

Studies on Polycarbazole-Modified Electrode and Its Applications in the Development of Solid-State Potassium and Copper(II) Ion Sensors

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ABSTRACT: Electrochemical synthesis of polycarbazole, having better stability and electrochromic activity, in dichloromethane containing 0.1 M tetrabutyl ammonium perchlorate (TBAP) is reported at 1.4 V versus Ag/AgCl. The electrochemistry based on cyclic voltammetric measurements in dichloromethane containing TBAP show redox behavior of the polymer associated to doping and de-doping of ClO_4^- ion within the polymer interstices. The polycarbazole matrix obtained by the potentiostatic and potentiodynamic modes of electropolymerization is characterized based on scanning electron microscopy, differential calorimetry, and infrared spectroscopy. De-doping of the polymer is studied by electrochemical reduction in TBAP-free dichloromethane followed by incubation of the polymer film in 1 M aqueous KCl solution for 24 h. The open circuit potential (OCP) of doped and de-doped polycarbazole modified electrode under the present experimental conditions is found to 462 and 19 mV, respectively, versus SCE in 0.1 M NH_4NO_3 . The de-doped polymer shows remarkable sensitivity and selective to Cu(II) ion compared to its sensitivity for Fe^{3+} , Ni^{2+} , Co^{2+} , Pb^{2+} , and Cu^+ ions. A typical response of the de-doped polymer electrode to Cu(II) ion is reported. On the other hand, ClO_4^- doped polymer is used in the development of solid-state K^+ ion sensors using dibenzo-18-crown-6/valinomycin as a neutral carrier-based, plasticized poly vinyl chloride matrix membrane assembled over a polymer-modified electrode. The doped polymer under this condition helps in maintaining charge stabilization across Pt/polymer and polymer/PVC interfaces. The lowest detection limit for the potassium ion sensor is 5×10^{-5} M with a slope of 58 mV/decade for valinomycin-based sensor and 6.8×10^{-5} M with a slope of 54 mV for dibenzo-18-crown-6 carriers with a wide linearity. The typical potentiometric results on the sensitivity, detection limits, and OCP to K^+ ion recorded using present polymer are compared with the data recorded earlier using polyindole and a similar neutral carrier-based PVC membrane. A comparison on electrode kinetics of these two polymer-modified electrodes also has been made using the data on Tafel plots to study the relative kinetic polarizability based on ion-exchange currents. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1749–1759, 2000

Key words: electropolymerization; conducting polymer; polycarbazole; potentiometry; solid-state ion sensor

INTRODUCTION

The electrochemical synthesis of polycarbazole^{1–3} and its characterization are of considerable inter-

est since not enough reports are available on this topic. The earlier reports^{1,2} on this polymer suggest poor quality of the electropolymerized film with respect to stability and electrochromic properties. The present investigation was undertaken to synthesize the polycarbazole in dichloromethane containing tetrabutyl ammonium perchlorate (TBAP), which shows better stability for practical applications. Cyclic voltammetry, scanning elec-

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tron microscopy, differential scanning calorimetry (DSC), and infrared (IR) spectroscopy have characterized the polymer. The doping and de-doping reactions of ClO_4^- anion are planned to study the behavior of the polymer for its technological application. The application of doped and de-doped polycarbazole is proposed in designing solid-state ion sensors, since the conducting polymer-modified electrodes have shown promising application in designing such ion sensors.^{4–11} The applications of polypyrrole,^{6,7} poly(3-octylthiophenes),^{8–10} and poly(*p,p'*-biphenol), as bridge layer between metal and poly vinyl chloride (PVC) matrix membrane, have been reported. Additionally, the de-doping reaction results in neutral polymer, leading to occurrence of free interstitial space within the polymer microstructure for the exchange of other ions; hence, it is of considerable interest to study the sensitivity of neutral polymer to other ionic species, and indeed, a remarkable result on the selective sensing of Cu(II) ion is reported.

We have recently studied the application of polyindole^{12,13} in the construction of solid-state, ion-selective electrodes (ISEs)^{4,5} based on a bilayer of polyindole and neutral carrier (dibenzo-18-crown-6)/valinomycin-incorporated PVC matrix membrane. The contribution of the polyindole layer was in stabilizing the potential difference across the metal/polyindole interface, which was associated with the presence of dissociated hydrophobic anions (ClO_4^-) in the oxidized form of the polymer. The objective of the present research was to make a comparative study on the use polycarbazole layer in place of polyindole layer under similar conditions for the construction of ISE. Additionally, electrode kinetic responses based on the Tafel plot are also proposed, to study relative kinetic polarizability to overpotential of both polyindole- and polycarbazole-modified electrode.

EXPERIMENTAL

Materials and Methods

Carbazole (AR grade) was obtained from Satureim export, Moscow; tetrabutyl ammonium perchlorate (TBAP) was obtained from Sigma Chemical Co.; PVC powder, dibutyl phthalate, valinomycin, and dibenzo-18-crown-6 were obtained from Aldrich Chemical Co. Tetraphenyl borate was obtained from the E-Merck, India, Ltd. The measurements were made in 0.1 M Tris-HCl

buffer, pH 7.0, using a double-junction calomel electrode containing sat. KCl in the inner junction and 0.1 M NH_4NO_3 in the outer junction. All the solutions were prepared in double-distilled deionized water.

Electrochemical Synthesis

The electrochemical measurements were performed with a Solartron Electrochemical Interface (Solartron 1287 Electrochemical Interface, UK) connected to a PC through the serial port. A one-compartment cell with a working volume of 5 mL, and a working electrode, Ag/AgCl reference electrode, and a platinum foil auxiliary electrode were used for the measurements.

