

Resistive-Type Humidity Sensors Based on PVP–Co and PVP–I₂ Complexes

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ABSTRACT: Poly(vinylpyrrolidone) films containing cobalt chloride or iodine were investigated to obtain information on their possible use as a humidity sensor element. FTIR and UV-VIS spectroscopies were used to characterize the PVP–I₂ and PVP–Co complexes. Infrared spectroscopy revealed a structural change of both shape and intensity of the carbonyl and lactam bands, indicating the formation of an ion-coordination polymer. The J – E curves for pure PVP, PVP–I₂, and PVP–Co films obey ohm's law at low voltages, deviate from the linear response at higher voltages, and finally display breakdown behavior. An increase in current density of the PVP matrix with iodine or cobalt doping is attributed to the formation of charge transfer complexes. The observed hysteresis of the I–V characteristics implies that there was some standing voltage in the film, which could be attributed to a disorientation of polar side groups of PVP. The electrical conductivities of the polymeric complexes were very sensitive to environmental humidity. An explanation of the humidity-sensing behavior of the PVP–I₂ and PVP–Co complexes is presented. © 2001 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 39: 459–469, 2001

Keywords: poly(vinylpyrrolidone); charge transfer complexes; electrical properties; humidity sensors; polymeric electret behavior

INTRODUCTION

The development of organic polymers with high electrical conductivity has opened up the possibility of new applications for polymers.¹ The most highly conducting polymers are polyacetylene, polyaniline or π -conjugated polymers, typified by poly-*p*-phenylene, polyphenylene vinylene, or polyphenylene ethynylene, doped with iodine or other dopants; such polymers can attain conductivities comparable to those of metals.^{2–8} These polymers, called Intrinsically Conducting Polymers (ICPs) become they can conduct electricity,

are characterized by a carbon backbone in which every second linkage between carbon atoms is made by a double bond. These materials have found limited applications owing to instability, irreproducibility, and lack of processability. Because of the large amount of double bonds, these polymers are very stiff and insoluble.

Electrical conductivity can be obtained in initially insulating polymer either by modifying the electronic structure of the polymer chain through doping with metallic ions or by filling the material with electrically conducting particles.^{9,10} Many studies have been directed toward understanding the role of dopant materials because the mechanical and physical properties of polymers can be tailored to a specific requirement by the admixture of a suitable dopant.

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The number of potential applications to which the use of metal-containing polymers can be considered include synthesis of conducting and semi-conducting polymers for applications in the area of magnetic materials,¹¹ sensors developments,¹² displays in electronic display panels,¹³ high-energy lithographic resists,¹⁴ lasers,¹⁵ electrocatalysis,¹⁶ photoelectrocatalysis,¹⁷ electrochromic devices,¹⁸ electroactive films,¹⁹ and electroluminescent devices.²⁰

The presence of a metal ion chemically bound to a polymeric matrix predetermines a series of interesting properties of metal-containing polymers (MCP), among which the electrophysical properties are of particular interest. In principle, the existence of metal ions in the polymer may lead to electroconductivity.

In addition to the patent literature, numerous publications have dealt with the polyvinylpyrrolidone structures as well as the complexes of these polymers with cobalt or iodine.^{20–24}

In this study charge transfer complexes obtained by complexation of poly(vinylpyrrolidone) (PVP) with iodine and cobalt were synthesized and characterized. The electrical and sensor humidity properties of the obtained complexes were investigated by conductivity measurements.

EXPERIMENTAL

Poly(N-vinyl-2-pyrrolidone) (PVP) was purchased from BASF ($M_v = 4.4 \times 10^4$). Iodine-doped PVP films were prepared by thermic reaction between PVP and I_2 . The PVP (1 mol based on monomer) was mixed intimately with 0.0772 mol of iodine and the mixture heated at 90 °C until no further decrease in thiosulfate-titrable iodine occurred. The obtained product, a red-brown powder, was readily prepared by solvent evaporation from methanol solutions of PVP (1.0% w/v). The complex PVP–Co was prepared via a melt reaction (170 °C) by the addition of the salt $CoCl_2$ to the PVP. The samples for carrying out the resistivity measurements were prepared by dispersing $CoCl_2$ in molten PVP (120 °C). The resulting mixture was stirred constantly during solidification to obtain satisfactory homogeneity. Before solidification, when the viscosity was suitable for avoiding the sinking of filler while still permitting flow, the mixture was poured into a disc-shaped die 16.0 mm in diameter and 9.0 mm thick. To avoid the formation of air bubbles, the mixture was pressed into pellets in an appropriate die. Silver

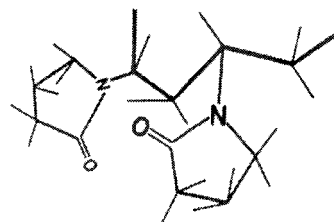
leaves were placed between the electrodes and the samples, ensuring good electrical contact.

