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BRILLIANT GREEN-BASED PVC MEMBRANE ELECTRODE FOR THE DETERMINATION OF SACCHARIN

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ABSTRACT. A conventional-type PVC membrane electrode which responds to $5x10^{-4}$ - $2x10^{-1}$ M saccharin has been developed based on Brilliant Green-saccharin ion-pair. The electrode body was designed from a Pyrex glass tube with a capillary at one end to hold the membrane phase eliminating the use of adhesives and/or O-rings which are the sources of mechanical difficulties in ion-selective electrode preparations. The electrode responded to saccharin sodium solutions within 15-60 seconds, with a slope of 56-58 mV per decade, at pH 4.7-8.3. Rapid determinations of saccharin sodium in commercial tablets, have been made using direct method, analate (dry sample), single standard, and multiple standard, addition techniques. The electrode was also found to respond to perchlorate ($1x10^{-5}$ - $2x10^{-1}$ M) and iodide ($1x10^{-4}$ - $2x10^{-1}$ M) and these ions interfere with the response of the electrode to saccharin.

INTRODUCTION

The use of triphenylmethane dyes, such as Brilliant Green and Crystal Violet, as ion-exchangers in liquid and polymer membrane electrodes selective to simple anions and anionic metal complexes has been recognized since 1973. Several electrodes selective to different organic and inorganic anions have been developed which include tetrathiocyanatozincate(II) (1,2), perchlorate (3), tetrafluoroborate (4), trifluoroacetate (5), salicylate (6), maleate (7), phthalate (8), and detergent anions (9). The use of these cationic dyes as ion-exchangers in these electrodes is based on the formation of ion-pairs extractable into water immiscible organic solvents. Brilliant Green is a typical monovalent cationic dye which forms such ion-pairs with anions.

The monovalent anion of the acid form of saccharin, $C_6H_4COSO_2NH$ (K_a = $2.5x10^{-2}$), also forms ion association salts with these dyes and the Brilliant Green form is utilized as saccharin ion-exchanger in a PVC membrane electrode. Saccharin sodium has been used, for many years, as non-calorie artificial sweetner in the diet of diabetic patients. It is also applied in pharmaceutical formulations such as aluminium hydroxide and magnesium trisilicate tablets, as well as in codein phosphate syrup.

The present investigation deals with the evaluation of the electroanalytical parameters and applications of a PVC membrane electrode based on Brilliant Green-saccharin ion-pair. The study also aims at eliminating the use of adhesives and O-rings in plastic-type electrodes which are the usual sources of mechanical difficulties in membrane preparations.

EXPERIMENTAL

Preparation of electroactive mixture. The Brilliant Green-saccharin salt was prepared by gradual mixing of 0.2%(w/v) aqueous solution of Brilliant Green with an excess of solution of 0.1 M saccharin sodium with stirring. The resulting mixture was saturated with sodium chloride to promote precipitation of the basic dye salt of saccharin. A highly viscous, sticky product was formed after standing overnight and isolated from the green aqueous phase by centrifugation. The product was washed twice with distilled water, and dried in an oven at 60°C for 4 hours. This ion-pair was used directly for electorde preparation without characterization. Brilliant Green-tetrathiocyanatozincate(II) was prepared by adding an excess of the Brilliant Green solution to a stirred solution containing stoichiometric proportion (1:4) of zinc acetate and ammonium thiocyanate (2). A polyvinyl chloride (PVC) solution was prepared by dissolving 100 mg of the polymer powder in about 3 ml of tetrahydrofuran (THF). The electroactive mixture was then prepared by mixing 15 mg and 5 mg of the basic dye salts of saccharin and tetrathiocyanatozincate(II) respectively, and 0.5 ml of 1-chloronaphthalene with the PVC solution.

