A potentiometric iodide (and other) ion sensor based on a conducting polymer film electrode
Part II. effect of electrode conditioning and regeneration techniques

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Abstract

A novel potentiometric halide sensor electrode for iodide, based on the entrapment of iodide/iodine/triiodide into a poly(3-methylthiophene) conducting polymer, had previously been developed using a potentiostatic technique for film formation. The effect of film thickness (with the film thickness controlled by the amount of charge passing in the electrolytic cell during the polymerization) has been studied. Also, the effects of various pre- and postconditioning parameters on the electrode performance and life time were examined and compared. The life time of the electrode was extended up to one year by storing its sensing tip in a newly designed cap. The cap consisted of two chambers linked with a special orifice; the first contained iodine adsorbed on silica or alumina and the second housed the electrode tip. The linear dynamic range of the new sensor electrode was 1×10^{-7}–5×10^{-1} M iodide and the detection limit was 1×10^{-8} M iodide. The working temperature range, response time and working pH range of the electrode are 0–50°C, 17–20 s and 2–11, respectively. The potential for bromide, chloride, and sulfite selective electrodes based on these conducting polymer films are also presented and compared to those obtained for iodide. Moreover, the effect of changing the type of conducting polymer using poly(3-methylthiophene), poly(N-methylpyrrole) or poly(aniline) are given and compared.

Keywords: Sensors; Potentiometry; Halide selective electrodes; Conducting polymers

1. Introduction

Studies of the electrochemical behavior of electrodes modified with polymeric materials are one of the most

rapidly growing and advancing areas of modern electrochemistry. The behavior of electrodes modified with conducting poly(thiophene) films have also been of great interest [1]. This is due to both the stability of poly(thiophene) films produced electrochemically and to their interesting electrochromic and conducting properties. The selective response of this class of polymers towards dissolved ions has made them useful in

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various applications as a new "generation" of ion sensors. Ohnuki et al. [2] reported that selective film permeation of H^+, Br^-, and Fe^{2+} was observed in some polymer coated electrodes. Poly(o-phenylenediamine) coated electrodes were also applied in voltammetric [3] and pH measurements [4]. The "unique" advantage of the electrochemical synthesis of the polymer films is that this procedure leads directly to the conductive polymers in a single-step process. Moreover, electrosynthesis of polymers also results in a "self-doped" film which incorporates a supporting electrolyte ion into the polymer [5]. The property of doping of the conducting polymers can be exploited in various ways from an analytical chemistry application point of view. For example, a polymer can be doped with an electroactive substance, which subsequently attains a thermodynamic equilibrium between the doping species and one in solution phase, forming the basis of a selective potentiometric electrode system. However, actual applications using these particular conducting polymers, such as poly(methylthiophene), poly(N-methylpyrrole) and poly(aniline), is rather limited [6].

The selective potentiometric response for chloride [6a] and perchlorate [6b] ions using poly(pyrrole), and for the selective response to iodide ion [6d] based on poly(N,N-dimethylaniline/poly(o-chloroaniline) dual-layer coated conducting film electrodes, are among the few studies cited in the literature on the application of conducting polymers in potentiometry. Our group has been studying [7] the electrosynthesis [7a–d,f–i], spectroscopic characterization [7e] and application [7l–q] of some conducting polymers.

In a previous work [7o], we reported the construction and properties of an iodide-selective electrode based on a poly(3-methylthiophene) conducting polymer film. This electrode suffered from short life times, up to a maximum of fifteen days, but possessed a relatively high selectivity coefficients towards most interfering anions. Also, some technical data, such as film thickness, working temperature range, etc. were not reported. In this study, we also introduce the design of a new cap for the storage of this electrode which resulted in extending its life time to more than a year. In addition, more data for this electrode concerning preparative and operating conditions are presented. The effect of changing the type of the conducting polymer used in the fabrication of this type of I⁻-selective elec-
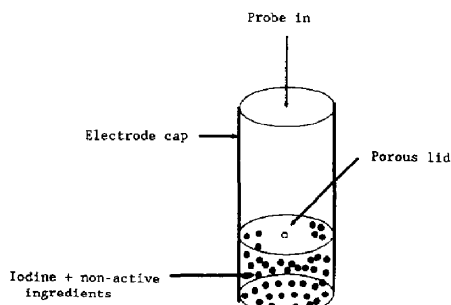

Fig. 1. Design of cap used for the activation/preservation of the iodide selective electrode.

trode is given and the responses are compared. Moreover, the efforts towards the fabrication of electrode sensors for other anions are discussed.

2. Experimental

2.1. Electrode construction

The fabrication of the electrode has been described previously [7o]. Fig. 1 shows a schematic diagram of the "storage" cap used for the electrode preservation. Electrochemical polymerizations were carried out with a three electrode cell where the working electrode was graphite of 2.544 cm² apparent surface area (Model Paroz-series 2003 Gr A 91EE075, AMP Inc., Cincinnati, OH). All the potentials in the polymerization and other measurements were referenced to an Ag/AgCl (3 M KCl) electrode. The auxiliary electrode was a 2×2 cm² or a 4×4.2 cm² platinum sheet. All the sensor electrodes were pretreated prior to the electropolymerization step as follows: The electrode was mechanically polished using metallurgical papers of successive grades 600 to 1200, and then the surface was treated by rubbing with filter paper, and finally with a fine tissue paper using an alumina/water suspension (10 μm) until no visible scratches were observed. Prior to immersion in the cell, the electrode was rinsed with distilled water, dried, and then thoroughly "degreased" in methanol. Finally, the electrode was rinsed with conductivity water, the solvent employed in the electropolymerization experiment, dried, and immediately put to use.

2.2. Electrolytic cells

All electrochemical measurements were performed in a conventional 100-ml flat bottom (Pyrex) glass cell which was fitted with five ground glass joints.

2.3. Chemicals and solvents

Tetrabutylammonium tetrafluoroborate (Aldrich, Milwaukee, WI), tetraethylammonium (Sigma, St. Louis, MO), hexylammonium tetrafluoroborate (Southwest Analytical Chemicals, Austin, TX), and lithium tetrafluoroborate, hexafluorophosphate, perchlorate, trifluoromethane sulfonate (Sigma) were used as supplied except for those experiments where samples were prepared for elemental or ESCA analyses. In such cases, the aforementioned electrolytic salts were recrystallized from a methanol/water mixture. Potassium and sodium salts of chloride, bromide, iodide, nitrate and sulfite (Aldrich) were used as supplied. All other salts, buffer solutions, HPLC-grade solvents, and reagents were purchased from Fisher Scientific. However, solvents used in the electropolymerization were distilled, purified as described in standard methods [8] and kept over molecular sieves, type A4, for at least 48 h prior to use. Aqueous solutions were prepared by dissolving a pre-weighed sample in conductivity water. The conductivity water was prepared from triple-distilled water which was subsequently passed through a Nanopure 4C-unit (Fisher). The water prepared in this way had a specific conductivity .of 1×10^{-17} to 1×10^{-18} S/cm. It should be noted that the conductivity increases when the water is left open to the atmosphere due to the dissolution of carbon dioxide. This water, which is known as "equilibrium water", was used only for rinsing purposes. All glassware and electrolytic cells were cleaned with a chromic–sulfuric mixture prepared by grinding chromium oxide with sulfuric acid or by using a cleaning mixture of alcoholic potassium hydroxide bath (either method yielded the same results). The cell was then washed with distilled water, equilibrium water, conductivity water, and was finally dried.

2.4. Electropolymerization

The conducting polymer films were electrochemically grown potentiostatically at 1.75 V on pretreated graphite surfaces (Paco Graphite, Decatur, TX). The electrosynthesis was achieved in a cell containing 50 mM 3-methylthiophene or N-methylpyrrole and 100 mM Bu_4NBF_4 in acetonitrile. The poly(aniline) polymer film was prepared from a solution containing 100 mM aniline in 1 M sulfuric acid. These films were then undoped by subjecting the working electrode to an applied potential of -0.2 V in the same synthesis solution for 45 min, where the current decreases to a 0.001 μA value within 5 min. The electrode was then removed from the synthesis cell, rinsed with acetonitrile, alcohol and water. The electrode was "activated" for subsequent use as a selective electrode for iodide, bromide, chloride and sulfite by one of the following methods; (i) the electrode was immersed in a cell containing aqueous solutions of 0.1 M KI, or KBr, or KCl, or K_2SO_3, and was subjected to a positive potential (determined by the oxidation potential of the anion of interest) in order to redope the film with the anion of interest. The electrode was then rinsed thoroughly with water; (ii) The electrode was alternatively "activated" by exposing its surface to one of the following gases: I_2, Br_2, Cl_2, or SO_2; the electrode was then rinsed with water and dried; or (iii) the "activation" was a combination of the electrochemical doping and the chemical treatment mentioned in (i) and (ii), respectively. The variation of the method of "activation" resulted in large differences in the potentiometric performance of the electrode.