The circuit used for DC electrical conductivity measurements was interfaced with a computer device and a Keithley 237 digital electrometer. The measurements were made at room temperature (25 °C). A voltage of 0–600 V was supplied to the samples, and the bulk resistance was measured after 2 min. Testing of the humidity response was carried out by using saturated salt solutions to provide a set of humidities ranging from 10 to 96%. The response of sensors to different humidities was measured with a Keithley 237 digital electrometer (applied AC voltage = 3V, $f = 1$ kHz).

UV-VIS spectra of iodine and cobalt-doped PVP membranes were recorded using a Shimadzu UV 2101 UV-VIS scanning spectrophotometer.

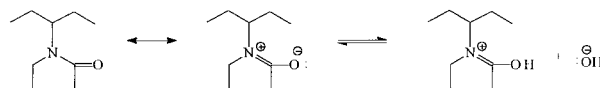
RESULTS AND DISCUSSION

Poly(vinylpyrrolidone) (PVP) is a vinyl polymer possessing planar and highly polar side groups due to the peptide bond in the lactam ring.²⁵ The structure of the PVP may be considered as:



PVP presents a lactam unity without any symmetry as well as a nitrogen atom with planar configuration that may be favorable to the complex formation with small molecules in solution or same in the solid state.²⁶

It is well documented in the literature that, in the presence of hydrogen donors, the mesomerism of the peptide linkage in PVP is significantly shifted as in the following scheme:^{27,28}



The above characteristics of PVP turn the lactam unit into an active binding site to form charge-transfer complexes with a wide variety of molec-

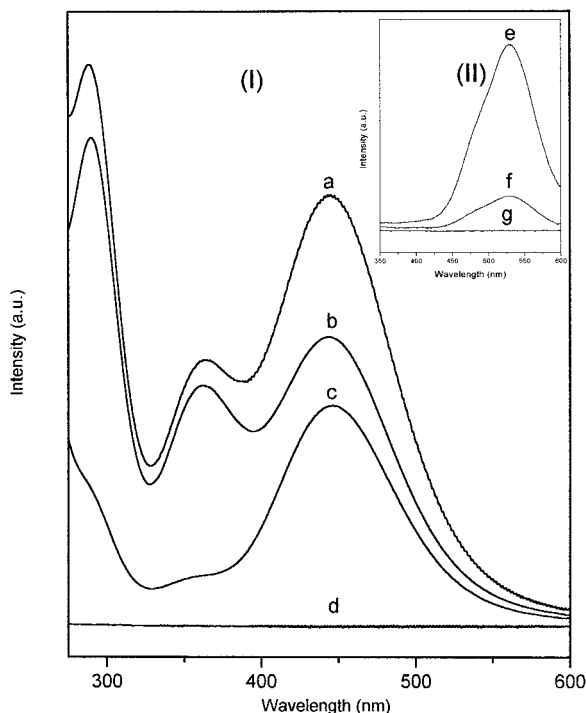


Figure 1. Absorption spectra of PVP-I₂ (I) and PVP-Co complexes (II) in methanol as solvent at 25°C. (I) Iodine concentration: 8.0×10^{-6} mol/L (a); 4.0×10^{-6} mol/L (b) and 2.0×10^{-6} mol/L (c). (II) CoCl₂ concentration: 4.0×10^{-6} mol/L (e); 0.90×10^{-6} mol/L (f), and pure PVP (d,g).

ular and ionic species, in the bulk state or in solution.^{29–36}

PVP forms a dark blue complex with cobalt, and it is known to form a red-brown complex with I₃⁻ under an iodide-rich condition at room temperature. The fact that PVP turns blue after addition of cobalt salt strongly suggests that Co, in the form of Co (II) ion, has a strong affinity for PVP.