PVC membrane electrode. A Pyrex tube (1.88 cm x 16 cm) with a 14/23 ground glass joint at one end and a capillary (1.5-2.0 mm internal diameter) at the other, was used as electrode body (Fig. 1). A drop of the electroactive mixture

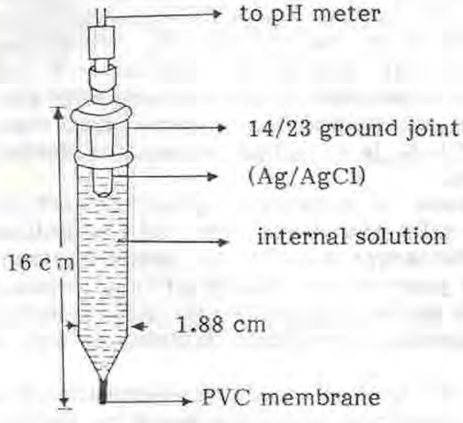

Fig. 1. PVC membrane electrode assembly.

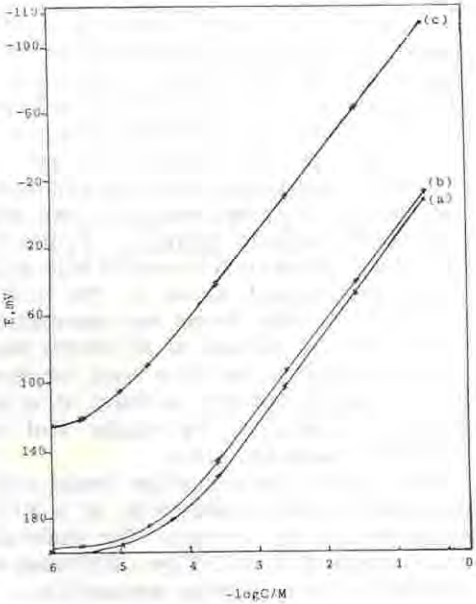

Fig. 2. Plot of potential response vs molar concentrations of (a) saccharin (b) iodide (c) perchlorate.

was carefully added to the capillary from the top of the tube using a long dropper. The tube was kept upright in air for about five minutes to dry the mixture from the lower end of the capillary. The electroactive mixture was further added until its level in the capillary was raised to 3-4 mm. The tube was then kept in the same position and the mixture was air-dried in a hood for about 24 hours. A 0.1 M solution of each in potassium chloride and saccharin sodium was introduced into the tube to a level at which an internal Ag/AgCl reference electrode would be in contact. The electrode was conditioned in 1.0×10^{-2} M aqueous saccharin sodium for about 24 hours before use. The tip of the electrode was always suspended in the conditioning solution when not in use.

Reagents. All chemicals used were of analytical reagent grade. Standard solutions of 2×10^{-6} - 2×10^{-1} M saccharin were prepared from pure saccharin sodium dihydrate. Buffer solutions of pH values 2.8-9.2 were prepared by mixing appropriate volumes of 0.05 M sodium hydroxide with 100 ml of 0.02 M actetic acid and diluted to 200 ml with distilled water. The solutions were stored in polyethylene bottles.

Stock solutions of several anions (0.2 M each) were prepared from their sodium or potaisium salts for interference studies. Solutions for potentiometric measurements were prepared by dissolving 20 tablets of commercial saccharin sweetner (Hermestas, Switzerland) in distilled water to make a one-liter solution.

Instrumentation. Potential measurements of solutions were made with the PVC membrane electrode against a calomel reference electrode using Philips PW 9409 digital pH/mV meter of 0.1 mV precision. All potential measurements were made one minute after continuous stirring with a Teflon-coated stirring bar. A complete cell is represented by the following scheme. The pH of the solutions were measured with a calibrated Beckman Chem Mate pH meter.

Internal Ag/AgCl	Cl^- (0.1 M)	PVC	Test	External calomel
reference electrode	saccharin (0.1 M)	membrane	solution	reference electrode

Potentiometric methods for saccharin determinations. Direct measurement of saccharin in the tablet solution was made after calibrating the electrode with the standard saccharin solutions. For dry sample (tablet) addition method, the potential of 50 ml of 2.0×10^{-3} M saccharin solution was first measured. The saccharin tablet was added to the same stirred solution and the new equilibrium potential was measured after the tablet completely dissolved. In the single standard addition method, the potential of a 50 ml tablet solution was initially measured. 1 ml of 2×10^{-2} M saccharin was then added to the sample solution and the new potential recorded. In multiple standard addition method (for Gran's plot technique), the same procedure was followed except that five successive additions of the standard were made and the steady potentials were recorded at each step. The method of calculation of saccharin content in the tablet soultion for each method is explained under Results and Discussions.

pH and interference effects. Two methods were used to study interference effects. In the mixed solution method (10), 10 ml solution of an interfering anion was added to 10 ml solution of 2.0×10^{-6} - 2.0×10^{-1} M saccharin and the potential recorded. In the separate solution method (11), potentials of equimolar solutions of saccharin and the interfering ion were measured independently. To study the potential dependence of pH, 10 ml of the buffer (pH 2.8-9.2) was mixed with a 10 ml saccharin solution of constant concentration.