2.5. Potentiometric measurement

Potential measurements were made with an Orion Model 601A ionalyzer using an Orion Model 90-02 double-junction reference electrode with a 10% KNO_3 solution in its outer chamber. As the ion selective electrodes respond to ionic activity, and as the readout is to be proportional to the analyte concentration, it is important that the activity coefficient, which relates these factors, is kept constant. In this respect, all the studied solutions contained 1×10^{-3} M KNO_3 as an ionic strength adjuster (except in the experiments where the interferences and the pH effect were investigated). These measurements were normally carried out at $23 \pm 0.5°C$ (except in the temperature range response measurements). Cyclic and double potential step experiments were performed using a BAS-100 instrument (BAS, West-Lafayette, IN).
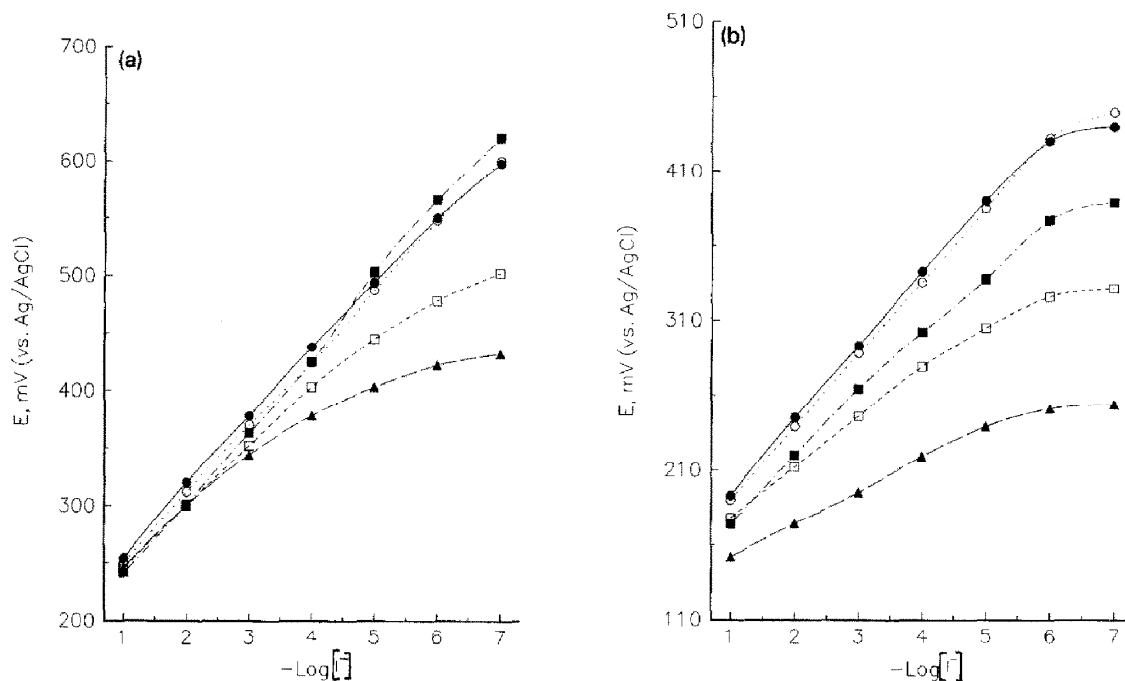
Fig. 2. Effect of doping potential on the response of 1000 thick film electrode of (a) PMT and (b) PA. 0.70 V (●), 0.80 V (○), 0.90 V (■), 1.00 V (□), 1.50 V (▲).

3. Results and discussion

3.1. Effect of electrode preconditioning parameters on electrode response

(i) Effect of doping potential.

The oxidation potential of I^-, Br^-, Cl^-, and SO_3^- solutions at the polymer film electrode was determined by a differential pulse voltammetry experiment. The doping (or more accurately, the activating) potentials were then applied using a potential slightly more positive than the oxidation "peak" potential determined from the differential pulse voltammetry experiment (ca. 50 mV). The effect of the doping potential on the response of the conducting polymer ion-selective electrode (CPISE) was studied for the poly(3-methylthiophene) (PMTCPISE) and the poly(aniline) (PACPISE) films. Figs. 2A and 2B. show the effect of the doping potential on the response of 1000 Å thick film electrodes of (PMT) and (PA), respectively. The effect of the applied potential for the doping step was found to depend on the nature of the doping ion and the type of the film under investigation. For example, Fig. 3A depicts the effect of the doping potential on the

response of a 1000 Å thick PMTCPISE (doped in 1×10^{-1} M KI solution for 45 s). It is evident that the films doped at a potential ≥ 1.2 V did not produce an acceptable linear dynamic calibration range. The films doped at potentials of $+0.70$, $+0.80$, or $+1.00$ V, on the other hand, produced calibration curves with a larger linear dynamic range (10^{-1}–10^{-7} M) and with correlation coefficients of 0.998, 0.999, and 0.998, respectively. Although the correlation coefficients of the calibration curves obtained for the electrode doped at $+0.70$, $+0.80$, and $+1.00$ V were comparable, the slopes obtained were different. For that doped at $+0.80$ V, the slope was 58.54 mV per decade. This is close to the expected value of 58.7 mV per decade (at 23°C). However, for the other two doping potentials the slopes were 57.42 and 64.54 mV per decade, respectively. All ensuing experiments were performed using films doped at $+0.8$ V for iodide ion determination. The relation between the doping potential and the "Nernstian" slope obtained from the calibration curves measured with the PMTCPISE for the determination of iodide is illustrated in Fig. 3A. It shows that the slope decreases significantly for films doped at potentials $> +1.00$ V. This phenomenon is probably a result of oxidative
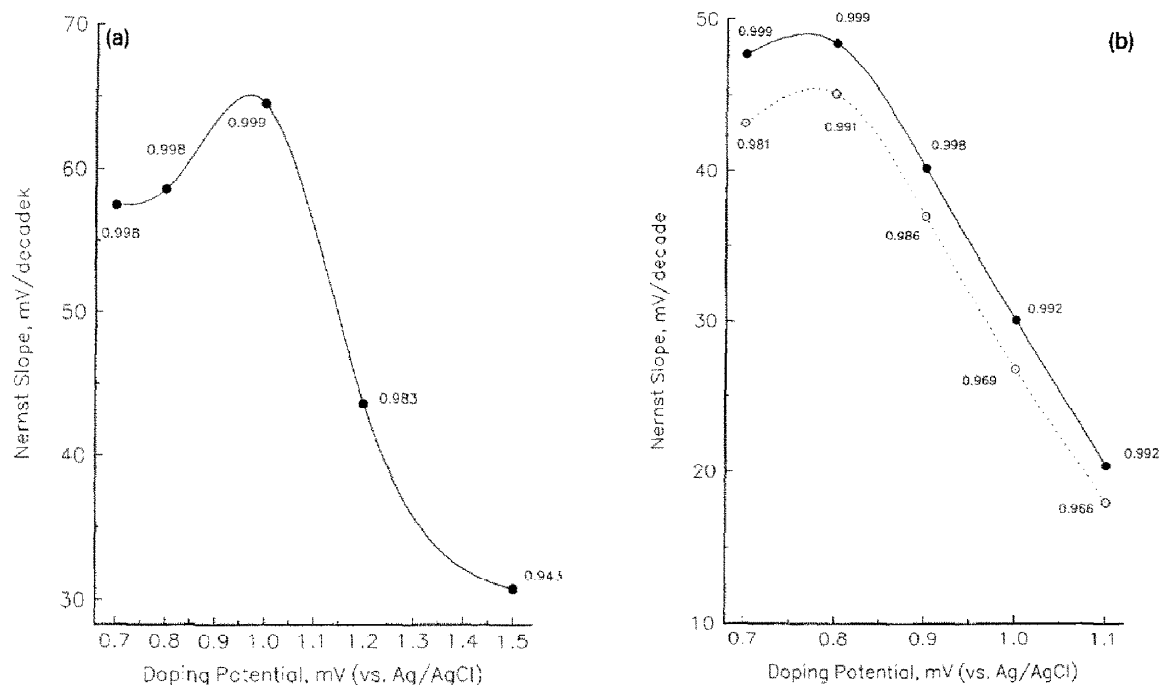
Fig. 3. The relation between doping potential and Nernst slope of the calibration for (a) PMT (film thickness 1000); and (b) PA: concentration range 1×10^{1} to 1×10^{-6} M (●), 1×10^{1} to 1×10^{-7} M (○). The correlation coefficient values are indicated for each calibration data.

effects caused by the iodine (I_2 gas) evolution at the film surface at the higher doping potentials. This will result in physical deterioration of the film. The oxidation peak potential of iodide at the PMT surface appeared at $+0.97$ V, as determined by the differential pulse voltammetric experiments. Similar behavior was also observed in the case of the PACPISE. However, the slope of the calibration curves were 20, 40, 48, and 46 mV/decade, with a conspicuous deviation from linearity at concentrations $\geq 10^{-6}$ M of iodide as depicted in Fig. 3B. Fig. 3B illustrates the relationship between the doping potential and the Nernst slope of the calibration curves. The slopes of the calibration curves decreased for films doped at potentials $> +0.80$ V. The magnitude of the doping potential at which the PACPISE response decreases occurs at less positive potentials than that of the PMTCPISE. A possible explanation for this behavior is attributed to the less positive oxidation potential for iodide at the PA film (ca. 682 mV, as measured from the DPV experiments). In general PMT electrodes had better analytical performance compared to PA and poly(N-methylpyrrole) (PNMP) as shown in Tables 1–3