The lactam groups in PVP are responsible for the UV-VIS absorption. Thus, the formation of PVP-I₂ and PVP-Co charge transfer complexes was studied by UV-VIS and fluorescence spectroscopies.

Figure 1 shows the visible and UV spectra of PVP as well as that of the PVP-I₂ and PVP-Co complexes. PVP exhibits no bands in the UV-VIS region studied, and the spectrum of iodine-doped PVP shows bands at 280 and 370 nm that may be attributed to the formation of charge-transfer complexes (CT). The band at 450 nm is due to molecular iodine.^{37–38}

The absorbance spectra of the PVP-Co complex has one maximum (λ_{\max}) at 529 nm (Fig. 1), and

this band may be associated with the coordination form of cobalt ion in the PVP matrix.³⁹

Figure 2 shows the relation between the absorbance of a complex and the concentration of added iodine or cobalt for PVP-I₂ and PVP-Co complexes, respectively. In each case, the absorbance approached asymptotically to a limiting value with increasing concentration of added iodine or cobalt. The saturation point may be interpreted as the maximum concentration of the ionic species (I₃⁻, I₅⁻, Co⁺²) that is bound to the lactam rings present in PVP.^{40,41}

Fourier-transform infrared (FTIR) spectra of PVP and PVP-I₂/PVP-Co complexes were determined to clarify the nature of the interactions between the polymer and the ionic species generated on the polymeric matrix. The influence of dopant on the vibrational spectrum of PVP can be seen in Figure 3. The complex formation between PVP and cobalt leads to lower carbonyl stretching frequency from 1653 to 1645 cm⁻¹, indicating that coordination occurs through the carbonyl groups. However, the complex formation between PVP and iodine leads to higher carbonyl stretch-

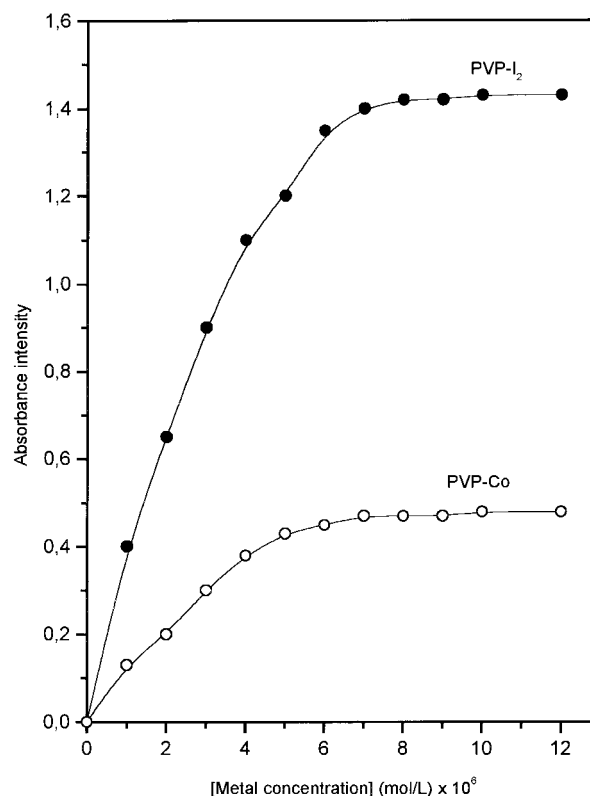


Figure 2. Dependence of absorbance at 280 nm on iodine (PVP-I₂) and at 529 nm for cobalt (PVP-Co) concentrations at 25°C.