The electrode body used for the construction of electropolymerized polycarbazole and subsequently ion-sensor, based on ionophore-impregnated PVC membrane, was made from a Teflon cylinder, as described in earlier publications.^{4,5} The platinum surface was polished with alumina slurry to a mirror finish, followed by drying under a nitrogen stream. The electrochemical polymerization of polycarbazole was carried out in CH_2Cl_2 containing 0.1 M TBAP and 5×10^{-3} M carbazole at constant potential of 1.4 V versus Ag/AgCl. The film was highly stable for practical applications and was characterized based on cyclic voltammetry in monomer-free dichloromethane containing 0.1 M TBAP. A platinum wire electrode (length, 8 mm; diameter, 0.45 mm) was used for the synthesis of polycarbazole for subsequent characterization of the film based on cyclic voltammetry. The Tafel plots of polyindole- and polycarbazole-modified electrodes were recorded in dichloromethane containing 0.1 M TBAP based on linear sweep voltammetry at the scan rate of 0.3 mV/s and were plotted from the data recorded as (E. versus Ag/AgCl) versus Log [i/A].

De-doping of electropolymerized polycarbazole was carried out by holding the electrode near cathodic potential for 15 min in monomer-free dichloromethane. The reduced polymer film was then incubated in 1 M KCl solution for 24 h at room temperature (26°C). The de-doping of the polymer was further carried out by the addition of Cl^- ion as KCl in aqueous medium (0.01 M Tris-HCl buffer, pH 7.0). The open-circuit potential of de-doped polycarbazole modified electrode in 0.01 M Tris-HCl, pH 7.0, was recorded as 19 mV versus the double-junction SCE electrode containing 0.1 M NH_4NO_3 in the second junction. The response of the electrode under this condition for

cations was measured by adding metal (Cu^{2+} , Ni^{2+} , Fe^{2+} , Co^{2+} , Cu^+ , and Pb^{2+}) acetate in the same buffer.

The construction of a K^+ ion sensor using electropolymerized polycarbazole was performed as follows. The electropolymerized oxidized (doped) film was washed in CH_2Cl_2 and dried under a stream of nitrogen. The solution of PVC-casting membrane was made in dried tetrahydrofuran (THF) of the composition; PVC fine powder (56 mg); valinomycin/dibenzo-18-crown-6 (1 mg); dibutyl phthalate (0.12 mL); tetraphenyl borate (0.75 mg); THF (2 mL). After complete dissolution of the membrane material; 70 μL of the solution was added to the recessed depth of the electrode body covered with the polycarbazole film. The solvent (THF) was allowed to evaporate slowly over a 20-h period at room temperature. On complete evaporation of the solvent, a transparent smooth layer of the sensing membrane remained at the surface of polycarbazole-modified electrode. The resulting electrode was conditioned for 12 h in 1 M KCl solution. The potentiometric responses of the ion sensor constructed above were carried out in 0.1 M Tris-HCl buffer, pH 7.0, and using a double-junction calomel electrode with the cell assembly.

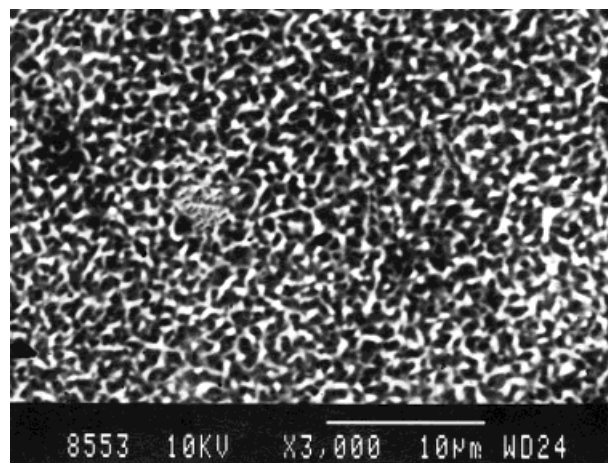
Calomel Electrode/KCl (Sat.)/0.1 M NH_4NO_3 /Test Solution/Polycarbazole-Modified Ion Sensor

As described in earlier publications,^{4,5} the ion sensor together with the double-junction reference electrode was dipped in the stirred electrochemical cell with a working volume of 15 mL. The electrode potential was monitored with an Orion pH meter, SA 520, and recorded with an Omniscribe series x-t recorder (Model 2000). At the steady-state potentiometric response, varying concentrations of the ionic solution were injected into the cell, and the new steady-state potential was recorded. The measurements were made with the polycarbazole-modified electrode with and without the ion-sensing membrane.

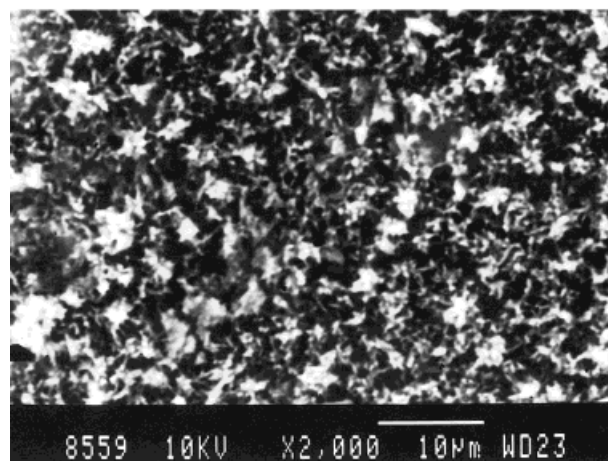
RESULTS AND DISCUSSION

Physical and Electrochemical Characterization of Polycarbazole-Modified Electrode

The potentiostatic mode of electrochemical synthesis of polycarbazole at 1.4 V versus Ag/AgCl has shown better stability with good yield com-



(a)



(b)

Figure 1 Scanning electron and micrographs of polycarbazole-modified film. (a) Made under potentiostatic condition at 1.4 V versus Ag/AgCl; (b) made under potentiodynamic condition between -0.2 and 1.6 V versus Ag/AgCl at the scan rate of 50 mV/s in dichloromethane containing 0.1 M TBAP at 25°C .

pared to that of potentiodynamic mode of synthesis. The color of polymer is dark green and has better physical stability on a metal surface with an amorphous structure. The scanning electron microscopy of surface structure of the polycarbazole synthesized under both the potentiodynamic and potentiostatic modes of electropolymerization is shown in [Figure 1(a,b)], respectively. The potentiostatic mode of electropolymerization (1.4 V versus Ag/AgCl) shows regular distribution of polymer domain and bathing electrolyte [Fig. 1(a)], whereas the potentiodynamic mode of electropolymerization shows relatively larger poly-

