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POTENTIOMETRIC SENSOR FOR POVIDONE-IODINE DETERMINATION

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A diiodobromide sensor with a plasticized polyvinylchloride membrane was developed. The sensor contained an ionic associate of diiodobromide and rhodamine B and had a linear response for I_2Br^- concentrations of $10^{-6} – 10^{-1}$ M with an electrode function slope characteristic of singly charged ions. The sensor was used as an indicator electrode for potentiometric determination of povidone-iodine in pharmaceuticals.

Keywords: diiodobromide sensor, potentiometry, povidone-iodine determination.

Iodine is an element that has several oxidation states [1, 2]. The determination of various iodine species, especially in pharmaceuticals, is of interest in analytical chemistry. Potentiometry using ion-selective sensors can perform this task [3, 4].

The goals of the present work were to study the possibility of using isolated ionic associates of diiodobromide and rhodamine B as an electrode-active component in plasticized sensor membranes and to fabricate from them a new potentiometric sensor for povidone-iodine determination.

EXPERIMENTAL PART

Stock solutions (10^{-2} M) of rhodamine B (RhB) were prepared by dissolving an accurately weighed portion of the previously purified compound in doubly distilled H_2O with a small amount of added EtOH. A standard solution (10^{-1} M) of diiodobromide was prepared by dissolving an accurately weighed portion of I_2 in KBr solution (0.2 M). A standard solution (0.1 M) of $Na_2S_2O_3$ was prepared from fixanal and also standardized by iodometry.

Ionic associates (IA) were prepared by precipitation from stirred solutions (10^{-2} M) of RhB and KI_2Br (1:1 ratio). The mixture was stirred and left at room temperature for 24 h. The resulting precipitate was filtered off, rinsed several times with cold distilled H_2O, and dried at room temperature for 4 d.

Plasticized polyvinylchloride (PVC) membranes were prepared according to recommendations [5]. PVC (0.1 g) and a certain amount of IA (1 – 15% of total membrane mass) were mixed, treated with plasticizer (0.1 mL) [dioctylphthalate (DOP), dibutylphthalate (DBP), dinonylphthalate (DNP), dinonylsebacate (DNS), or tricresylphosphate (TCP)] and solvent (0.7 mL) (cyclohexanone or tetrahydrofuran), thoroughly mixed to produce a homogeneous mass, transferred into a form (ring of diameter 1.5 cm), preliminarily polished, glued to a glass substrate, and dried in air for 5 – 7 d. Membranes (0.7 cm in diameter) were cut from the obtained films and glued to the ends of PVC tubes. The degree of homogeneity of the membranes was estimated using a METAM P-1 metallographic microscope.

Potentiometric measurements were taken from an I-160.M ion-meter at room temperature using an EVL-1MZ AgCl standard electrode.

TABLE 1. Electrochemical Characteristics of Diiodobromide Sensors

Plasticizer, 45%	S, mV/pC	$E = f(\log C)$, M	c_{min}, M
TCP	61 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$5.1 \cdot 10^{-5}$
DOP	69 ± 1	$1 \cdot 10 – 4 – 1 \cdot 10^{-1}$	$3.8 \cdot 10^{-5}$
DNP	42 ± 1	$1 \cdot 10^{-6} – 1 \cdot 10^{-1}$	$1.7 \cdot 10^{-6}$
DBP	73 ± 1	$9 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$1.2 \cdot 10^{-5}$
DNS	43 ± 1	$1 \cdot 10^{-5} – 1 \cdot 10^{-1}$	$1.2 \cdot 10^{-5}$

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TABLE 2. Determination of Povidone-Iodine in Pharmaceuticals ($n = 3$; $P = 0.95$)

