- > SCN^- > I^- > Sacc > HP^- > ClO_3^- > NO_3^- > Br^- > BrO_3^- \approx Cl^- > F^-$. Such patterns were observed for other liquid membrane anion-selective electrodes and generally hold true for some solvents including nitrobenzene, irrespective of the cationic ion-pairing agent [24, 25]. Reinsfelder and Schultz [24], for example, showed similar selectivity order for a nitrate-selective liquid membrane electrode. Such regularity in selectivity order is attributed to the hydration energy of the anions, which in turn is

related to ionic radius. The correlations with hydration energy [26] and ionic radii [27] are shown in Figures 3 and 4. The observations are in agreement with the theoretical arguments made in Ref. [28, 29] which relate selectivity to free energy of exchange between the aqueous and the organic phase. The free energy of exchange is in turn determined by the solvation energy in the liquid membrane solvent, hydration energy, and the radius of the anion.
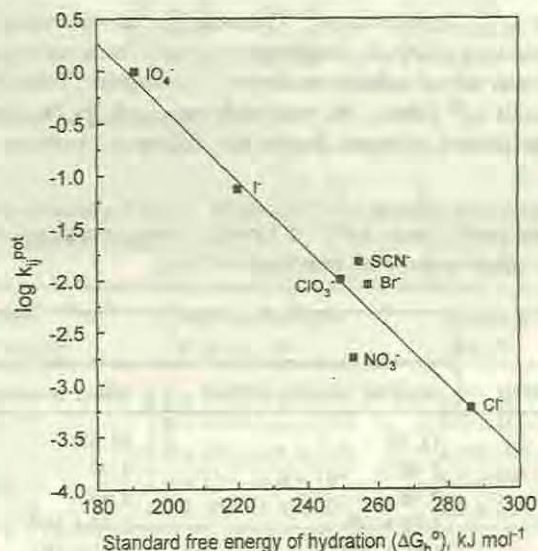

Figure 3. Correlation between the standard free energy of hydration (ΔG_h°) of anions [26] and the k_{ij}^{pot} values of the Crystal Violet-perchlorate liquid membrane electrode.

Since the electrodes respond to a number of anions, the presence of one with any other of the anions could evidently cause interferences. The selectivity of the Crystal Violet-perchlorate electrode to iodide, saccharin, and H-phthalate is less by two orders of magnitude compared to those of perchlorate and periodate (see Table 4).   This multi-selective behaviour, typical of other liquid membrane electrodes [29], is governed by the partition coefficient and stability of liquid membrane solute in both phases [30]. It is of course evident that some analyte species may not commonly occur and the electrode could still be useful in analysis. Multi-component analysis with the same transducer, such as the reported electrodes here, could be made in flow injection analysis [31] and liquid chromatography (LC). Phthalate and nitrate detections were, for example, made in LC using a liquid membrane electrode [32].

Applications

Determination of perchlorate. The Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent) was applied for the determination of perchlorate in aqueous solutions by direct (calibration) and standard addition potentiometric methods. Six replicate determinations were made on solutions containing $0.01 - 2.0$ mg.mL^{-1} of perchlorate by each method. The results showed an average recovery of 99.2% and a mean standard deviation of 1.9% (Table 5). Hence the electrode can be used to determine perchlorate in aqueous samples with reasonable precision and accuracy.
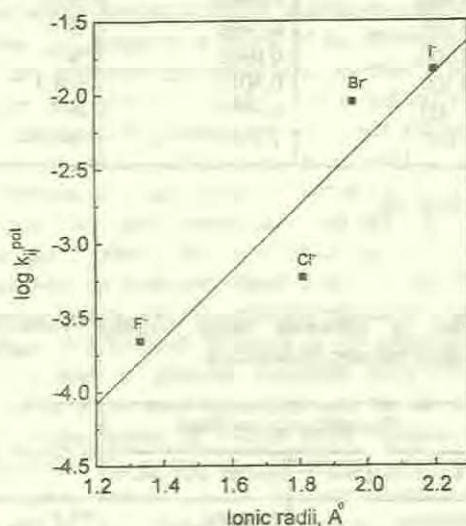

Figure 4.   Correlation of ionic radii (r_i) of halide ions [27] with their k_{ij}^{pot} values of the Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent).