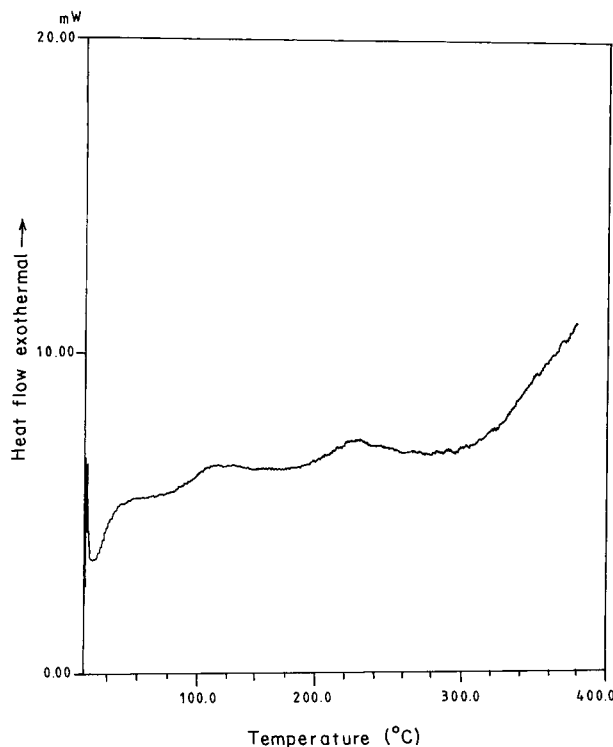


Figure 2 Differential scanning calorimetry of polycarbazole at the scan rate of 10°C/min.

mer domain size [Fig. 1(b)], with pits even after prolonged application of potential cycle scans (100 cycles at the scan rate of 50 mV/s, between -0.2 and 1.6 V versus Ag/AgCl). On the other hand, polyindole synthesized under potentiodynamic condition shows regular distribution of polymer domain and interstices with doped electrolyte.⁵ The oxidation potential of carbazole is larger (>1.2 V versus Ag/AgCl), whereas the oxidation potential of indole is <1.0 V versus Ag/AgCl.

Differential Scanning Calorimetry

The DSC of the polycarbazole was carried out at the scan rate of 10°C/min using a 2-mg sample. The results of DSC are shown in Figure 2. The data show that the polymer is stable for >450 °C. The data also show exothermic behavior on increasing temperature, suggesting an association of the polymeric domain and a subsequent change in polymer morphology, possibly associated to increasing in chain length.

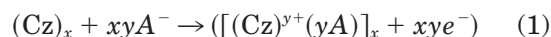
IR Spectroscopy

IR spectra of polycarbazole-modified electrodes are shown in Figure 3. IR spectra of the polycar-

bazole film in a KBr matrix show a strong N—H stretching band at 3440 cm^{-1} and C—H stretching band at 1637 cm^{-1} . The bands for C—C and C—N stretching were observed in the range of 1600 to 1450 cm^{-1} and a C—H stretching for the trisubstituted ring is observed in the range of 800 to 750 cm^{-1} .

Electrochemical Characterization

The cyclic voltammograms of polycarbazole synthesized under potentiostatic mode in dichloromethane containing 0.1 M TBAP are shown in Figure 4 at different scan rates. The electrochemistry shows peaked reversible redox behavior at slower scan rates (5 and 10 mV/s), whereas at higher scan rates it shows a plateau, and oxidation/reduction peaks are not well defined, which is associated with a shift in oxidation and reduction peak potential. On the other hand, polyindole synthesized under potentiostatic mode shows well-defined, reversible electrochemistry at all the scan rates (inset to Fig. 4). The redox behavior of the polymer is associated with doping and de-doping of the ClO_4^- anion within the polymer interstices. The electrochemical anion doping, also known as p-doping, since introduction of the anion into the polymer correlates with the appearance of positive charge in the polymer, and de-doping reactions can be represented as follows



where $(\text{Cz})_x$ is polycarbazole, x is the degree of polymerization, y is the doping level, and A^- is the univalent anion (ClO_4^- ion). The forward reaction of eq. (1) results in doping, whereas the reverse is de-doping.

Response of De-Doped Polycarbazole-Modified Electrode to Cu(II) Ion

The de-doping reaction eq. (1) results neutral polymer; hence, the interstices of the polymer microstructure are vacant for other ions in the absence of ClO_4^- ion in the reaction medium. We studied the interaction of de-doped polymer to several cations. Figure 5 shows the typical response of the de-doped polycarbazole [open circuit potential (OCP) = 19 mV] on the addition of varying concentrations of copper(II) acetate. The response is very fast and is similar to the response recorded using PVC matrix membrane electrode.