RESULTS AND DISCUSSION

Response characteristics. Our first attempt to prepare a plasticized PVC membrane electrode was based on Brilliant Green-saccharin salt alone. The electrode response was 54-56 mV per decade to aqueous solutions of saccharin which confirmed the formation of a 1:1 Brilliant Green-saccharin salt during the preparation. The salt in the membrane, however, dissolved into the test solution with concentrations less than 10^{-4} M saccharin imparting a green colour to the solution. Consequently, the slope of the electrode decreased gradually and had a life-time of only 12-24 hours. Previous work from this laboratory(2) has shown that Brilliant Green-tetrathiocyanatozincate(II) in presence of PVC and 1-chloronaphthalene, could serve as electroactive salt in a coated-wire electrode (CWE) with a life-time of at least six months. The CWE did not impart a green colour to the colourless test solution showing that the salt is much less soluble than the corresponding saccharin salt. This suggests that Brilliant Green-tetrathiocyanatozincate(II) could be used to maintain the concentration of the basic dye anion-exchanger in the PVC phase of the saccharin electrode. Addition of the salt improved the electrode behaviour, increasing its life-time to at least eight weeks. Best response characteristics were obtained when the mass ratio of the PVC, the saccharin and tetrathiocyanatozincate(II) salts of the basic dye, respectively, was 20:3:1 to 20:3:2.

It seems that 1-chloronaphthalene also acts as a solvent to the electroactive salts in addition to its plasticizing the PVC. This has been shown by the recovery of electrode response when 1-chloronaphthalene was applied, with a paper towel, to the tip of the PVC phase which lost its response upon storage in air for over fifteen days.

Potential measurements in aqueous saccharin solutions using the PVC electrode prepared under the prescribed procedure gave a negative slope of 57.0 ± 1.0 mV per decade suggesting an ion-exchange equilibrium between the membrane and aqueous phases:

$$^{*}\text{saccharin}^{-}\ (\text{membrane}) + \text{saccharin}^{-}\ (\text{aq}) \rightleftharpoons \text{saccharin}^{-}\ (\text{membrane}) + {}^{*}\text{saccharin}^{-}\ (\text{aq}).$$

The electrode also responded linearly to aqueous solutions of $1.0\text{x}10^{-5}$ $2.0\text{x}10^{-1}$ M perchlorate and $1.0\text{x}10^{-4}$ - $2.0\text{x}10^{-1}$ M iodide with slopes of 57 ± 3 mV and 54±1 mV per decade respectively (Fig. 2). This multi-anion selective electrode can thus be potentially useful as electrochemical detector to these ions.

The major difficulty in the preparation or assembly of PVC membrane electrodes is while mounting the PVC membrane on the electrode body using adhesives or O-rings. After fixing the membrane, it is common to observe a continuous drift of potential, when in use, due to a difficultly detectable leakage of the internal reference electrolyte. In the present work, a capillary drawn from a Pyrex glass tube was used to hold the membrane phase without the need of an adhesive or an O-ring. This completely eliminated the mechanical difficulities associated with the preparation or assembly of the PVC membrane electrode. One advantage of this electrode body is that one electroactive organic ion-exchanger can be easily discharged and replaced by another. Moreover, the smallness of the membrane tip (1.5-2.0 mm internal diameter) compared to that of a conventional electrode sensor (typically of diameter 10-11 mm) provides an alternative to miniaturization of polymer membrane electrodes for application to small sample volumes.