(ii) Effect of polymer film thickness

The effect of film thickness on the potentiometric response of the modified PMTCPISE and PACPISE electrodes is illustrated in Figs. 4A and 4B, respectively. For the PMTCPISE, the correlation coefficients and slope values are given in Tables 1–3 for two different concentration ranges and indicate that all five electrodes (films grown at a constant deposition potential of $+0.8$ V, and with thicknesses corresponding to apparent 250, 500, 1000, 1500, and 2000 Å, respectively) exhibit acceptable calibration plots, with the 1000 Å thick film having the closest slope value to the expected Nernstian slope. The PACPISE, on the other hand, exhibited a different trend; thin films of 500 Å thickness had closer to Nernstian behavior than those for greater thickness, as shown in Tables 1–3. Fig. 5 illustrates the effect of film thickness on the performance of the PMTCPISE and the PACPISE, respectively. The optimum slope and correlation coefficients for the calibration curves for the PMTCPISE and PACPISE are 58.55 mV/decade, and 1.00; and 51.18 mV/decade, and 0.997, for films having 1000 and 500 Å thickness, respectively. This can be explained in terms of the difference in the morphology of the film (the

Table 1

(A) Effect of various preconditioning parameters on the correlation coefficients (R) and slope (S) of calibration graphs for different concentration ranges for PMTCPISE

Parameter	Value	Concentration range (M)			
		$10^{-1}–10^{-5}$		$10^{-1}–10^{-6}$	
		R	S	R	S
Film thickness (Å)	250	0.996	57.86	0.995	57.33
	500	0.999	57.43	0.997	56.78
	1000	1.000	58.54	0.999	56.89
	1500	0.999	54.43	0.999	57.45
	2000	0.999	48.57	1.000	56.31
Dopant concentration (M)	10^{-3}	0.999	56.10	0.999	54.5
	10^{-2}	1.000	57.35	0.999	53.64
	10^{-1}	0.998	58.81	1.000	58.54
	10	1.000	48.55	0.955	42.54
Doping period (s)	30	1.000	57.98	1.000	58.54
	60	0.999	58.67	0.999	58.71
	120	0.999	56.78	0.999	55.46
	240	1.000	45.62	0.989	40.57
Doping potential (mV)	700	0.999	58.56	0.998	57.43
	800	1.000	60.20	1.000	58.54
	1000	1.000	59.21	0.999	64.54
	1200	0.992	51.01	0.984	43.57
	1500	0.981	44.32	0.944	30.75

Table 2

Effect of various preconditioning parameters on the correlation coefficients (R) and slope (S) of calibration graphs for different concentration ranges for PACPISE

Parameter	Value	Concentration range (M)			
		$10^{-1}–10^{-5}$		$10^{-1}–10^{-6}$	
		R	S	R	S
Film thickness (Å)	250	1.000	52.14	0.998	48.86
	500	0.999	51.67	0.997	51.18
	1000	0.997	49.04	0.990	45.11
	1500	0.995	48.11	0.990	40.82
	2000	0.997	42.21	0.995	38.04
Dopant concentration (M)	10^{-3}	0.999	54.11	0.999	41.50
	10^{-2}	0.999	50.88	0.997	42.14
	10^{-1}	1.000	55.51	0.991	45.11
	10	0.985	45.16	0.966	34.39
Doping period (s)	30	0.999	50.34	0.991	45.11
	60	0.998	50.12	0.998	44.00
	120	1.000	40.98	0.982	33.86
	240	0.998	32.45	0.927	29.89
Doping potential (mV)	700	0.999	47.71	0.981	43.14
	800	1.000	48.46	0.991	45.11
	1000	0.998	40.20	0.985	36.98
	1200	0.992	30.06	0.969	26.75
	1500				

difference in morphology between thin and thick films) [7n,q].

(iii) Effect of dopant concentration.

The effect of concentration of iodide in the doping solution was investigated using electrodes having 1000 Å thickness films of PMT and PA, respectively. All dopant concentration studies were conducted on films doped at $+0.8$ V for 45 s. As can also be observed in Figs. 6A and 6B and Tables 1 and 2, increasing the dopant concentration results in a decreasing value of the linear dynamic range for the PMTCPISE and PAC-PISE. This deviation can probably be attributed to the increased oxidation of the electrode surface with the increase in the iodide ion concentration.

(iv) Effect of doping period

For a given film thickness of 1000 Å and a dopant solution concentration of 0.1 M KI, the effect of the doping period on the linear dynamic range and the slope of the calibration curve of the PMTCPISE and the PAC-PISE were also investigated. For this given set of con-

ditions, the optimum doping period was found to be in the range of 30 to 60 s, for both types of films, as illustrated by Figs. 7A and 7B, and Tables 1 and 2.

The data presented so far indicate that in order to obtain an iodide selective electrode from the conduct-

Table 3

Effect of various preconditioning parameters on the correlation coefficients (R) and slope (S) of calibration graphs for different concentration ranges for PPCPISE

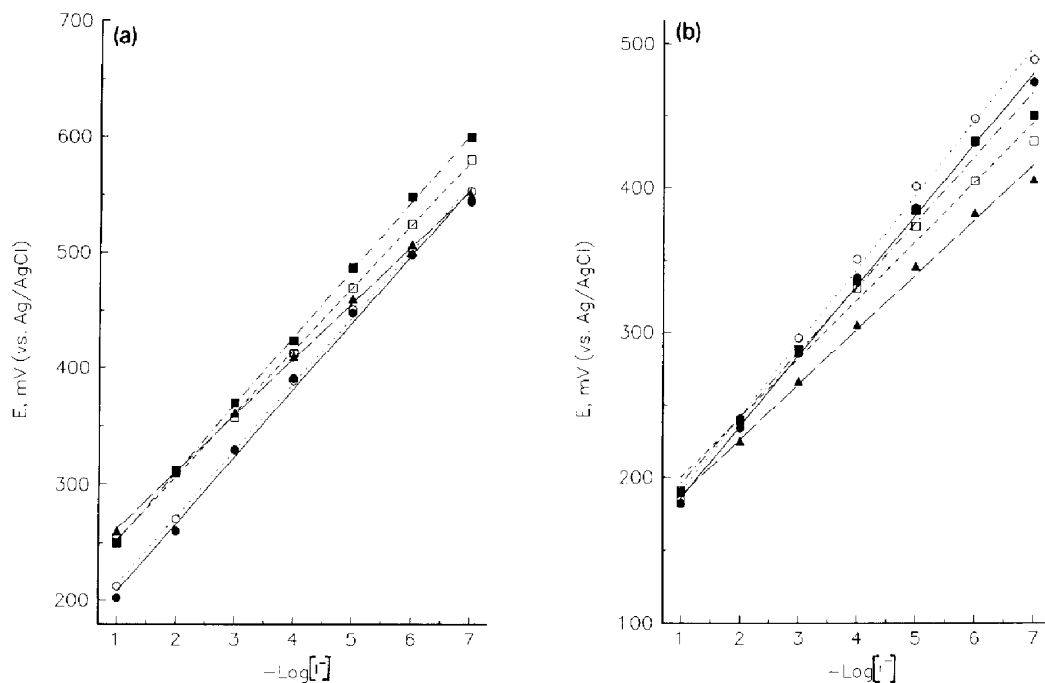| Parameter	Value	Concnetration range (M)			
		$10^{-1}–10^{-5}$		$10^{-1}–10^{-6}$	
		R	S	R	S
Film thickness (Å)	500	0.901	35.21	0.865	24.16
	1500	0.893	30.45	0.774	22.28
Dopant concentration (M)	10^{-2}	0.945	29.70	0.843	25.67
	10^{-1}	0.798	34.89	0.679	29.45
Doping period (s)	60	0.923	32.55	0.832	20.34
	120	0.945	28.38	0.712	19.05
Doping potential (mV)	700	0.967	38.90	0.756	30.48
	1000	0.877	34.22	0.652	26.83

Fig. 4. Effect of polymer film thickness on the potentiometric response of (a) PMT and (b) PA: 250 (●), 500 (○), 1000 (■), 1500 (□), 2000 (▲).

ing polymer films with a wide linear dynamic range and a near Nernstian slope, there must be an optimum amount of iodide/iodine incorporated into the film matrix (which should have, in turn an ideal thickness). However, the amount of iodide/iodine should be restricted to the minimum amount required to generate a surface redox potential within the polymer film. Exceeding such level of doping proved to be destructive to the physical integrity of the film resulting in an inferior response. Thus, as the film thicknesses are increased, the concentration of the dopant required for an optimum electrode performance also increased as illustrated in Figs. 8 and 9. However, for PMTCPISE films with a 2000 Å thick film, the effect of doping periods between 30–240 s seems to be insufficient. The PACPISE shows a comparable trend in the case of films of 500 Å thickness. The relationship between the film thickness, the doping period, and the Nernst slope of the PMTCPISE for the determination of iodide ion is represented in Fig. 9. It can be seen that a large variation exists in the values measured for the slope as the film thickness changes. The increase in the film thickness leads to a noticeable drop in the value of the slope. However, for films of ≥ 1000 Å thick, the increase in

doping time did not change the Nernst slope. This appears to confirm the previously mentioned destructive effect of excessive exposure of the films to iodine evolution throughout the doping process. Fig. 8 shows the potential response of PMTCPISE with different film thicknesses towards various iodide ion concentration of the doping solution. Optimum response is found to occur for 1000 Å thick films doped for a period of 30 s in the 0.1 M KI/0.1 M NaNO$_3$ at +0.8 V.