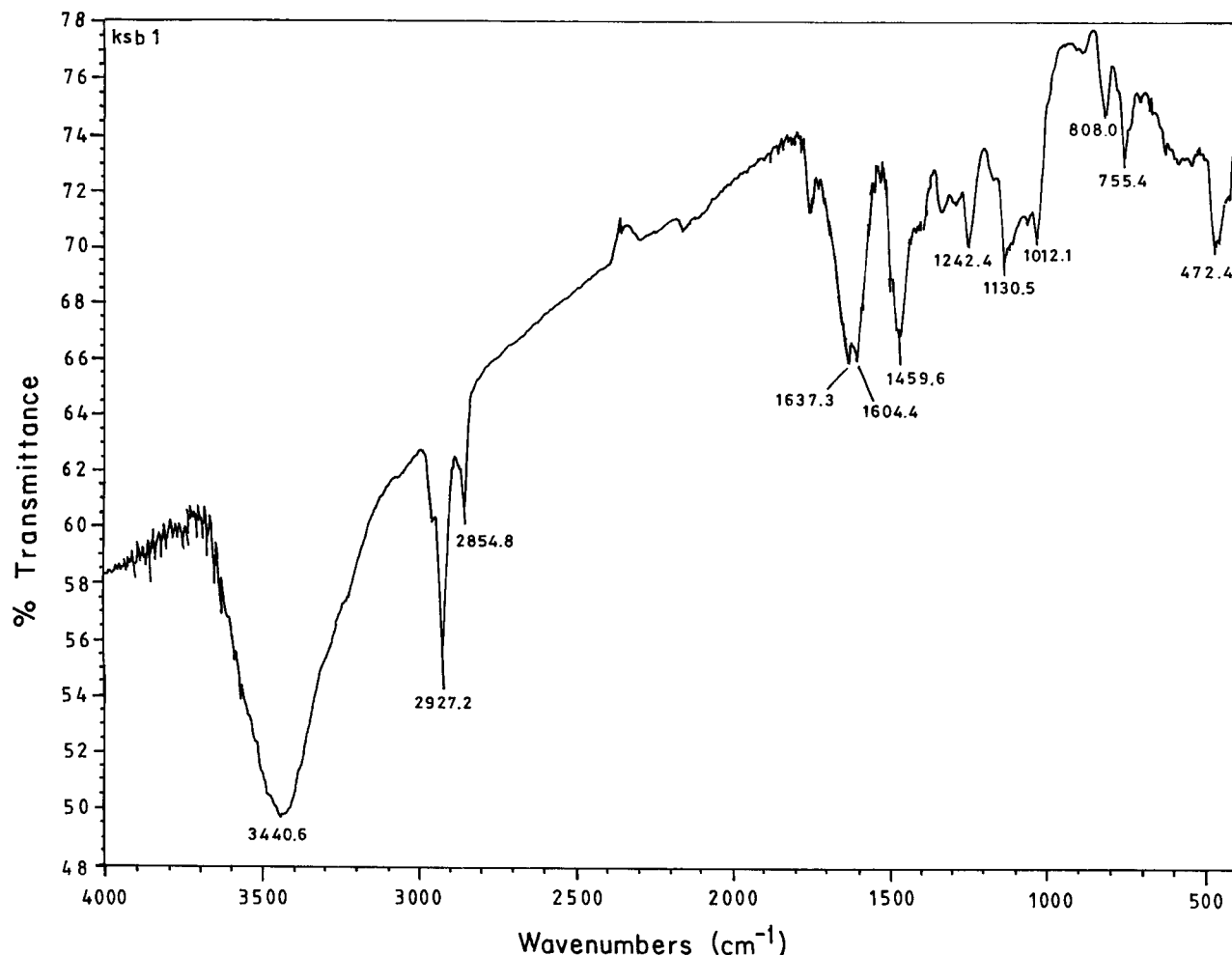


Figure 3 IR spectra of polycarbazole in KBr matrix.

The nature of response curve is very interesting, as shown in Figure 6. The linear range of the calibration curve is even less than one decade; however, the slope within this range is calculated to be 99.4 mV/decade, which reflect super Nernstian behavior of the de-doped polymer-modified electrode to the Cu(II) ion. The selectivity of the de-doped polycarbazole-modified electrode also was studied on the addition of the acetate salts of various metal i.e. Ni²⁺, Co²⁺, Fe³⁺, Zn²⁺, and Pb²⁺. No detectable response of the sensor to Ni²⁺, Co²⁺, Fe³⁺, and Zn²⁺ was observed, whereas sluggish response to Pb²⁺ was recorded with a slope of 19 mV/decade, with longer response time compared to the response time recorded for Cu²⁺. The polymer electrode even shows negligible potentiometric response to the Cu⁺ ion.

The behavior of the response curve of the polycarbazole-modified electrode to Cu²⁺ is mainly

due to the formation of symmetrical interstices, which possibly help in the formation of host-guest linkage or due to doping of Cu²⁺ within the polymer interstices. The size of Cu²⁺ ion and geometry of the polymer interstices possibly contribute the selective response of the sensor.

Neutral Carrier-Based PVC Membrane Solid-State Ion Sensors

The potentiometric sensors based on double layer of polycarbazole and the neutral carrier-incorporated PVC matrix membrane have been developed by coupling Pt/polycarbazole and polycarbazole/PVC interfaces. The PVC membrane was incorporated with either valinomycin or dibenzo-18-crown-6. The resulting solid-state ISE shows better potentiometric behavior for practical application compared to other ISEs based on blocked