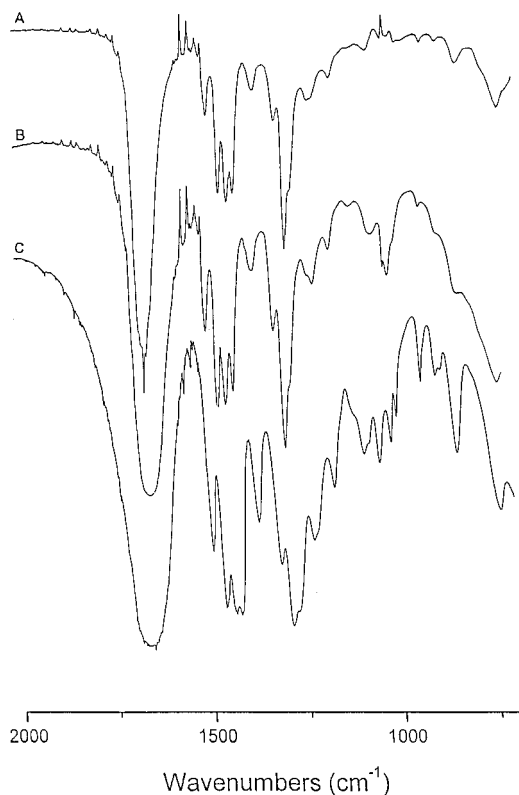


Figure 3. Infrared spectra (FTIR/ATR) of PVP (A), PVP-Co (B), and PVP-I₂ (C) films. The iodine and cobalt concentrations are 8.0×1.0^{-6} mol/L, respectively.

ing frequency from 1653 to 1671 cm^{-1} . The broadness and shift to lower frequencies may be due to the higher concentration of coordinated lactam units.⁴²

The stretching motion corresponding to the C=N of lactam groups presents in PVP (1425 cm^{-1} , Fig. 5) visibly undergoes profound changes with the iodine or cobalt addition to the polymeric matrix.

This observation indicates that the complexation of iodine or cobalt with PVP takes place not only at the carbonyl groups of the lactams but also involves the C—N bond, which results in an appreciable decrease in the conjugation of the peptide linkage and loss of partial double bond character of the C—N bond.⁴³

The sorption and diffusion of water vapor in polymeric membranes is a subject of great technological importance for the design of polymeric humidity sensors.^{44,45}

For a plane polymer sheet, the mechanism of water vapour transport in the PVP-I₂ or PVP-Co complexes may be described by the Fick's second law⁴⁶:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

where C represents the concentration of the water vapor at distance x from the contacting surface and D represents the diffusion coefficient.

If the initial concentration, C_0 , of the water vapor is constant at the surface and reaches a value C_{max} at equilibrium, then the solution of eq. (1) gives:⁴⁷

$$\frac{C - C_0}{C_{\text{max}} - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{n=\infty} \frac{(-1)^n}{2n+1} \times \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{L^2} \cos \frac{(2n+1)\pi x}{L} \right] \quad (2)$$

where n is an integer.

The mass M , of water vapor taken up by the polymer as a function of time, is obtained by integrating eq. (2) over the entire thickness, L , for obtaining:

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left[\frac{-D(2n+1)^2 \pi^2 t}{L^2} \right] \quad (3)$$

where M_t is the mass of water vapor sorbed at time t , M_∞ is mass sorbed at equilibrium time, and the L is the initial thickness of the polymer film. Sorption results before attainment of 55% equilibrium saturation have been fitted to the empirical relationship^{48,49}:

$$\frac{M_t}{M_\infty} = Kt^n \quad (4)$$

where M_t/M_∞ is the fractional water uptake by the polymer, K is a constant characteristic of the system, and n is an exponent characteristic of the mode of transport of the penetrant.

Figure 4 present the dynamic swelling curves for the PVP, PVP-I₂ and PVP-Co systems. As is evident from the data in Figure 4, the level of water uptake decreases with the cobalt or iodine doping.

In case I or Fickian transport, where the rate of diffusion is much less than the rate of relaxation, $n = 0.5$; in case II transport, where diffusion is very rapid compared to rate of relaxation, $n = 1$. Non-Fickian systems lie between case I and case