(v) Effect of exposure time to iodine vapor

In this section, the effect of changing the method of activation of the ISE is discussed. As mentioned earlier in the experimental section (electrode preparation), an alternative method for the activation of the polymer was employed; the film was "exposed" to iodine vapors for a given period of time. The exposure of the surface was made possible using the "modified" cap shown in Fig. 1. The cap contained iodine adsorbed on activated alumina or silica gel. This cap was used for "storage" or when the electrode was not in use in order to retain the "activity" and the response of the film for extended periods of time. The effect of the exposure time on the response of the PMTCPISE is illustrated in
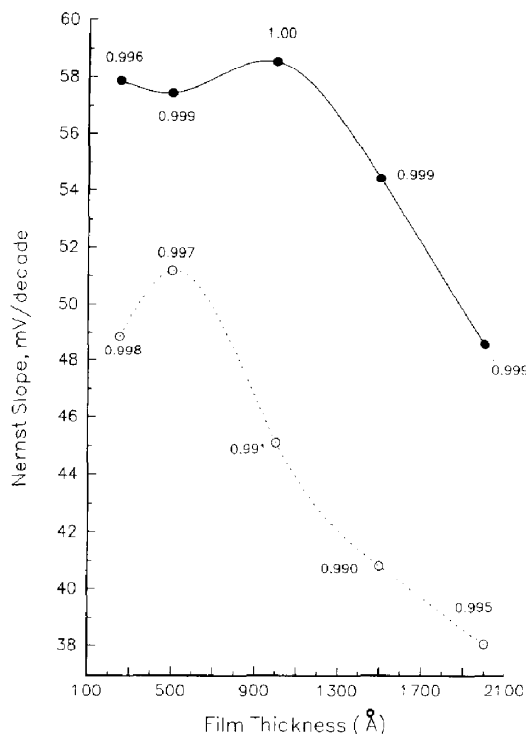
Fig. 5. Effect of polymer film thickness on the Nernstian slope of PMT (●) and PA (○). The correlation coefficient values are indicated for each calibration data.

Fig. 10. The amount of iodine used was 0.0500 g, which was thoroughly mixed with 1.2000 g of silica gel or activated alumina. A diaphragm that contains 10 peripheral and one central orifices of 1 mm diameter each was used to separate the electrode tip from the iodine/alumina containing compartment. The cap-chamber capacity is 1.3 cc and was filled with the doping mixture just prior to the preconditioning step. The previous conditions were found optimum for the electrode response. As can be learned from Fig. 10, the exposure of the PMT film to the iodine vapor for 30 s exhibited near Nernstian behavior and a larger linear dynamic range (1×10^{-7} to 1×10^{-1} M) than for films exposed for a period of time between 60 to 120 s. The previously observed damaging effect which results from prolonged periods of exposure to iodine under electrolysis conditions was also observed in the iodine vapor exposure study.

Thus, the calibration curves obtained for films doped for periods > 120 s showed a deviation from linearity in the calibration curves for concentrations $\leq 1 \times 10^{-5}$ M iodide analyte and had lower slopes and correlation

coefficients, as can be seen from Fig. 11 and Table 4. Films preconditioned using a combination (hybrid) of the two methods showed superior characteristics over those preconditioned using only one method. A comparison of the three activation procedures are given in Table 5. The most important advantages of the "hybrid" method of activation were observed in the lifetime of the electrode, reduced interference by other ions, and improved (near Nernst) slopes for long exposure periods to the analyte solution, as can be seen from Fig. 11.

3.2. Electrode reproducibility and response time

During the course of this study a large number of electrodes had been prepared to test the reproducibility of the potential response with electroactivation parameters. In order to determine the reproducibility of electrode preparation, the data were examined for a set of electrodes that had been prepared under the same conditions. Table 6 shows the reproducibility of electrode measurements for (a) the electrodes having 1000 Å thick films, doped electrochemically with 1×10^{-1} M KI + 1×10^{-1} M NaNO$_3$ at +0.8 V, and (b) for those both electrochemically doped and also exposed to iodine vapors for 60 s as described above. The data in Table 6, which were extracted from thirty seven measurements obtained over a period of nine months, show a reasonable degree of precision in electrode preparation, as demonstrated by the standard deviation of the potential values for a given analyte concentration. The uniformity of the electrode preparation is also demonstrated as shown in Fig. 12 for those films prepared using the "hybrid" technique.

The response time of the electrodes studied in this work was reported as the time required for the potential to come to a final steady value of ± 1 mV/min. Replicate measurements using the same electrode showed a considerable variation of $\pm 28\%$. This parameter was examined for the electrodes responding to both concentration increases and decreases. The experimental procedures for the determination of this parameter were as follows: (i) the two electrodes, the indicator (CPISE) and the reference were connected to a strip-chart recorder, (ii) then immersed in a solutions containing the KI of different concentrations and 1×10^{-3} M NaNO$_3$, and (iii) the time between the time at which the immersion of the iodide-selective electrode and a
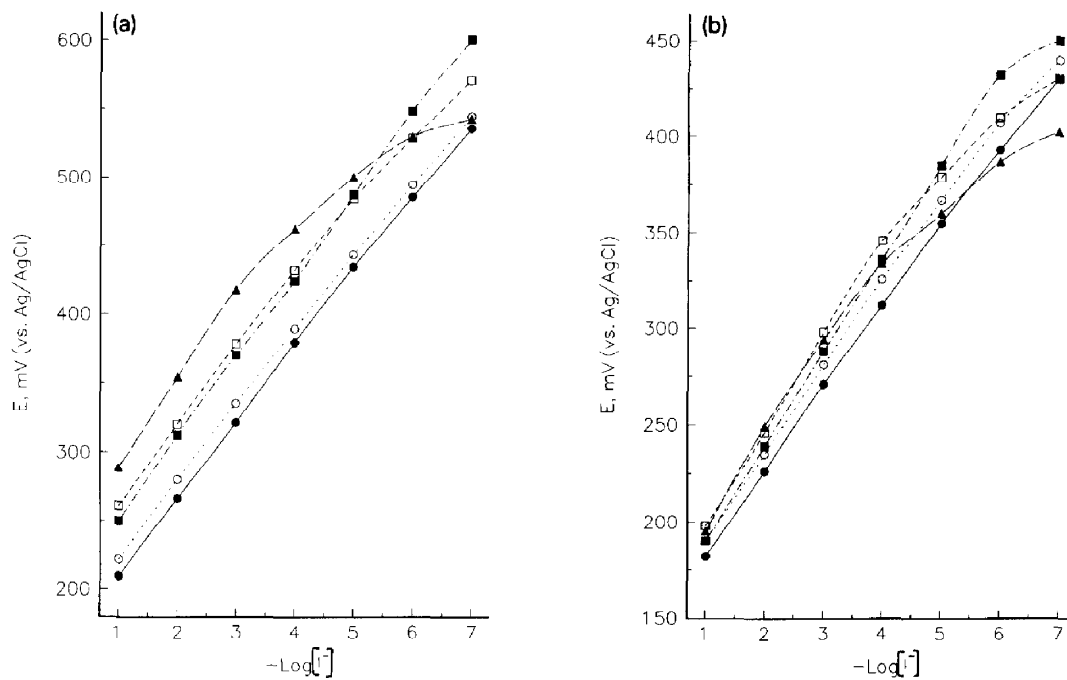
Fig. 6. Effect of iodide concentration used for doping on the potentiometric response of (a) PMT and (b) PA: 1×10^{-3} M ($\bullet$), 1×10^{-2} M ($\bigcirc$), 1×10^{-1} M ($\blacksquare$), 5×10^{-1} M ($\square$), 1×10^{1} M ($\blacktriangle$).
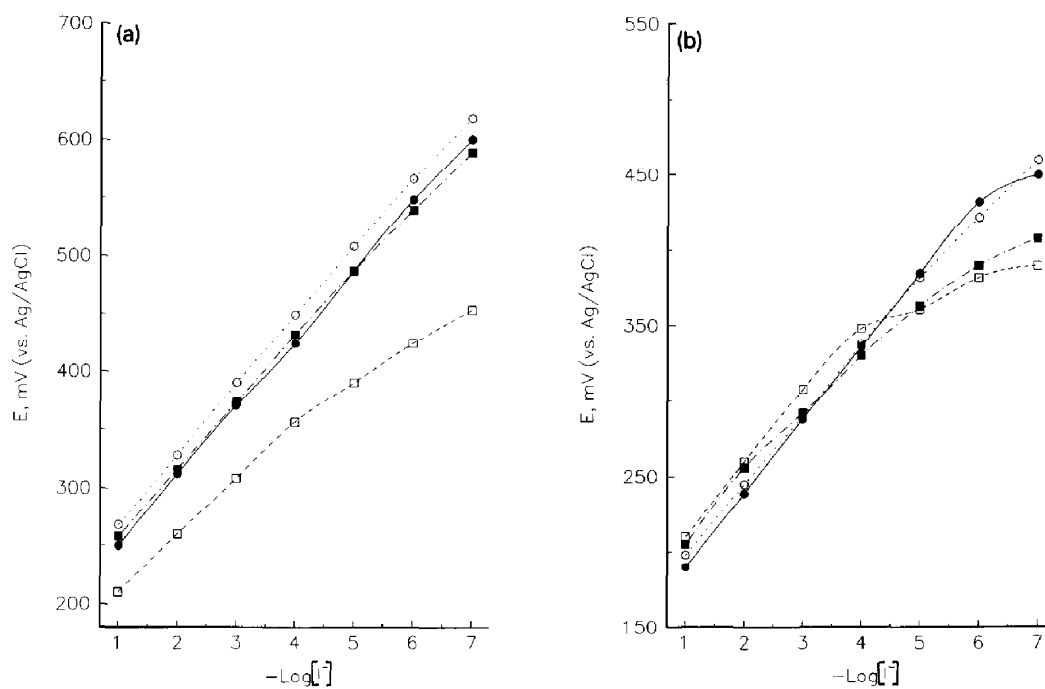