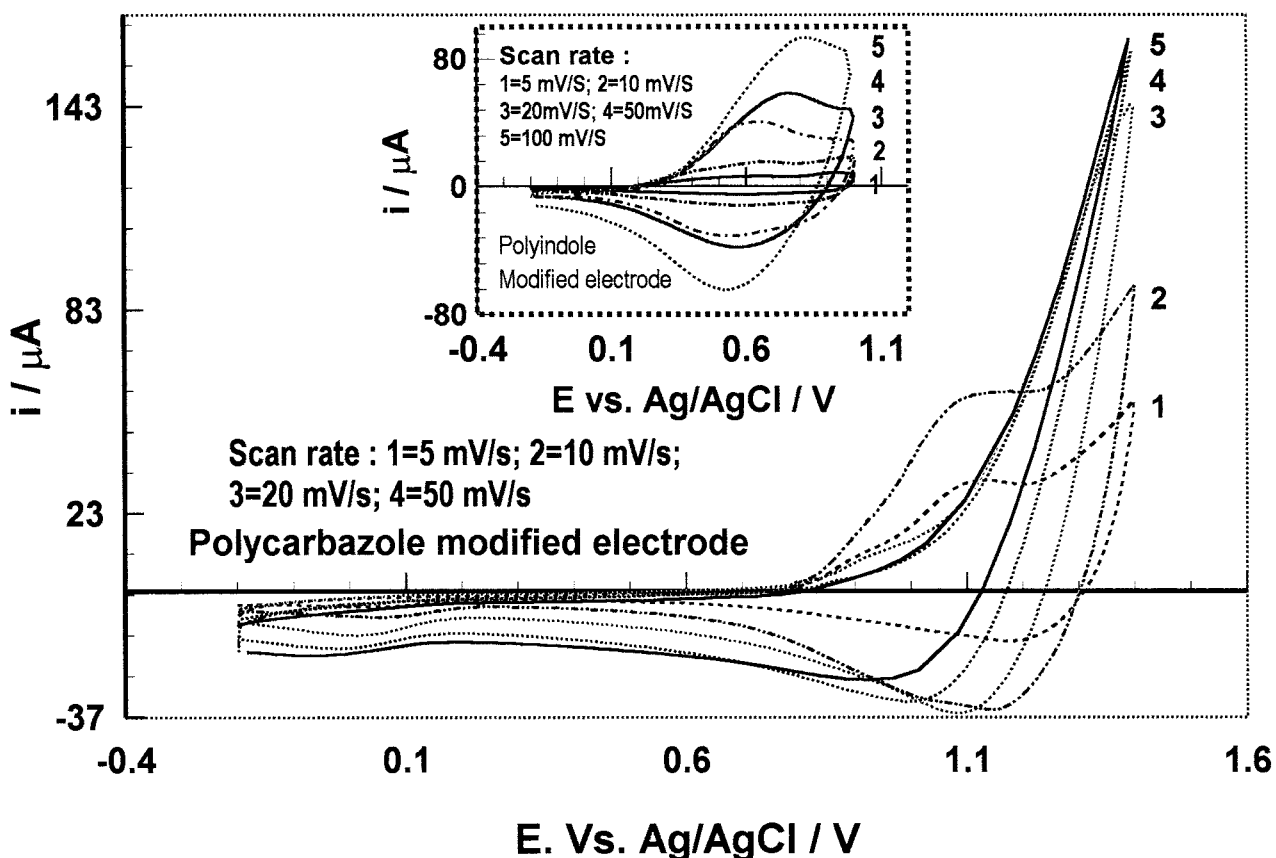


Figure 4 Cyclic voltammogram of polycarbazole-modified electrode in dichloromethane containing 0.1 M TBAP at various scan rates (mV/s); (1) 5, (2) 10, (3) 20, (4) 50, and (5) 100 in dichloromethane containing 0.1 M TBAP. The inset shows the cyclic voltammograms of polyindole-modified electrode in dichloromethane containing 0.1 M TBAP at various scan rates (mV/s); (1) 5, (2) 10, (3) 20, (4) 50, and (5) 100.

interface. Figure 7 shows the typical potentiometric response of the valinomycin-mediated ion sensor on the addition of varying concentrations of K^+ as KCl. The response is very fast, with a detection limit of 5.8×10^{-6} M. The detection limits were determined as described earlier.^{4,5} Figure 8 shows the typical potentiometric response of the dibenzo-18-crown-6-mediated ion sensor on the addition of varying concentrations of K^+ . The response is very fast with the detection limit of 6.8×10^{-6} M.

Figure 9 shows the typical calibration curve of ion sensor made with polycarbazole/valinomycin on the addition of primary and interfering analytes. The order of selectivity is found to be $K^+ > NH_4^+ > Na^+$. Figure 10 shows the typical calibration curve of the dibenzo-18-crown-6 ion sensor. The order of selectivity was found to be $K^+ > Na^+ > NH_4^+$. The response of the ion sensor is highly selective to K^+ , with extended linearity to

K^+ over almost five decades. The slope within the Nernstian response is calculated to be 58 mV/decade for polycarbazole/valinomycin sensor and 54 mV/decade for polycarbazole/dibenzo-18-crown-6-mediated ion sensor. The life time of the typical ion sensors based on the polycarbazole- and polyindole-modified electrodes is recorded in Table I. In each case, the slopes were determined using the small data range, where maximum sensitivity to cation was recorded.

Comparative Studies on the Polyindole/Polycarbazole-Modified Electrodes Kinetics

The Tafel plots of the polycarbazole- and polyindole-modified electrode are shown in Figure 11. These plots were obtained by plotting the data recorded on linear sweep voltammetry at the scan rate of 0.3 mV/s (-0.3 to 1.6 V versus Ag/AgCl for polycarbazole; -0.2 to 1.1 V versus Ag/AgCl for

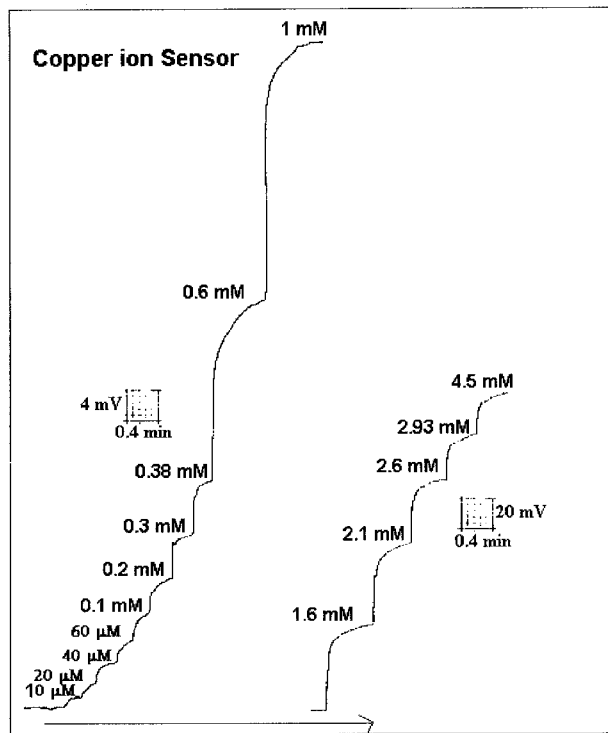


Figure 5 Typical potentiometric response of the deposited polycarbazole-modified electrode on the addition of copper(II) acetate in 0.1 M Tris-HCl buffer, pH 7.0, at 25°C.

polyindole). The equilibrium kinetic potentials calculated by making a horizontal straight line at the inversion of cathodic to anodic current (from