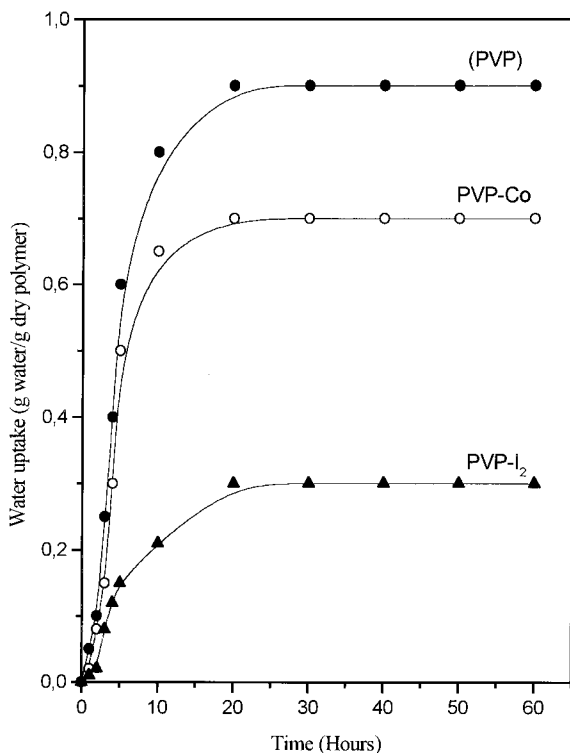


Figure 4. Water uptake per dry polymer weight (g/g) at room temperature (298 K) for PVP, PVP-Co, and PVP-I₂ systems. Water activity (a_w) = 1.

II, and n takes an intermediate value between 0.5 and 1.

Table I shows the n values for water vapor sorption of PVP-I₂ and PVP-Co complexes at room temperature (25 °C). In general, the results indicate Fickian behavior independently of the iodine or cobalt concentrations, indicating that the chain relaxation is not important as the phenomenon of penetrant transport in the swelling/deswelling processes.

The mathematical relation to calculate D at long diffusion times is important for polymer membrane applications under continuous water vapor exposure conditions. The relation to calculate long-term diffusivity can be deduced from eq. (3) to give:

$$\ln\left(1 - \frac{M_t}{M_\infty}\right) = \ln\left(\frac{8}{\pi^2}\right) - \frac{D\pi^2 t}{L^2} \quad (5)$$

Thus, according to eq. (4), the plot of $\ln(1 - M_t/M_\infty)$ as a function of t should be linear at long diffusion times, and slopes of these lines are proportional to diffusivity. The results are given in

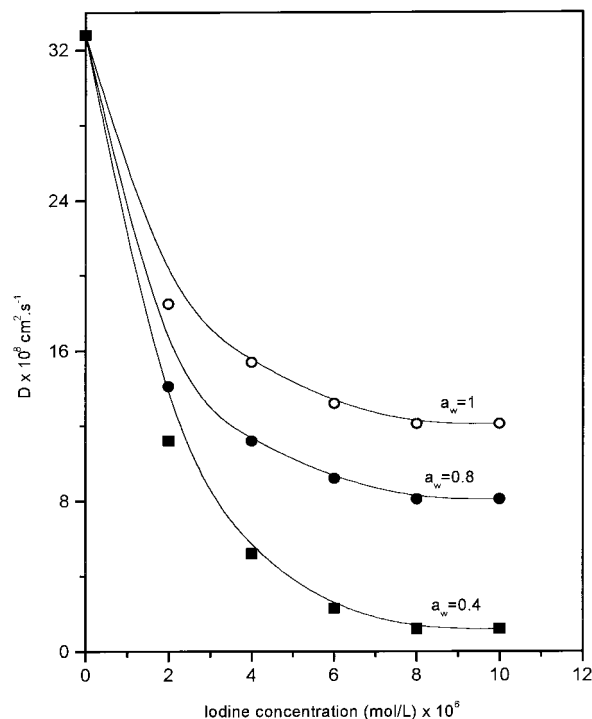


Figure 5. Dependence of water vapor diffusion coefficients on the iodine concentration of PVP matrices at 25°C.

Figures 5 and 6. The water diffusion coefficients decreased with increasing metallic ions in the PVP matrix, indicating that the motional freedom of the water molecules becomes more restricted.

Figure 7 depicts the amount of water absorbed into PVP and PVP-I₂/PVP-Co complexes, as a function of relative pressure at room temperature. As it is evident from the data displayed in Figure 7, the PVP matrix is a much more hygroscopic polymer than PVP-I₂ or PVP-Co complexes. It is reasonable to suppose that iodine or cobalt molecules may occupy the interstitial sites between the polymer chains of the amorphous

Table I. Water Sorption Data n Value of the PVP-I₂ and PVP-Co Complexes at Room Temperature (25 °C)

Metal Concentration (mol/L × 10 ⁶)	$n_{\text{PVP-Co}}$	$n_{\text{PVP-I}_2}$
0	0.38 ± 0.075	0.45 ± 0.090
2	0.25 ± 0.051	0.51 ± 0.110
4	0.36 ± 0.060	0.47 ± 0.102
6	0.29 ± 0.037	0.39 ± 0.087
8	0.36 ± 0.034	0.46 ± 0.075