Fig. 7. Effect of doping period for 1000 thick film on the potentiometric response of (a) PMT and (b) PA: 30 s ($\bullet$), 60 s ($\bigcirc$), 120 s ($\blacksquare$), 240 s ($\square$).
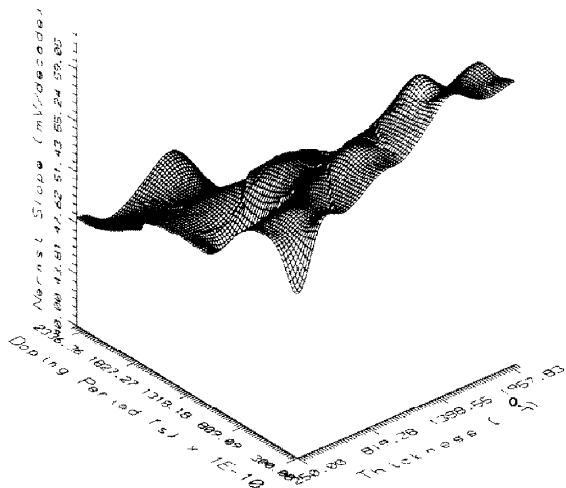
Fig. 8. Potential response of PMT electrode of different thicknesses towards various iodide ion concentrations.
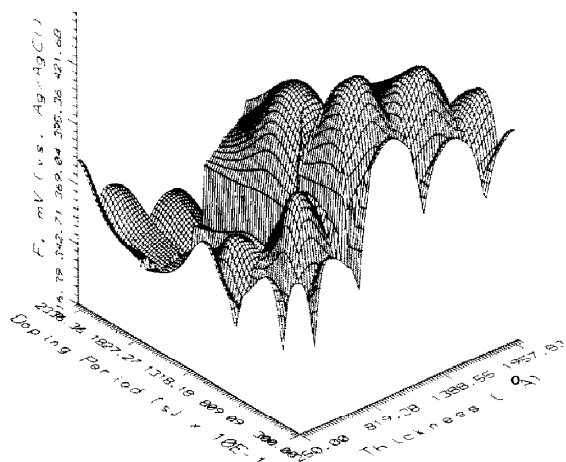
Fig. 9. Relation between film thickness, doping period, and the Nernst slope of the PMT electrode for the determination of iodide ions.

new potential plateau reached was taken as the response time. The results for the response time at the PMTCPISE and the PACPISE prepared by (a) the electrochemical doping, or (b) the hybrid-electro-chemical-chemical doping are given in Table 5. For concentrations $\geq 1 \times 10^{-5}$ M KI, the response time was in the range of 21 to 26 s with a standard deviation of ± 2.45 for electrodes preconditioned using method (a), and 17 to 20 s with a standard deviation of ± 0.67 for method (b), for a set of 14 electrodes each. A significant decrease of the response time of the CPISE preconditioned using method (b) was observed for iodide ion solutions with concentration $\leq 1 \times 10^{-6}$ M. The electrodes preconditioned via method (a) showed
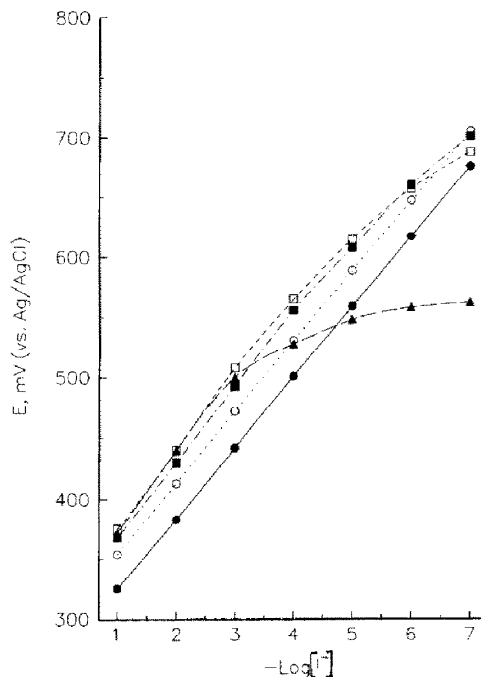

Fig. 10. Effect of exposure time of the PMT electrode to the iodine vapor on the response to iodide ion of different concentrations. 60 s (●), 90 s (○), 120 s (■), 300 s (□), 600 s (▲).
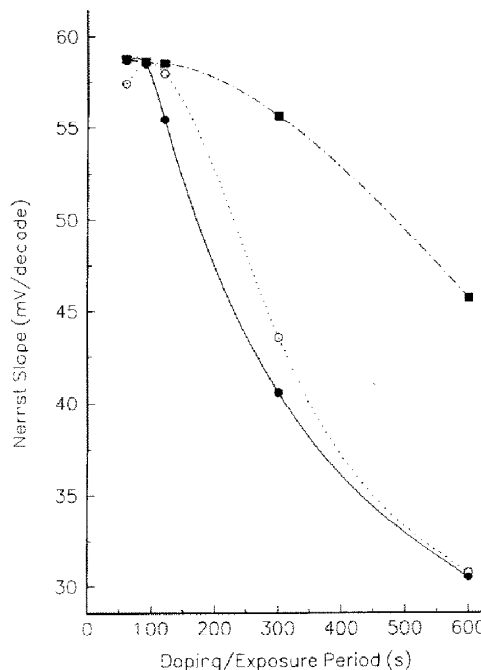

Fig. 11. Effect of exposure time on the Nernst slope of the PMT electrode response in the determination of iodide ions. Method of preparation: electrochemical (●), chemical (○), hybrid (■).

Table 4
Effect of exposure time of the PMTCPISE to the iodine vapor on the response to the iodide ion solutions

Exposure time (s)	Concentration range (M) 10^{-1}–10^{-4}	
	R	S
60	1.000	58.50
90	1.000	58.50
120	0.996	56.21
300	0.985	52.86
600	0.860	30.50

a response time of ca. 47 to 54 s for the dilute solutions of iodide, and those prepared using method (b) displayed values of ca. 26 to 34 s. The response time for some commercial iodide ion selective electrodes have been reported as follows: (i) Radiometer America, Inc. reported that the response time of their ion-selective electrodes in general varies from 10 s to several minutes, depending on the concentration of the iodide ion, the composition of the sample, etc.; (ii) Orion Research, Inc. reported that 99% of their iodide selective electrodes responded in one minutes or less; (iii) Corning/Fisher Scientific reported simply < 30 s response times for their ion selective electrodes. All the previously mentioned commercially available electrodes reported their values without mentioning any concentration range for the iodide ion. Thus the iodide ion selective electrode based on conducting polymer films showed comparable or superior response time characteristics over these commercially available ones.