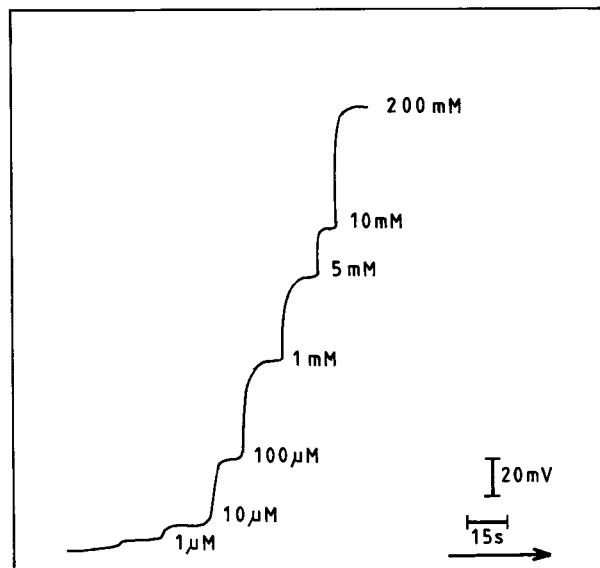


Figure 7 Typical potentiometric response of the polycarbazole/valinomycin ion sensor in 0.01 M Tris-HCl buffer, pH 7.0, at 25°C.

curve 1 for polyindole and from curve 2 for polycarbazole) associated with doping and de-doping reactions as shown in eq. (1) suggest that it is greater in the case of the polycarbazole-modified electrode (0.36 V. versus Ag/AgCl) compared to the polyindole-modified electrode (0.18 V versus Ag/AgCl). A comparison of ion-exchange current

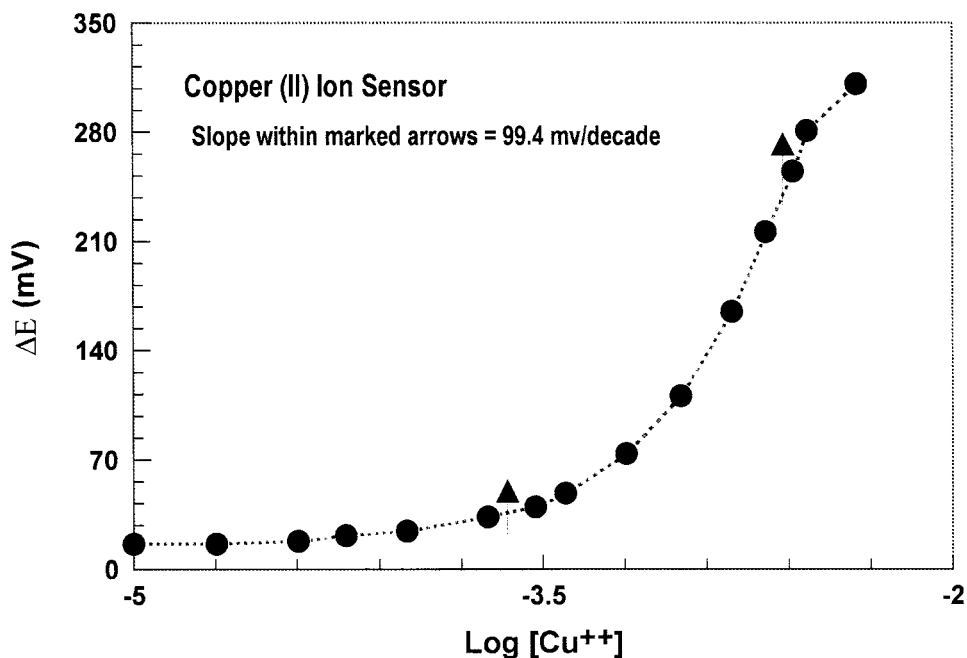


Figure 6 Calibration curve of ion sensor to Cu^{2+} in 0.1 M Tris-HCl buffer, pH 7.0.

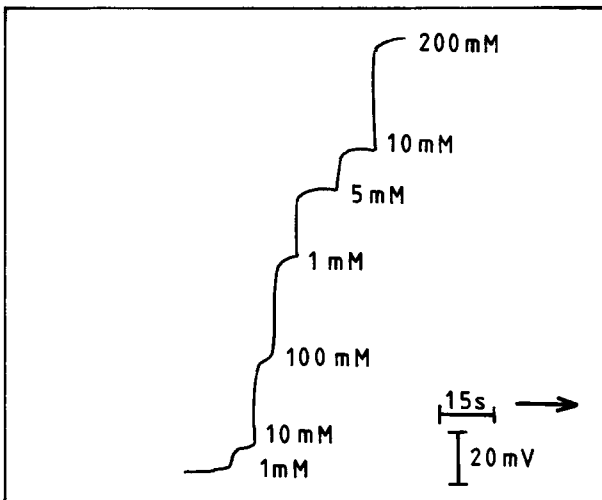


Figure 8 Typical potentiometric response of the polycarbazole/dibenzo-18-crown-6 ion sensor in 0.01 M Tris-HCl buffer, pH 7.0, at 25°C.

density also can be made from these curves, and the data suggest that the polycarbazole-modified electrode is relatively least kinetically polarizable compared to the polyindole-modified electrode based on the comparative values of the ion exchange current densities obtained from Fig. 11.

Doped and De-Doped Polymer Interstices and Ion-Sensing of Polymer-Modified Electrodes

The steady-state potentiometric response of an electrode is the function of thermodynamic equilibrium potential and is the dipolar potential developed at electrode/solution interface. The polymer with doped ions as shown in eq. (1) creates a positive charge in the polymer having a dissociated negative charge within the polymer interstices, resulting in the development of thermodynamic equilibrium dipolar potential. However, the polymer interface is susceptible to exchange of other ions present in a aqueous/nonaqueous solution. The redox behavior of the polymer, based on the cyclic voltammetric results (Fig. 4), is only recorded when the experiments are conducted in CH_2Cl_2 containing the doped anion (ClO_4^-). When the voltammograms is not recorded in similar medium, the polymer-modified electrodes do not show reversible redox behavior. Thus, the steady-state value of the thermodynamic equilibrium potential depends on the stability of doped anions. When the doped polymer-modified electrode is incubated in aqueous medium that contains other anions, for example, Cl^- , Br^- , NO_3^- , OH^- , CH_3COO^- instead of the ClO_4^- ion, the perchlorate ion may be exchanged by these hydrophilic anions, which do not follow