Response time and stability of the membrane. The response time required for the conditioned electrode to reach a potential within ±1.0 mV of the equilibrium value (12) was 10-20 seconds for 10^{-3} M (or greater) and upto 60 seconds for concentrations lower than 10^{-3} M saccharin. This allowed the measurement of 15-30 samples of saccharin per hour using the four test methods. The electrode exhibits a day-to-day reproducibility of ±1.0 mV for 10^{-3} - 10^{-2} M saccharin. The net potential shift within four weeks was about 10 mV to more negative values.

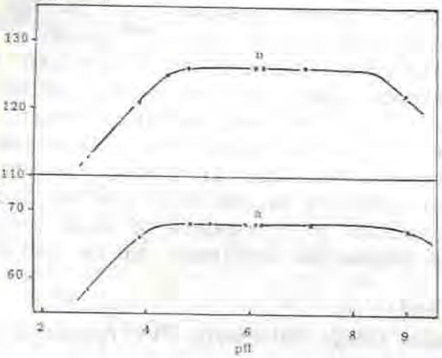

Fig. 3 Effect of pH on the potential of the Brilliant Green - saccharin based PVC membrane electrode (a) 10^{-2} M (b) 10^{-3} M saccharin sodium.

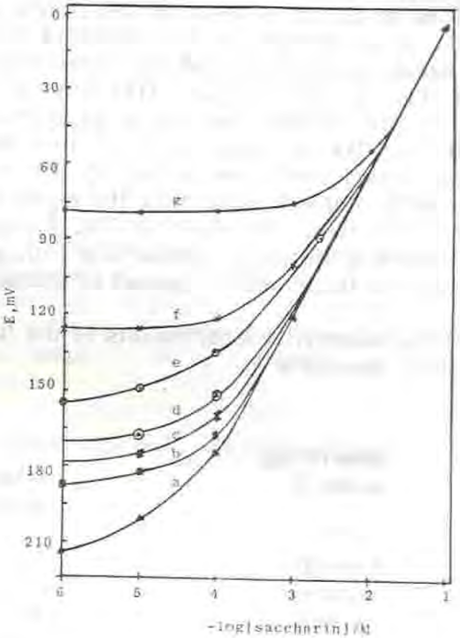

Fig. 4 Potential response of the PVC membrane electrode to (a) pure saccharin sodium, and in presence of (b) 0.1 M sulphate (c) 0.1 M acetate (d) 10^{-5} M perchlorate (e) 0.1 M chloride (f) 0.1 M maleate (g) 0.1 M nitrate.

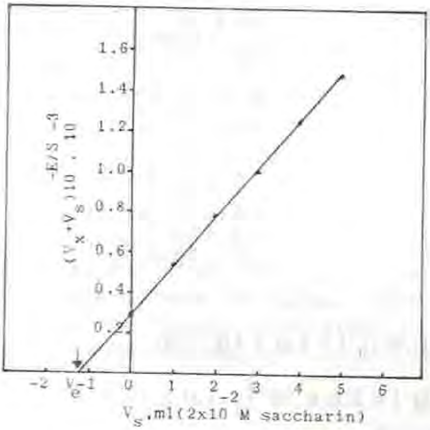

Fig. 5 Gran's plot for the multiple standard addition method (1 tablet / 50 ml solution).

Influence of pH on potential. The influence of pH on the potential of the electrode is shown in Fig. 3. The potential is independent of pH in the range 4.7-8.3. This pH range is nearly within the pH range for the stability of aqueous saccharin solutions which is 3.3-8.0. In more acidic and basic media saccharin hydrolyzes to the respective sulphobenzoic and o-sulphaminobenzoic acids (13,14). The most negative potentials may probably be due to the reponses of the anions of these acids and the acetate ion used in the buffer.

Selectivity of the membrane. The potentiometric selectivity coefficient (K_{ij}^{pot}) of an ISE is an index of selectivity toward an ion of interest i over another ion j. It is defined by the modified Nernst equation (15). The K_{ij}^{pot} values of the saccharin electrode for the interfering ions (Table 1) were obtained by mixed (10) (Fig. 4) and separate (11) solution methods. The variation in the values by the two methods are due to experimental differences such as ionic strength. It should also be noted that K_{ij}^{pot} for a given ion j is not necessarily a constant unless ions i and j are sensed by the electrode with identical slopes. Despite this, both methods show that the highest intereference comes from perchlorate and iodide ions. As shown in Fig. 2, the electrode also responds to these ions with more selectivity. Hence this multianion responsive electrode can be useful to measure these ions in aqueous solutions.