Determination of periodate. Since the Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent) also responds to periodate ion, the electrode was applied for the direct determination of periodate in aqueous solutions by direct (calibration) and standard addition potentiometric methods. Six replicate determinations were made on solutions containing $0.01 - 2.0$ mg.mL^{-1} of periodate by each method. The results showed an average recovery of 99% and a mean standard deviation of 1.9% (Table 6). Thus the electrode can be used to determine periodate in aqueous samples with reasonable precision and accuracy. Furthermore the periodate ion is a strong oxidizing agent and the electrode does not respond to the iodate ion, i.e., the reduction product of the periodate ion. Hence the electrode can also be used for the indirect determination of reducing substances.

Table 5. Determination of perchlorate using Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent).

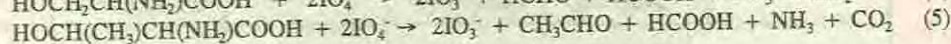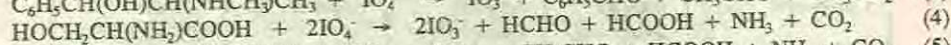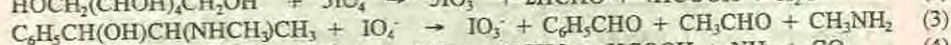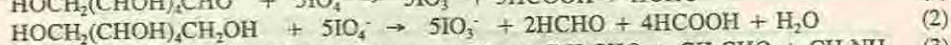| Method	Perchlorate concentration		Recovery (%)	Standard deviation (%)
	Taken (mg.mL^{-1})	Found* (mg.mL^{-1})		
Direct potentiometry	0.010	0.0098	98.0	2.2
	0.050	0.0492	98.4	1.8
	0.100	0.1002	100.2	2.0
	0.500	0.4990	99.8	1.6
	1.000	0.9950	99.5	1.4
	2.000	1.9840	99.2	1.7
Standard addition	0.010	0.0098	98.0	2.1
	0.050	0.0498	99.6	2.4
	0.100	0.0988	98.8	1.8
	0.500	0.5015	100.3	1.5
	1.000	0.9970	99.7	1.9
	2.000	1.9680	98.4	2.2

* Average of three determinations.

Table 6. Determination of periodate using Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent).

Method	Periodate concentration		Recovery (%)	Standard deviation (%)
	Taken (mg.mL^{-1})	Found* (mg.mL^{-1})		
Direct potentiometry	0.010	0.00978	97.8	2.5
	0.050	0.0496	99.2	2.1
	0.100	0.0986	98.6	1.5
	0.500	0.5010	100.2	1.7
	1.000	0.9980	99.8	2.0
	2.000	1.9680	98.4	1.6
Standard addition	0.010	0.00976	97.6	2.3
	0.050	0.0492	98.4	1.8
	0.100	0.1004	100.4	2.0
	0.500	0.4985	99.7	1.6
	1.000	0.9920	99.2	1.4
	2.000	1.9780	98.9	1.9

* Average of three determinations.

Determination of glucose, mannitol, ephedrine, serine, and threonine. Polyhydric alcohols are known to react selectively and stoichiometrically with periodate at room temperature (Malaprade reaction) [11]. Similarly α-amino alcohols are also known to react selectively

and stoichiometrically with periodate at room temperature [11]. The reactions of glucose, mannitol, ephedrine, serine, and threonine with periodate are given by the following equations:

$$HOCH_2(CHOH)_4CHO + 5IO_4^- \rightarrow 5IO_3^- + 5HCOOH + HCHO \qquad (1)$$
$$HOCH_2(CHOH)_4CH_2OH + 5IO_4^- \rightarrow 5IO_3^- + 2HCHO + 4HCOOH + H_2O \qquad (2)$$
$$C_6H_5CH(OH)CH(NHCH_3)CH_3 + IO_4^- \rightarrow IO_3^- + C_6H_5CHO + CH_3CHO + CH_3NH_2 \qquad (3)$$
$$HOCH_2CH(NH_2)COOH + 2IO_4^- \rightarrow 2IO_3^- + HCHO + HCOOH + NH_3 + CO_2 \qquad (4)$$
$$HOCH(CH_3)CH(NH_2)COOH + 2IO_4^- \rightarrow 2IO_3^- + CH_3CHO + HCOOH + NH_3 + CO_2 \qquad (5)$$

These reactions were used for the indirect determinations of glucose, mannitol, ephedrine, serine, and threonine with the Crystal Violet-perchlorate electrode (nitrobenzene as membrane solvent) by the standard subtraction method. Known amounts of the compounds were allowed to react with an excess of $NaIO_4$ and the consumption of the periodate was followed by monitoring the change in potential of the electrode. The completion of the reaction was easily ascertained when the steady-state potential of the electrode was reached. It was found that a reaction time of 15, 3, and 2 min, at ambient temperature, was adequate for the quantitative oxidation of glucose, mannitol, and ephedrine, respectively. The oxidation of serine and threonine with periodate was found to proceed slowly at ambient temperature and the completion of the reaction required 1 and 2 h, respectively. Hence the reactions were carried out on heating over water bath and reaction times of 5 and 30 min were adequate for the quantitative oxidation of serine and threonine, respectively.