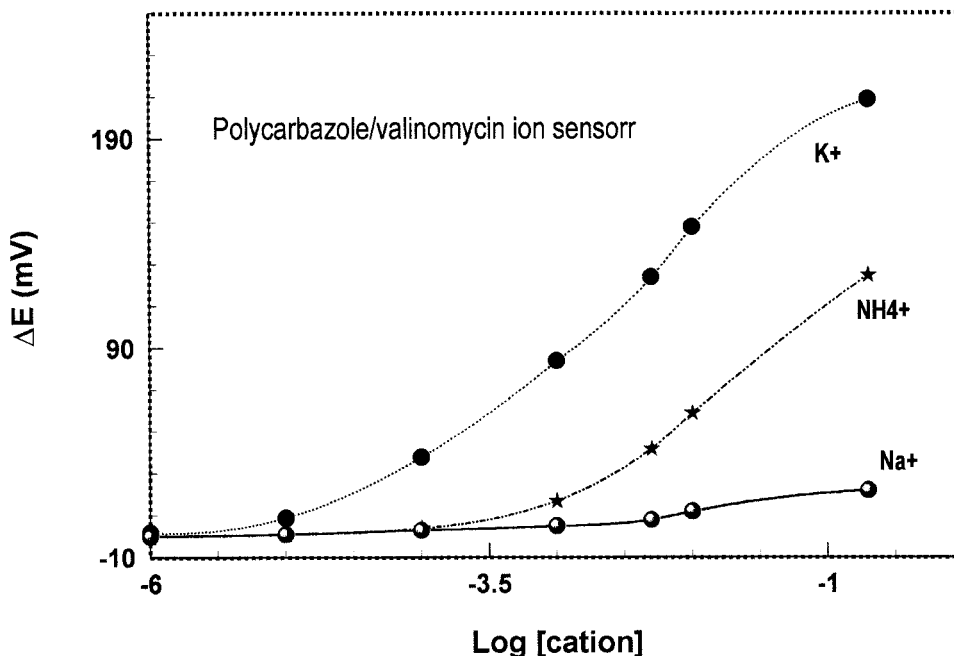


Figure 9 The calibration curves to K^+ , Na^+ , NH_4^+ ions of the polycarbazole/valinomycin ion sensor in 0.01 M Tris-HCl buffer, pH 7.0, at 25°C.

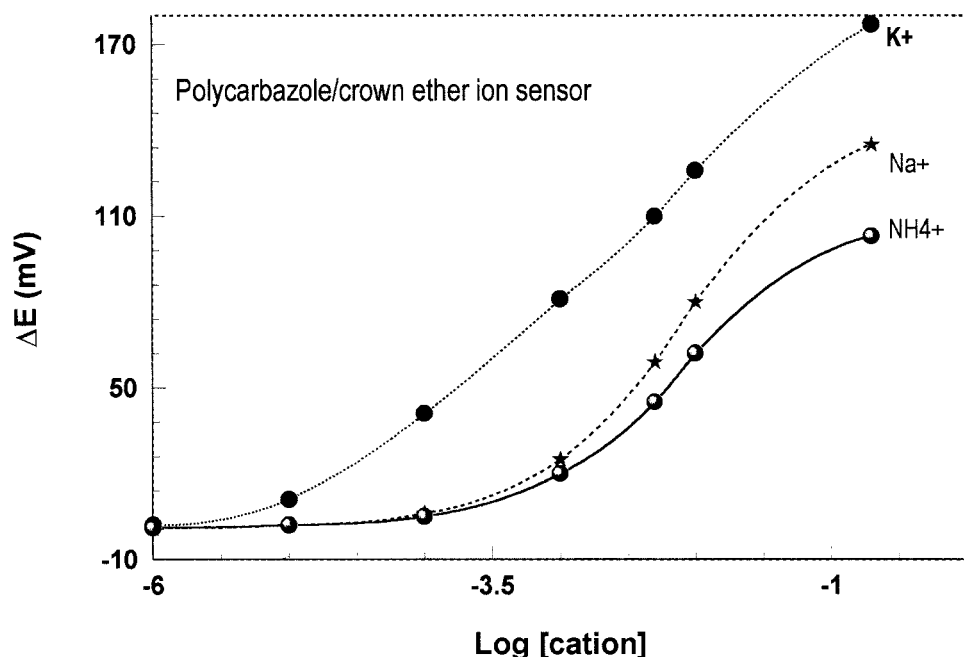


Figure 10 The calibration curves to K^+ , Na^+ , NH_4^+ ions of the polycarbazole/dibenzo-18-crown-6 ion sensor in 0.1 M Tris-HCl buffer, pH 7.0, at 25°C.

the doping/de-doping reactions, and accordingly, a positive charge is not created in the polymer and is converted into neutral polymer, as evidenced by the electrochromic activity of the polymer. We observed that the relative capability of exchanging the ClO_4^- ion is on the order of $Cl^- > Br^- > NO_3^- > CH_3COO^-$. The interstices of neutral polymer may be occupied by any other cations/anions, depending on the geometry of polymer interstices and ions. Thus, neutral polymer is analogous to organic neutral carriers,

which form host-guest linkage and have been extensively studied in the construction of ion-selective electrodes. The mechanism for yielding Cu^{2+} ion sensing of neutral polymer-modified electrode may be explained from these arguments. On the other end, when the oxidized polymer with doped anion is used in the construction of neutral carrier-incorporated PVC matrix membrane, the dipolar potential developed across Pt/polymer, and polymer/PVC interfaces is maintained for a relatively longer time, since the PVC

Table I Life Times and Drifts in Baselines of a Typical Ion Sensor

Day	Polycarbazole			Polyindole		
	Detection Limit (M)	Slope (mV/decade)	OCP (mV) ^a	Detection Limit (M)	Slope (mV/decade)	OCP (mV)
a. Valinomycin-based ion sensor						
1	5.0×10^{-6}	59	460	6.0×10^{-6}	59	163
2	6.4×10^{-6}	57	452	6.0×10^{-6}	58	160
5	7.3×10^{-6}	56	441	8.0×10^{-6}	58	155
10	1.2×10^{-5}	56	420	1.0×10^{-5}	58	142
b. Dibenzo-18-crown-6-based ion sensor						
1	6.8×10^{-6}	54	511	7.0×10^{-6}	53	30
2	7.4×10^{-6}	53	507	7.8×10^{-6}	52	22
5	8.1×10^{-6}	53	496	8.3×10^{-6}	52	10
10	1.3×10^{-5}	52	465	1.0×10^{-6}	52	-5

^a OCP, open circuit potential.