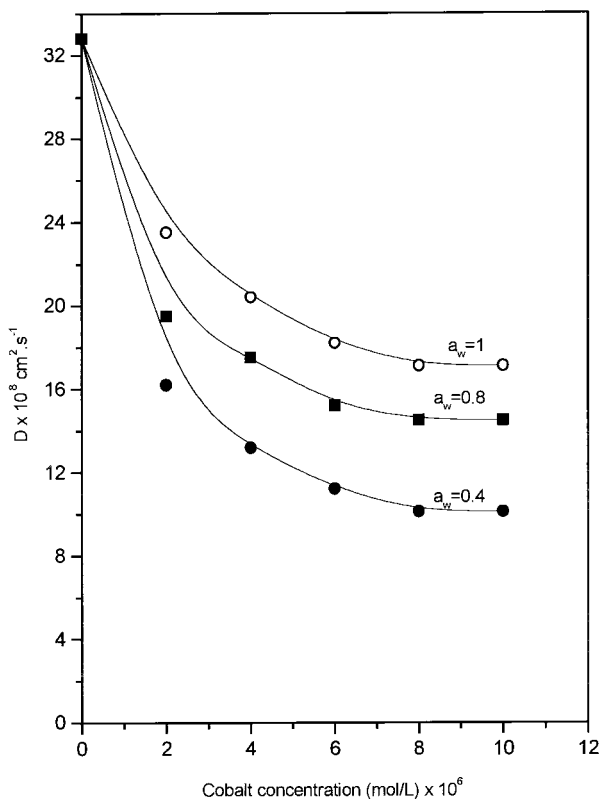


Figure 6. Dependence of water vapor diffusion coefficients on the cobalt concentration of PVP matrices at 25°C.

phase and link them with some type of bonds due to charge transfer processes between the iodine (or cobalt) and the lactam groups of the poly(vinylpyrrolidone) molecules.

The exponential increase of the water sorption with increasing water activity, a_w , may be a result of a plasticization effect of sorbed water on the polymeric systems. The lower a_w shoulder observed in the PVP isotherm has been attributed to the polymer transition from the glassy to the rubber-like state.⁵⁰ However, at low a_w , the polymeric complexes do not exhibit an initial shoulder. The most likely explanation is due to filling an unrelaxed hole free volume frozen in glassy PVP with absorbed water.

The current density-electric field characteristics (J - E) of PVP, PVP-I₂, and PVP-Co films measured at room temperature (25 °C) and under vacuum (10^{-5} mmHg) are shown in Figures 8–10. For all J - E measurements, the current density increased with increasing applied voltage. In particular, the J - E curves for all of the films obey ohm's law at lower voltages, deviate from the linear response at higher voltages and finally dis-

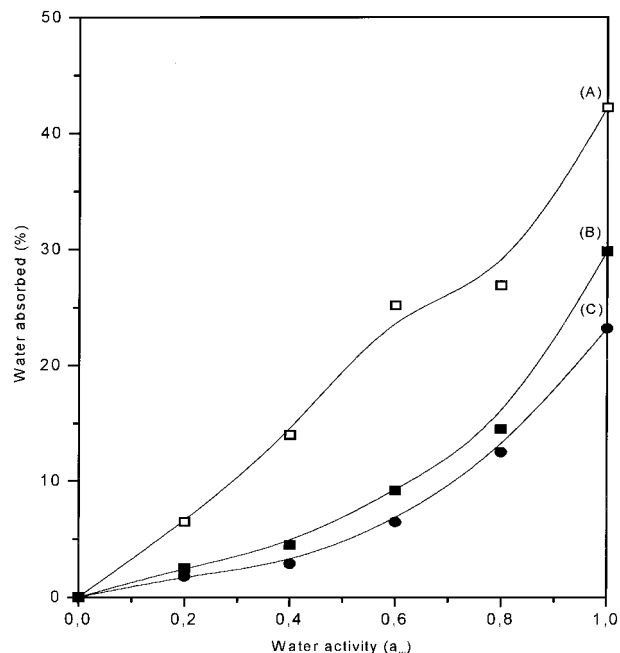


Figure 7. Water vapor absorption isotherms for PVP (A), PVP-I₂ (B), and PVP-Co (C) complexes at 25°C.