Name and manufacturer	Composition	Regulated	Metrological characteristics
IOX, Aibeks	Povidone-iodine, propyleneglycol, levomenthol, citric acid monohydrate, sodium citrate dihydrate, 96% EtOH, H_2O	4.25 g in 50 mL	$\overline{X} = 4.13$, $S = 0.01$, $S_r = \pm 0.17$ %, $\Delta X = \pm 0.02$, $\varepsilon = 1.33$ %
Betadine, Alkaloid AD, Skopje	Povidone-iodine, macrogol 1000	200 mg	$\overline{X} = 198.7$, $S = 0.07$, $S_r = \pm 0.04$ %, $\Delta X = \pm 0.2$, $\varepsilon = 0.67$ %

Ionic strengths of solutions were maintained using KBr solution (0.2 M). Solution pH values were maintained using a universal buffer and were monitored by potentiometry using a glass electrode.

RESULTS AND DISCUSSION

The effect of the plasticizer on the sensor electrochemical characteristics was studied. The results in all instances showed that an electrode function was observed in the I_2Br^- concentration range $10^{-6} – 10^{-1}$ M. The slope of the electrode function for membranes plasticized with DOP, DBP, and TCP was 61 – 73 mV/pC with a minimum determined concentration of $n \cdot 10^{-5}$ M. Sensors with DNS and DNP plasticizers showed a Nernst function of slope 42 – 43 mV/pC with a minimum determined concentration $n \cdot 10^{-6}$ M (Table 1). It can be seen that lengthening the plasticizer hydrocarbon chain on going from DOP to DNP gave a more heterogeneous membrane and caused the electrode function slope to decrease.

Acidity also affected the potential of the I_2Br^- sensors. It was found that the sensor operating range with respect to acidity was pH 2 – 10. The large potential increase of the sensor at pH > 10 was due to hydrolysis of I_2Br^-.

The response time of the developed sensors showed that the potential was established in 2 – 3 sec for solutions with $[I_2Br^-] = 10^{-4} - 10^{-1}$ M and 5 – 7 sec for those with $[I_2Br^-] = 10^{-8} - 10^{-5}$ M.

The potentiometric selectivity coefficients ($-\log K_{i,j}^{pot}$) of the I_2Br^- sensors for Cl^- (5.0), Br^- (4.6), I^- (4.3), NO_3^- (4.6), SCN^- (4.2), ClO_4^- (4.1), SO_4^{2-} (5.0), HPO_4^{2-} (5.0), etc. were determined by the mixed solutions method and were >4. Model solutions showed that the excipients did not affect the analytical chemical characteristics of the sensors. This indicated that they could be used as analytical indicator electrodes, e.g., to determine povidone-iodine in pharmaceuticals.

Method for determining povidone-iodine

IOX formulation. An aliquot (2 – 5 mL) of the formulation was taken and treated with KBr (0.2 M) and H_2SO_4 (2 M) solutions. The reference electrode was AgCl; titrant, $Na_2S_2O_3$ solution (10^{-3} M).

Betadine formulation (suppositories). Povidone-iodine was determined by dissolving a suppository with heating in distilled H_2O (20 mL). The resulting solution was cooled, treated with KBr (0.2 M) and H_2SO_4 (2 M) solutions, and titrated potentiometrically. Three parallel measurements ($p = 0.95$) were made. The analytical results were calculated using mathematical statistics (Table 2).

Povidone-iodine reacts with thiosulfate according to the equation:

$$R^+I_2Br^- + 2S_2O_3^{2-} \xrightarrow{H^+} R^+ + 2I^- + Br^- + S_4O_6^{2-}.$$

It was shown that the synthesized ionic associate of I_2Br^- and RhB could be used as an electrode-active compound for an I_2Br^--sensitive potentiometric sensor. The operating conditions of the proposed sensor were investigated (effect of solution pH, plasticizer, I_2Br^- concentration, response time, etc.). The selectivity of the sensors was studied. Based on the results, a new sensitive and selective method that was simple to use was developed for potentiometric determination of povidone-iodine and was tested for determining it in pharmaceuticals.

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