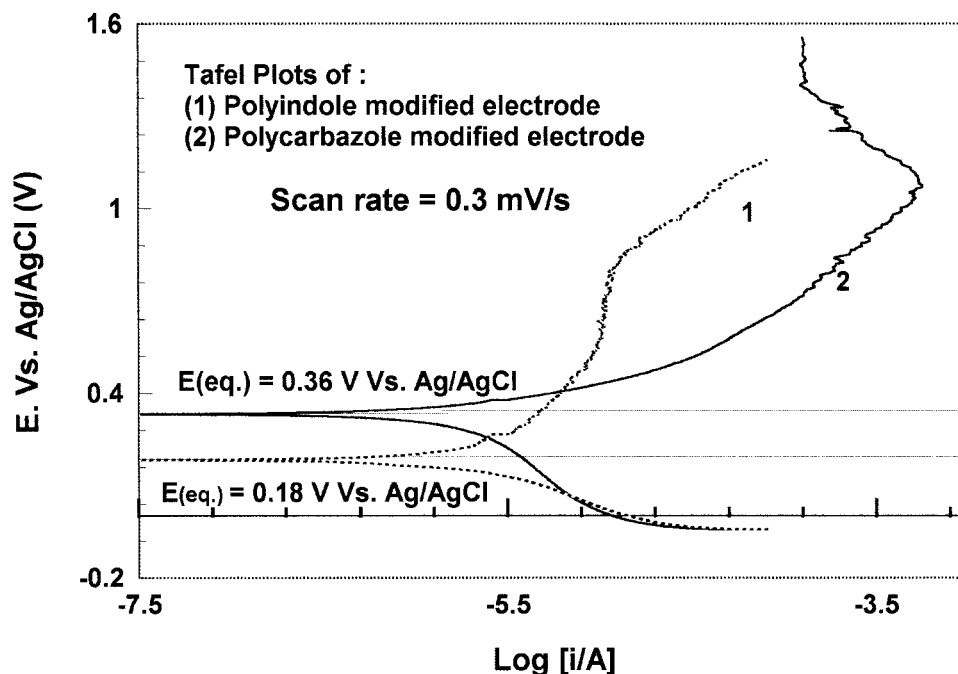


Figure 11 Tafel plots of polyindole- (1) and polycarbazole- (2) modified electrodes recorded in dichloromethane containing 0.1 M TBAP at 25°C.

matrix prevents the leaching out of the hydrophobic perchlorate ion, which is a carrier of cations. The mechanism for yielding the Nernstian response of the sensor having interfaces generated using bilayer film, as described above, is attributed to (i) redox behavior of the conducting polymer films that contribute by stabilizing the charge exchange process at interfaces and by establishing the thermodynamic equilibrium electrode potential at the (polycarbazole or polyindole/PVC) interface (ii) better stability of the polymer film having doped hydrophobic anions (ClO_4^-), leading to reproducible baseline potential recovery. The plasticized PVC film is prepared over the oxidized and anion-doped polycarbazole/polyindole. Although polycarbazole/polyindole has no site for cation exchange, the oxidized polymer together with dissociated and relatively hydrophobic anions contribute to maintaining a stable potential difference across the polycarbazole/polyindole/PVC interface.

Another way for maintaining constant dipolar potential across the polymer/PVC interface is incorporation of ion exchanger within the polymer interstices as described by Momma et al.⁶ which establishes a symmetric cell configuration (ion-in, ion-out), since the presence of ion exchanger, that is, polysulfonate behaves as a K^+ exchanger with

least selectivity and the neutral carriers (valinomycin/dibenzo-18-crown-6) are a relatively selective K^+ ion exchanger. Even after incorporation of polysulfonate, the dipolar potential decays in a regular pattern⁶ associated with leaching out of the ion exchanger from the polymer matrix. The present ion-selective electrodes described in this work avoid the application of any ion exchanger and maintain relatively stable dipolar potential compared to solid-state the K^+ sensor described by Momma et al.,⁶ which shows the advantage of the present design. Based on the approach to design solid-state, ion-selective electrodes of the present configuration, other similar ion-selective electrodes have been designed using doped polypyrrole⁷ and poly(3-octylthiophene).⁸⁻¹⁰ The performance of the present design as given in Table I supercedes the earlier developed solid-state, ion-selective electrode in terms of stability and reproducibility of OCP for a longer time, which is mainly attributed to the relatively high hydrophobicity of the polymer film, with doped anion having been synthesized in a nucleophilic reagent-free solvent (dichloromethane). The polycarbazole-based K^+ ion initially shows better slope and sensitivity, as defined by detection limits; however, relative deterioration of OCP with time is better when the polyindole layer was used

as a bridge between the Pt and PVC layer (Table I). Additionally, the values of OCPs recorded using these two polymer-modified electrodes show that the magnitude of OCP for polycarbazole is greater (460; 511 mV) compared to the values recorded for polyindole (163; 30 mV). These thermodynamic equilibrium potential values follow the similar trend as recorded for the kinetically polarizable potential values as shown in Figure 11.

CONCLUSIONS

The electropolymerization of carbazole monomer in CH_2Cl_2 containing 0.1 M TBAP results in highly stable, electroactive-conducting polymer. The behavior of de-doped and doped polymer was studied. The de-doped polymer behaves as Cu^{2+} ion sensor, whereas doped polymer helps in the construction of the K^+ -selective electrode using valinomycin/dibenzo-18-crown-6-incorporated PVC membrane. The ion sensor was highly selective to K^+ , with extended linearity over almost five decades. A comparison of the potentiometric response physical structure and electrochemistry of polyindole and polycarbazole was made.

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