3.3. Stability of potential measurements

The effect of subsequent runs on the measured potential of a given electrode for identical analyte concentration was also examined for electrodes preconditioned using (a) the electrochemical and (b) the hybrid elec-

Table 5
Effect of preconditioning parameters on the characteristics of the PMTCPISE in the determination of iodide

Parameter	Value		
	Electrochemical	Chemical	Hybrid [a]
Film thickness (Å)	1000	1000	1000
	$R(0.999),S(56.78)$	$R(1.000),S(57.31)$	$R(1.000),S(58.31)$
Dopant concentration (M)	10^{-1} I$^-$	Sat. I$_2$	Sat. I$_2$, 10^{-1} I$^-$
	$R(1.000),S(58.54)$	$R(1.000),S(58.75)$	$R(1.000),S(59.23)$
Doping period (s)	60	120	60, 120
	$R(0.999),S(58.71)$	$R(1.000),S(59.23)$	$R(0.999),S(58.62)$
Doping potential (mV)	800	–	800
	$R(1.000),S(58.54)$		$R(0.999),S(58.62)$
Lifetime (days)	15	23	> 120
Selectivity coefficient			
Cl$^-$	2.57×10^{-3}	3.55×10^{-3}	1.21×10^{-4}
Br$^-$	4.71×10^{-3}	2.33×10^{-3}	4.56×10^{-4}
NO$_3^-$	5.62×10^{-3}	1.66×10^{-4}	2.78×10^{-5}
ClO$_4^-$	2.12×10^{-3}	3.51×10^{-4}	5.16×10^{-5}
SCN$^-$	3.78×10^{-3}	5.67×10^{-4}	1.04×10^{-4}
H$_2$PO$_4^-$	4.61×10^{-4}	1.24×10^{-4}	4.66×10^{-5}
SO$_4^{2-}$	3.66×10^{-4}	2.71×10^{-4}	5.29×10^{-5}
CO$_3^{2-}$	2.79×10^{-3}	3.84×10^{-4}	1.34×10^{-4}
S$_2$O$_3^{2-}$	6.88×10^{-3}	2.33×10^{-3}	6.77×10^{-4}
OH$^-$	2.30×10^{-1}	4.10×10^{-1}	1.18×10^{-1}
CN$^-$	8.34×10^{-1}	6.45×10^{-1}	2.11×10^{-1}
Response time (s)	21–26, $\sigma(2.45)$	20–25, $\sigma(1.65)$	17–20, $\sigma(0.67)$
Temperature range (°C)	0–80	0–80	0–80

[a] In the hybrid method both electrochemical and chemical doping were used. The electrode was kept all the time in a cap containing the activating agent.

trochemical/chemical techniques. For a given electrode, potentials were measured over a period of four months in which the electrode was left (i) standing in air, (ii) in distilled/deionized water, (iii) 1×10^{-1} M KI solution, or (iv) in the previously described regeneration cap in Fig. 1 containing iodine between measurements. Each electrode was equilibrated first in stirred deionized water prior to the next set of measurements. Comparison of Figs. 13a and 13b shows: (i) For an electrode doped electrochemically (A) the calibration curves were shifted to less positive potentials on subsequent measurements. An electrode doped chemically/electrochemically (B) showed an insignificant change in the calibration curves; (ii) after a two weeks period, the slopes of the calibration curves showed a departure from the expected Nernst value of 58.7 mV/decade for electrode (A), while the slopes of the calibration curves for electrode (B) remained practically the same; and (iii) a change in the linear dynamic range, which was reduced to 1×10^{-1} to 1×10^{-6} M KI after the first day of preparation for electrode (A); On the other hand, electrode (B) maintained the same dynamic range of ca. 1×10^{-1}-- 1×10^{-7} M for the whole testing period. It was concluded from the above studies that the electrodes kept in the cap (containing the iodine) gave the best results relative to reproducibility and long term stability. These conclusions can also be drawn from in Fig. 14, where the slopes of the calibration curves for electrode type (B) kept in air were compared to that kept in the cap within the same time period.

3.4. Selectivity coefficients

As no electrode is entirely selective towards the ions specified, the presence of other ions can seriously
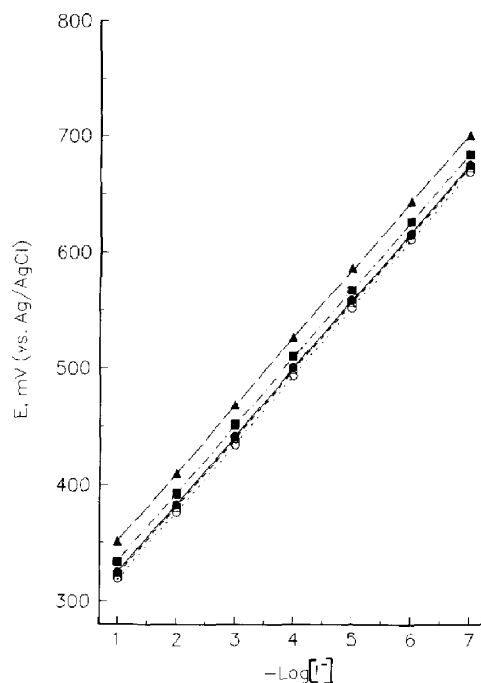

Fig. 12. Uniformity of preparation of PMT electrodes preconditioned with the hybrid method. Electrode 1 (O), 2 (□), 3 (■), 4 (●), 5 (▲).

impair electrode performance. Such interferences can take several forms, depending on the type of electrode material used and on the method of surface activation. The electrode behavior can be represented by an equation first used by Nicolsky [9] for the glass electrode showing a mixed response to hydrogen and sodium ions, which can be adopted for the study of the interference effects on the CPISE:

$$E = \text{constant} \pm k \log(C_i + k_{ij}C_j) \tag{1}$$

or for the case of other halides as:

Table 6
Uniformity of electrode preparation. Comparison between electrodes preconditioned electrochemically, and using the hybrid technique

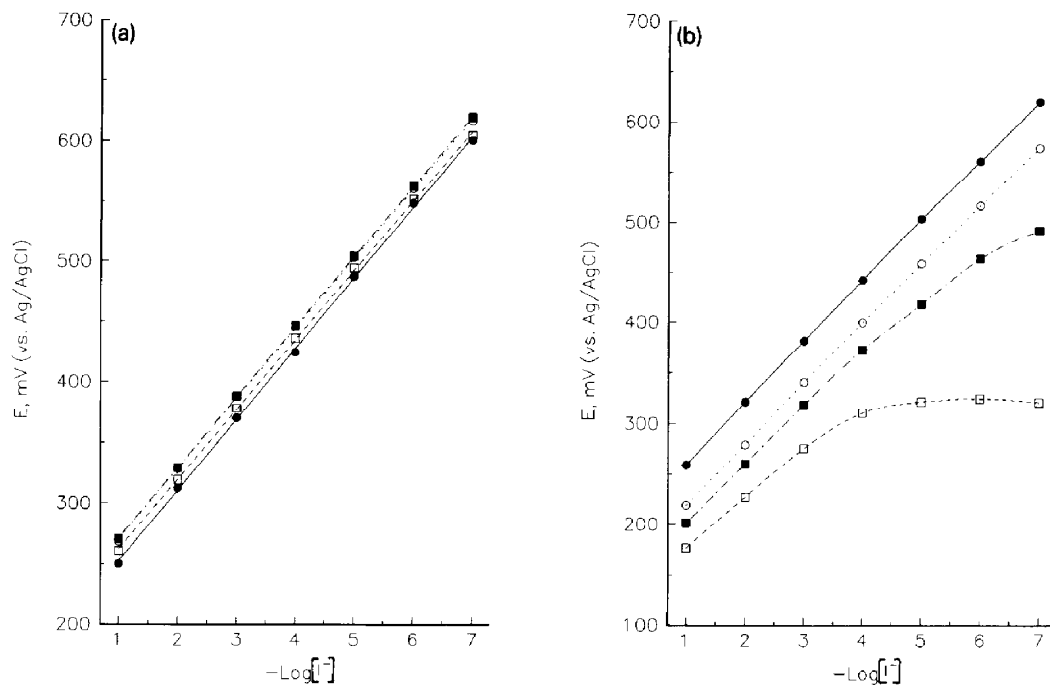| Concentration (M)	Electrochemical doping		"Hybrid" doping	
	E, Mean (mV)	σ_n (mV)	E, Mean (mV)	σ_n (mV)
1×10^{-1}	254	6.53	323	2.45
1×10^{-2}	315	7.19	382	2.29
1×10^{-3}	376	6.95	439	2.54
1×10^{-4}	435	6.82	501	5.49
1×10^{-5}	490	10.87	559	5.78
1×10^{-6}	540	21.25	618	5.52
1×10^{-7}	553	21.67	676	5.49

Fig. 13. Stability of potential measurements of (a) PMT and (b) PA: 1 day (●), 7 days (○), 30 days (■), 120 days (□).

$$E = \pm \frac{RT}{zF} \ln \left[a_i + \sum_j k_{ij}^{\text{Pot}} a_j \right] + \text{constant} \qquad (2)$$

where i and j are two similarly charged ions, k_{ij} is the selectivity coefficient, and k_{ij}^{Pot} is the ratio of the solubility products and activity coefficients.