play the breakdown behavior. A much larger current, by an average of one more order of magnitude, has been observed for the polymeric com-

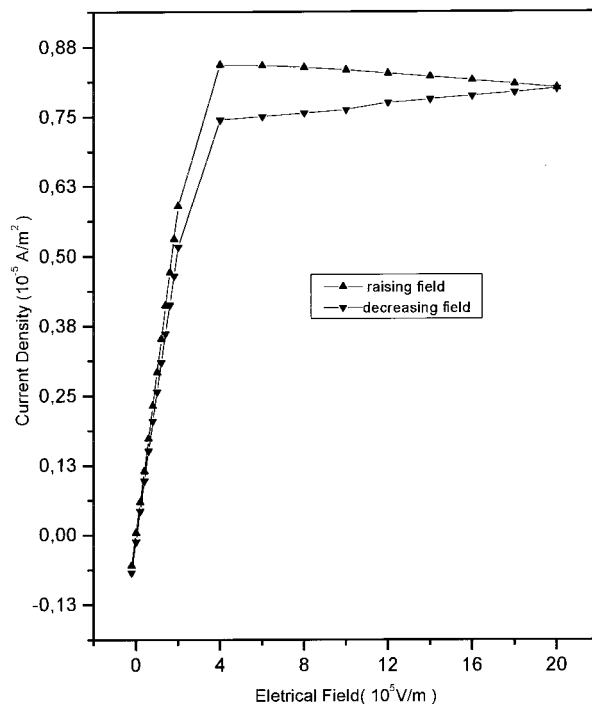


Figure 8. J - V characteristics of pure PVP at 25°C.

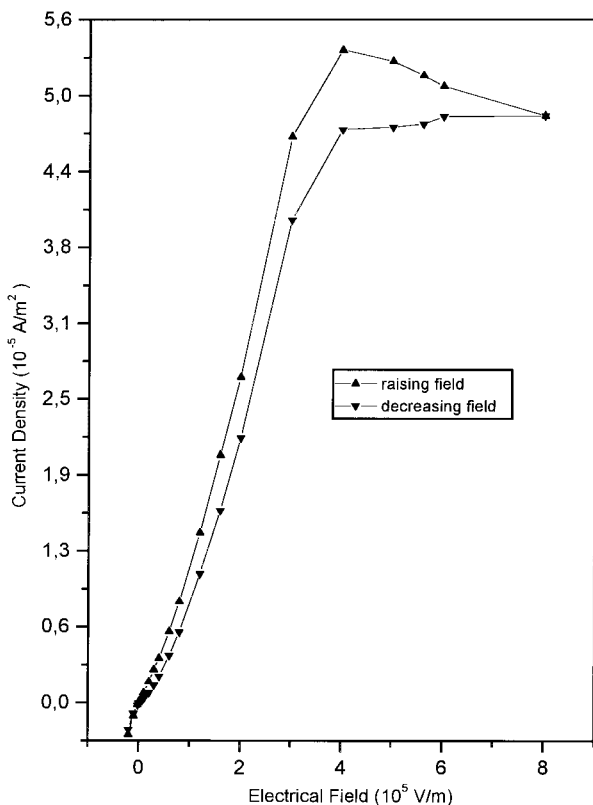


Figure 9. J-V characteristics of the PVP-I₂ complex at 25°C. Iodine concentration in the film: 8.0×10^{-6} mol/L.

plexes relatively to the PVP matrix. The increase in current on iodine or cobalt doping may be attributed to the formation of charge transfer complexes. The observed hysteresis of the I-V characteristics implies that there was some standing voltage in the film, which could be attributed to a disorientation of polar side groups of PVP.^{51,52}

At higher electric fields, the current density J can be considered to be related to the applied field E by the following expression:⁵³

$$J = J_0 \{ e^{[q(E-IR_b)]/nkT} - 1 \} \quad (6)$$

where J is the current density, J_0 is the reverse saturation current, and n is the ideality factor.