The results obtained for the determination of 0.05 - 5.0 mg.mL^{-1} of glucose, mannitol, ephedrine hydrochloride, serine, and threonine showed an average recovery of 99% and a mean standard deviation of 2% (Table 7) based on the consumption of 5, 5, 1, 2, and 2 moles of periodate per mole of glucose, mannitol, ephedrine, serine, and threonine, respectively. These results are in good agreement with the above equations.

In conclusion, the higher selectivity and the rapid response of the Crystal Violet- and Brilliant Green-perchlorate electrodes to perchlorate and periodate ions in wider concentration ranges make them useful for the determination of these ions in aqueous samples. The electrodes are also useful for the indirect determination of many reducing substances that react with periodate.

Table 7. Determination of glucose, mannitol, ephedrine, serine, and threonine by oxidation with $NaIO_4$ using the Crystal Violet-perchlorate liquid membrane electrode (nitrobenzene as membrane solvent).

Compound	Amount added (mg)	Amount found[a] (mg)	Recovery %	Standard deviation (%)
Glucose	0.20	0.203	101.5	2.1
	1.00	0.984	98.4	1.9
	1.50	1.49	99.4	1.8
	3.00	2.96	98.7	2.0
Dextrose[b]	4.00	3.95	98.8	1.8
	40 %	39.5 %	98.8	1.8
Mannitol	0.10	0.099	99.0	2.3
	0.50	0.493	98.6	2.1
	1.00	1.011	101.1	2.0
	2.00	1.954	97.7	1.8
Ephedrine.HCl	0.20	0.197	98.5	2.2
	1.00	0.98	98.0	1.9
	2.00	1.98	99.0	1.8
	5.00	4.98	99.6	1.6
	10.00	9.82	98.2	1.7
Serine	0.40	0.41	102.5	2.2
	1.00	0.98	98.0	2.0
	2.00	1.95	97.5	2.4
	4.00	3.94	98.5	1.8
	10.00	9.82	98.2	1.9
Threonine	0.40	0.392	98.0	2.0
	1.00	1.01	101.0	1.7
	2.00	1.96	98.0	1.9
	4.00	3.94	98.5	1.8
	8.00	7.86	98.2	1.8

[a] Average of three determinations.
[b] Injection USP obtained from Arab Otsuka Pharmaceutical Co.

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Table 7.   Determination of glucose, mannitol, ephedrine, serine, and threonine by
            oxidation with $NaIO_4$ using the Crystal Violet-perchlorate liquid membrane
            electrode (nitrobenzene as membrane solvent).

Compound	Amount added (mg)	Amount found[a] (mg)	Recovery %	Standard deviation (%)
Glucose	0.20	0.203	101.5	2.1
	1.00	0.984	98.4	1.9
	1.50	1.49	99.4	1.8
	3.00	2.96	98.7	2.0
Dextrose[b]	4.00	3.95	98.8	1.8
	40 %	39.5 %	98.8	1.8
Mannitol	0.10	0.099	99.0	2.3
	0.50	0.493	98.6	2.1
	1.00	1.011	101.1	2.0
	2.00	1.954	97.7	1.8
Ephedrine.HCl	0.20	0.197	98.5	2.2
	1.00	0.98	98.0	1.9
	2.00	1.98	99.0	1.8
	5.00	4.98	99.6	1.6
	10.00	9.82	98.2	1.7
Serine	0.40	0.41	102.5	2.2
	1.00	0.98	98.0	2.0
	2.00	1.95	97.5	2.4
	4.00	3.94	98.5	1.8
	10.00	9.82	98.2	1.9
Threonine	0.40	0.392	98.0	2.0
	1.00	1.01	101.0	1.7
	2.00	1.96	98.0	1.9
	4.00	3.94	98.5	1.8
	8.00	7.86	98.2	1.8

[a] Average of three determinations.
[b] Injection USP obtained from Arab Otsuka Pharmaceutical Co.

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