The selectivity coefficients of the CPISE for the commonly encountered anions were determined by the commonly used method adopted by Srinivasan and Rechnitz [10], known by the "fixed interference method". The results for common interfering anions are summarized in Table 5, which shows that for the large majority of anions the selectivity coefficients are of the order of 1×10^{-3} or smaller. The poorer selectivity coefficients observed with the CN^- and OH^- can be explained in terms of the following reactions [11]:

$$I_2 + 2OH^- \rightleftharpoons IO^- + I^- + H_2O \qquad (3a)$$

$$3IO^- \rightleftharpoons 2I^- + IO_3^- \qquad (3b)$$
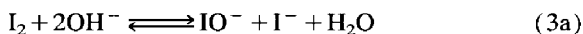
Hence the concentration of iodine in the film will decrease with a concomitant increase of iodide in the aqueous phase. From Eq. 3 it follows that electrode potential will shift to lower values as a result of the above reaction, and this will be reflected as an interfer-
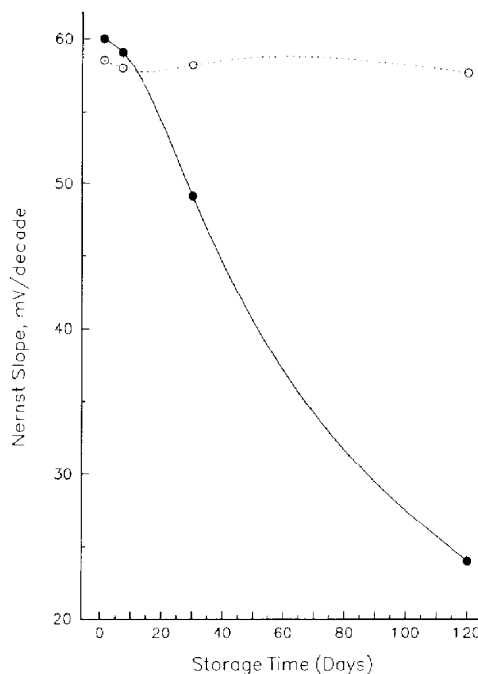

Fig. 14. Nernst slopes of the calibration curves for PMT electrode preconditioned by the hybrid method and kept in the cap (○) and left in the air (●).
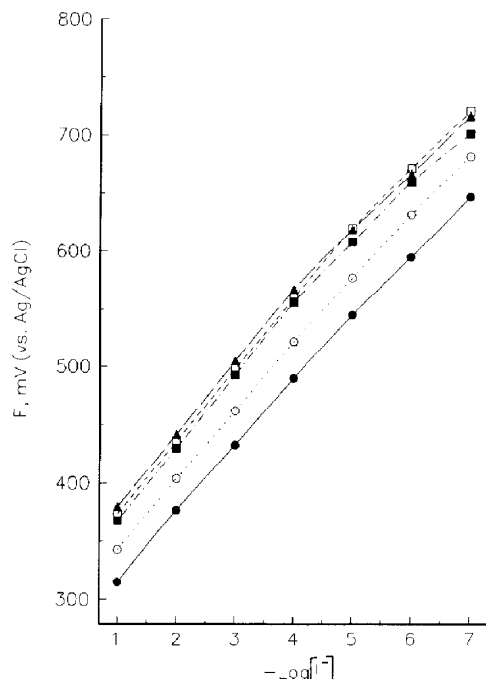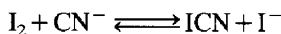
Fig. 15. Temperature effect on the potentiometric response of PMT electrode preconditioned using the hydrid method. 0°C (●), 10°C (○), 20°C (■), 50°C (□), 80°C (▲).

ence. Similarly, the cyanide effect can be accounted for by the following reaction [12]:

$$I_2 + CN^- \rightleftharpoons ICN + I^-$$

It can also be expected that any redox system which can reduce iodine or oxidize iodide would interfere with the measurements.

3.5. Effect of temperature on the CPISE

The theoretical temperature coefficient value is 0.198 mV/decade/K [13]. The effect of temperature on the performance of the CPISE was examined for the electrodes preconditioned using the "hybrid" method. The temperature coefficients calculated from the data obtained in Fig. 15 are on the order of c.a 0.09 to 0.15 mV/decade/K. Working temperatures > 80°C proved to be detrimental to the life time of the electrode.

3.6. The nature of the response of the CPISE

The oxidation of iodide in aqueous solutions on solid electrodes has been widely investigated. For instance,

iodide gives two voltammetric anodic waves on a platinum electrode, the first of which corresponds to the oxidation of iodide to iodine and the second to the oxidation of iodine to iodate [14]. On a pyrolytic graphite electrode three waves are found, which have been attributed to the successive oxidation of iodide to iodine, I^+ and iodate [15]. I^- may be oxidized to either I_2 or I_3^- in the same potential region [16]:

$$I_3^- + 2e^- = 3I^-; \quad E° = 0.545 \text{ V}$$

$$I_{2(s)} + 2e^- = 2I^-; \quad E° = 0.535 \text{ V}$$
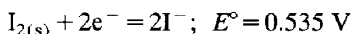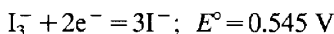
Therefore, on oxidation of I_2 may occur initially; then, with subsequent reaction with I^-, I_3^- formation may take place in relatively concentrated ($> 2.5 \times 10^{-3}$ M) I^- solutions [17]. We do not have direct evidence as to what type or in what ratio the oxidation products exist inside the polymer matrix. However, analogous to work concerning the oxidation of iodide at an electrodeposited poly(carbazole) film electrode [18], it tentatively was suggested that iodine is fixed on the polymeric electrode and at the same time I_3^- is formed in the diffusion layer. The formation of I_3^- seems essential for electroneutrality of the oxidized film. Alternatively it is suggested that a substantial fraction of I_3^- leaches out to the water during the equilibration of the electrode prior to the potential measurements. Assuming that iodine predominantly prevails on the polymer, the potential of the electrode can then be expressed by the following relationship:

$$E = E^{°\prime} + \left(\frac{RT}{2F}\right)\ln\frac{(a_{I_2})_f}{(a_I^-)_w^2} \tag{3}$$

where (aI_2) denotes activity in the polymer film and $(aI^-)_w$ denotes the activity in the aqueous phase. For dilute solutions, the activity terms can be replaced by concentration terms, so that at 25°C:

$$E = E^{°\prime} + 0.0296 \log[I_2]_f - 0.0592 \log[I^-]_w \tag{4}$$

From Eq. 4, it follows that the potential of this electrode depends on the concentration of iodine in the polymer film and on the concentration of iodide in both film and aqueous phase. If, however, $[I_2]_f$ can be kept constant, Eq. 4 converts to:

$$E = \text{constant} - 0.0592 \log[I^-] \tag{5}$$

at 25°C. A liquid-state iodide selective electrode based on a carbon rod impregnated with iodine from an

organic phase was described by Ruzicka and Rald [19]. The data regarding the longevity and stability tests of the PMTCPISE, which are represented in Figs. 13a and 13b, indicate that the electrode potential drifts to lower values (for those electrochemically doped or preconditioned with use) and the rate of drop decreases with each new set of measurements and time. The drift of the potential to lower values can be interpreted as the leaching out of I_2 from the polymer body. As indicated in Fig. 13a, this process apparently continues until a stable value for $[I_2]_f$ is reached or, alternatively it slows down to the extent that Eq. 5 holds for all practical purposes. The electrode performance is unfortunately altered at that stage and the slope deviates from the expected Nernstian value. The electrodes preconditioned using the "hybrid" method, on the other hand, and kept in the cap containing iodine as the active agent displayed more stability and longevity, as shown in Fig. 13b.

Electrochemically produced iodine can adsorb on unmodified graphite electrodes [20]. Therefore, it has been suggested that a simple iodide-treated graphite electrode can function in the same way as a polymer-coated iodine/iodide-doped electrode, and the need for a polymer coating can be questioned. However, uncoated graphite electrodes activated with the same procedures as described for the polymer-coated ones showed a response but with non-Nernstian slopes. Moreover, iodine-doped-graphite electrodes proved to be unstable and have a noticeable decrease in response upon repetitive measurements. The method employed by Dong and co-workers [6a,6b] and [21] was also examined and compared to ours. The polymer electrode was undoped at -0.2 V for 45 min, then was subjected to different final potential values varying in the range of 0 to $+0.8$ V for 5 to 30 min in 0.1 M KI solution before subjecting the electrode to potentiometric assays. The precision of the potential readings with the electrodes preconditioned using this method was poor, and the average lifetime of the electrode was only 1 to 2 days.

3.7. Chloride, bromide, and sulfite-chemical sensor based on conducting poly-3-methylthiophene

The selective determination of chloride, bromide and sulfite using a poly(3-methylthiophene)-modified electrode was investigated in order to demonstrate the multifaceted nature of this class of conducting polymer as an ion-selective probe. Three different techniques were used for the "preconditioning/activation" of the polymer film for a given anion. (i) The first method adopted the same procedures as reported by Dong et al. [6a,6b] for PNMP preconditioning. Thus, the PMT was formed potentiostatically as described above; the film was "undoped" at a negative potential of -0.20 V for 45 min; this was followed by immersing the electrode in solutions containing varying concentrations of the "doping" anion (0.01–1.00 M Cl^-, Br^- or SO_3^{2-}) for 5 h (and for varying periods of time between 1 to 3 days). (ii) The polymer film was alternatively activated by the electrochemical method described in the Experimental section of this paper. (iii) The third method depends on the use of a supporting electrolyte containing the anion under investigation (i.e. Cl^-, Br^-, or SO_3^{2-}) during the electrosynthesis step. In this case the following precautions were taken in order to ensure only the incorporation of the anion of interest in the film; the supporting electrolyte used was of a high purity grade, the final synthesis potential was $+1.80$ V in all cases, and the electrode was rinsed in an aqueous solution containing the counter anion.