Table 1. Selectivity Coefficients of the Brilliant Green Saccharin-PVC membrane electrode

Interfering anion (j)	K_{ij}^{pot}	
	Mixed solution method*	Separate solution method*
Acetate	1.3×10^{-3}	8.0×10^{-4}
Benzoate	5.9×10^{-2}	4.0×10^{-2}
Chloride	4.2×10^{-3}	1.0×10^{-3}
Iodide	1.3	1.2
Maleate	5.4×10^{-2}	4.5×10^{-2}
Nitrate	5.6×10^{-2}	5.0×10^{-2}
Perchlorate	84.7	67.0 - 72.3
Sulphate	2.7×10^{-4}	7.5×10^{-4}
Hydrogen phosphate	4.5×10^{-2}	3.0×10^{-2}
Oxalate	6.0×10^{-3}	5.1×10^{-3}
Tartarate	8.1×10^{-3}	7.1×10^{-3}

*[j] for all ions = 0.1 M except for $[ClO_4^-] = 1.0 \times 10^{-5}$ M

**[j] = 0.1 M except for $[ClO_4^-]$ and $[I^-] = 5.0 \times 10^{-4} - 1.0 \times 10^{-1}$ M)

Determination of saccharin sodium in tablets. The saccharin content of the sweetening tablet, with a certified value of 12.5 mg of saccharin sodium per tablet, was determined using the four potentiometric methods. In direct potentiometry, the concentration of the sweetner was determined from a calibration plot of E [mV] vs -log [saccharin]. To maintain constant activity coefficient of the sensed anion, no ionic strength adjustment was made to avoid possible interference. Alternately, a narrow range of saccharin concentration, $1.0 \times 10^{-3} - 3 \times 10^{-3}$ M, which encompasses that of the tablet solution, was used to calibrate the electrode. For the same reason, less than a two-fold change over the original concentration of saccharin was made in the three addition methods.

The content of saccharin sodium per tablet by the dry sample addition method was evaluated on the basis of single point calibration method from the difference in potential ($E_s - E_t$) before and after dissolving the tablet into the standard saccharin solution C_s. The new concentration of saccharin (C_t) is calculated using $C_t = C_s.10^{(E_s - E_t)/S}$ where S is the electrode slope. Thus $C_{s}[10^{(E_s - E_t)/S} - 1]$ gives the the concentration of saccharin due to the added tablet. Equation 1 has been used (16) to calculate the concentration of saccharin in the tablet solution where $E_t - E_s$ is the potential change after adding the standard, and V_x and V_s are volumes of the sample and standard solutions, respectively.

$$C_x = C_s \left[10^{(E_t - E_s)/S} . \left(1 + \frac{V_x}{V_s}\right) - \frac{V_x}{V_s}\right]^{-1} \qquad (1)$$

Gran's plot was made following the method for anions by Liberti and Mascini (17). The plot of $(V_x + V_s)10^{-E/S}$ (= y) vs V_s (= x) gives a linear relation of the type y = a + bx. The straight line obtained (Fig. 5) intercepts the absissa for an equivalent volume V_e of the standard where $C_x V_x = -C_s.V_e$. The initial saccharin concentration is calculated from $C_x = -C_s V_e / V_x$. The quantity V_e has been reliably calculated from $V_e = -a/b$ after evaluating the slope of Gran's plot, b, and the intercept at the y-axis, a, (when $V_s = 0$) by the method of least squares.

Table 2. Content of saccharin sodium per tablet containing 12.5 mg of pure saccharin sodium

Method	Found* (mg)	Percent recovery	Standard deviation
Direct	12.81	102.5	0.44
Dry sample addition	12.20	97.6	0.35
Single standard addition	12.65	101.2	0.30
Multiple standard addition	12.80	102.4	0.31

*Average of five determinations.

The results of analyses of saccharin sodium content per tablet using the four potentiometric methods (Table 2) are in good agreement with the certified value. The electrode methods are very rapid compared to the current methods which involve hours of tedious refluxing, distillation and titration (13,14). The electrode can also be potentially useful for measuring perchlorate and iodide ions in aqueous samples.

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