Best results were obtained for films activated using a combination of the first and third methods. For example, for a chloride ion selective electrode, a typical preparation method was as follows: The polymer film (1000 Å thick) is formed potentiostatically from a solution containing 0.05 M monomer/0.10 M Bu_4NCl in acetonitrile. The electrode is rinsed with acetone, dried, then rinsed with a solution containing 0.1 M KCl, and finally immersed in the KCl solution for 3 days. The electrodes were thoroughly rinsed with distilled water prior to the potentiometric measurements. Representative potential response of the Cl^-, Br^-, and SO_3^{2-}-doped poly(3-methylthiophene) film electrodes are given in Figs. 16a, 16b, and 16c, respectively. The data in Figs. 16a, 16b, and 16c revealed that the chloride, bromide, and sulfite-selective-conducting polymer-based electrodes prepared by the above method have common features. These can be summarized as follows: (i) the linear dynamic range is limited (1×10^{-1} to 1×10^{-5} M concentration), (ii) the slope is in the range of 45 to 48 mV/decade, and (iii) the detection limits are in the order of 1.2–8.9×10^{-6} M. Moreover, their average lifetime was in the range of 2
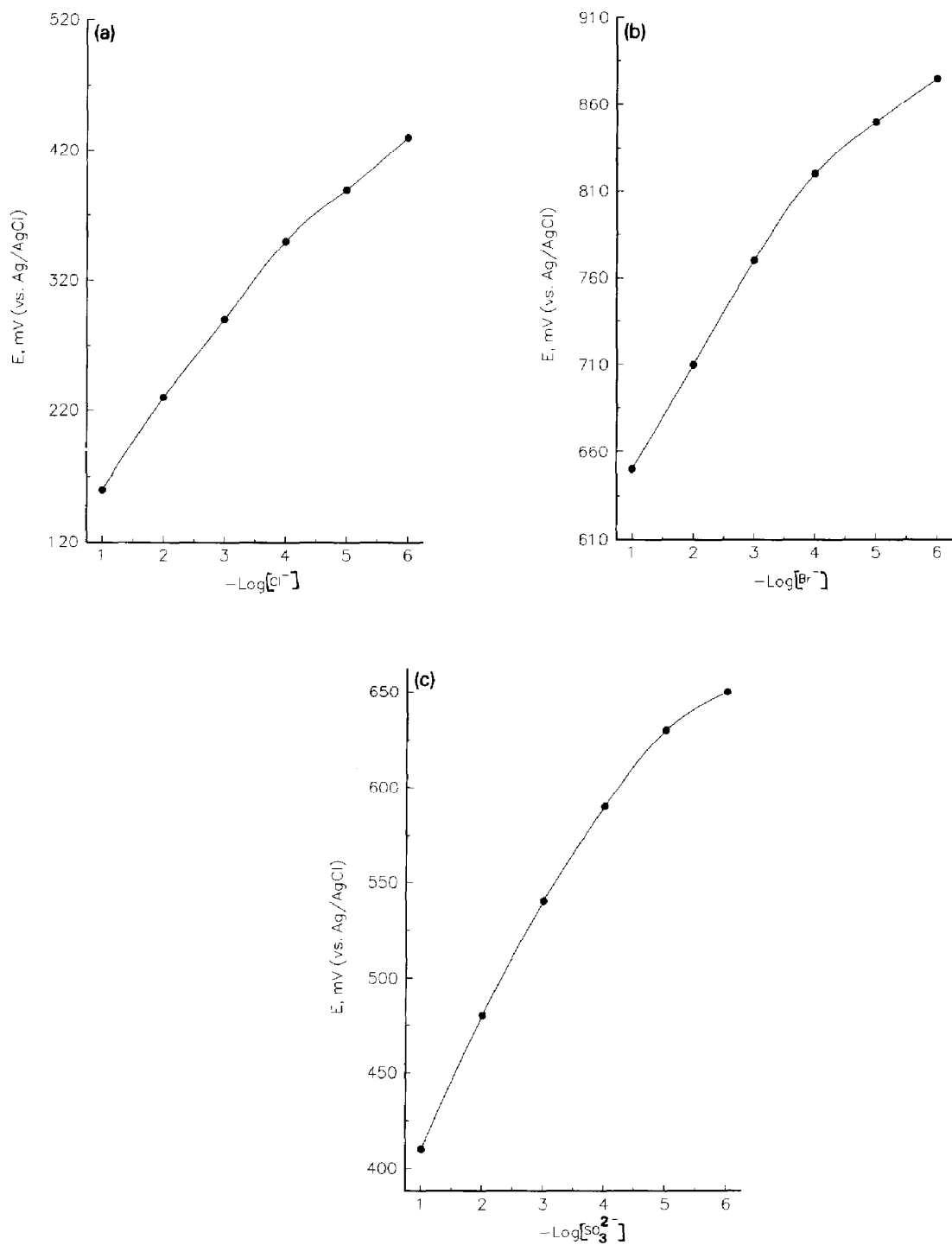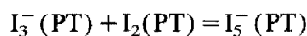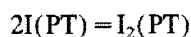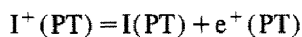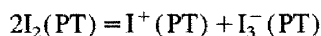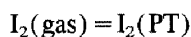
Fig. 16. Representative potentiometric response of PMT electrode towards (a) Cl^-, (b) Br^-, (c) SO_3^{2-}

to 3 days. The longevity of the electrode could only be extended upon keeping the electrode immersed in a 0.1 M solution of the ion under investigation.

The "superior" performance of the conducting polymer film which was preconditioned for the potentiometric detection of iodide ion over those devised for other anions could be explained in terms of the nature of interaction of the film with the species under investigation. Thus, absorption of gaseous iodine by films of poly(thiophene) was found to be fully reversible, the doping process appeared to be similar to the case of conventional semiconductors, and I_2, the electrically active dopant, behaves as an acceptor [22]. Moreover, Kim and Reiss [22] suggested the following equilibria to be associated with the iodine-polymer film interaction:

$$I_2(gas) = I_2(PT)$$

$$2I_2(PT) = I^+(PT) + I_3^-(PT)$$

$$I^+(PT) = I(PT) + e^+(PT)$$

$$2I(PT) = I_2(PT)$$

$$I_3^-(PT) + I_2(PT) = I_5^-(PT)$$

It can be concluded that the I_2, I^+, I, I_3^-, and I_5^- are all present in the polymer film at some given concentration ratios. The equilibrium established between the I^- in solution and species in the polymer gives rise to the observed potentiometric response. It is important to note that the renewal of the film response by its exposure to the iodine vapor in the cap suggests this. These peculiar reversible iodine-polymer interactions are probably not found with other anions. Therefore, the inclusion of I_2/I^- would lead to physically change film morphology.

3.8. pH effects

The ion selective electrode is affected by large hydrogen or hydroxyl ion activities, and the analyte under investigation may react with them. The iodide electrode, for example, responded over a limited pH range of 3.0 to 10.0 for 1×10^{-2} M I^- and 4.0 to 9.0 at the 1×10^{-4} M concentrations. The poor response beyond these limits could be explained as follows: at high pH values it responds to the hydroxyl ion (cf. the selectivity coefficient for hydroxyl ion in Table 5), while, at low pH, iodide (similar to fluoride) and
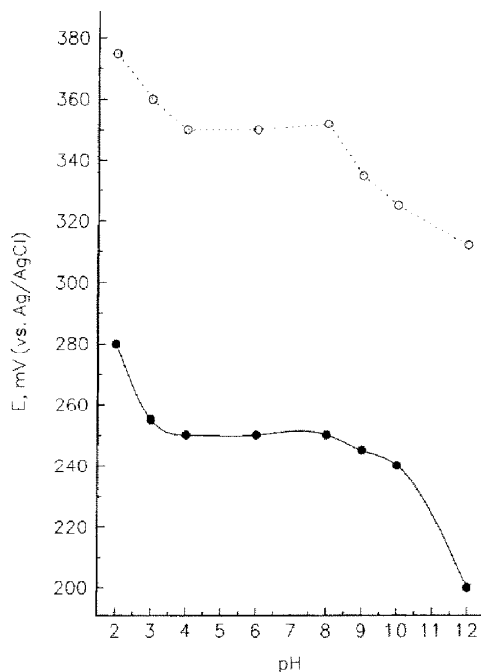

Fig. 17. pH effect on the potentiometric response of PMT electrode towards iodide. Iodide ion concentrations: 1×10^{-4} (O), 1×10^{-2} (●).

hydrogen ions react to form undissociated hydrogen iodide. Fig. 17 shows the effect of pH on the PMTCPISE performance is displayed.

4. Conclusions

In conclusion, the "hybrid" technique used for the "preconditioning" of the electrode proved to extend the lifetime of the iodide selective electrode. The working temperature range, the selectivity coefficients, and response time of this sensor electrode are comparable to those commercially available. The preparation of bromide, chloride or sulfite selective electrodes was successful, however, extended lifetimes for such electrodes was difficult. The "unique" response of iodine-doped poly(3-methylthiophene) electrode towards iodide and its superior behavior over that of poly(aniline) or poly(N-methylpyrrole) is explained in terms of the specific interaction of iodine with the poly(3-alkylthiophene). In a paper by Winokur et al.

[23], the authors demonstrated that poly(3-alkylthio-phenes) undergo continuous structural transformations upon doping with iodine vapor. In their discussion [23], the authors showed that an unusual reorganization can occur in the doped phases of alkyl-substituted conducting poly(thiophenes). Therefore, the iodine-induced structural changes in the poly(3-meth-ylthiophene) may be different than that of other polymers. Moreover, the chloride, bromide and sulfite interactions with the polymer films can be explained similarly.

Acknowledgements

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