The linear relationship between $\log J$ and the electrical field (Figs. 11–13) in the low voltage region suggests the formation of a Schottky barrier. The slope of the straight line, corresponding to the low voltage region in Figures 11–13, yields the ideality factor (n). The obtained n values of 5.64 (PVP), 1.27 (PVP-Co) and 1.34 (PVP-I₂) indicate that the systems are nonideal showing n

> 1 . The n values obtained in this work may be attributable to the recombination of electrons and holes in the depletion region, and also to the increased effect of the diffusion current on increasing the applied voltage.⁵⁴

Electret behavior of poly(vinylpyrrolidone) (PVP) has been studied in detail, but no work has been reported on the effect of iodine or cobalt doping on the charge storage by PVP complexes.⁵⁵

The presence of iodine or cobalt in the PVP matrix may favor homocharge. The dopants may reside at the amorphous/crystalline boundaries and diffuse preferentially through the amorphous regions forming charge transfer complexes (CTCs), or it may exist in the form of molecular aggregates between the polymer chains. The possibility of the formation of CTCs reduce the barrier at the amorphous/crystalline interfaces and provide conducting paths for the charge carriers through these boundaries. Such phenomena would increase the mobility of carriers during polarization, and hence, would not favor the carrier localization into traps. However, if the iodine or cobalt forms molecular aggregates, then the motion of carriers would be impeded and the

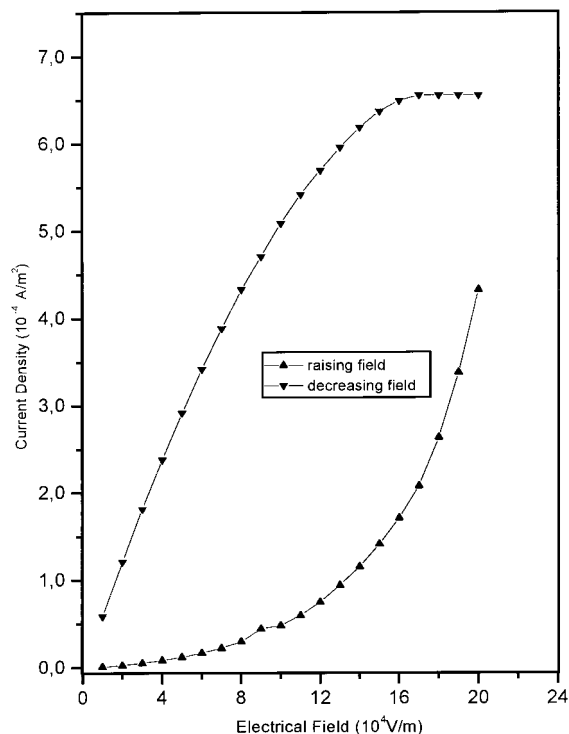


Figure 10. J-V characteristics of PVP doped with cobalt at 25°C. CoCl₂ concentration in the film: 8.0×10^{-6} mol/L.

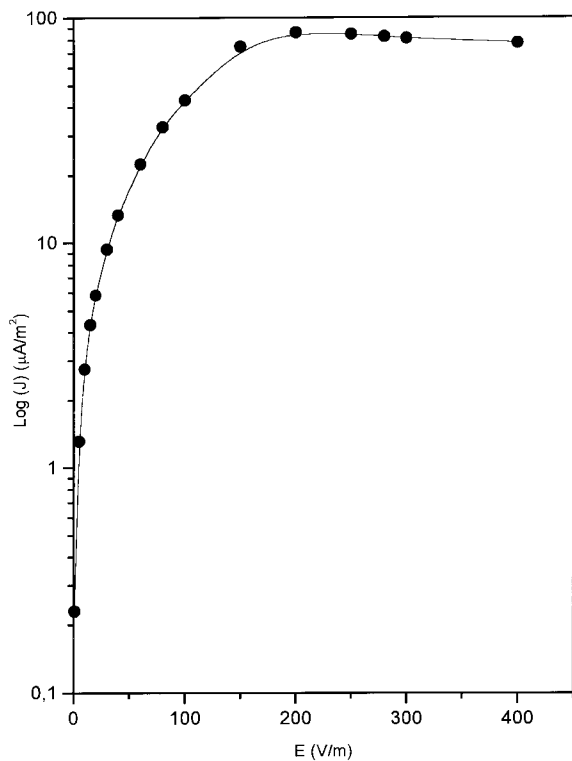


Figure 11. The current density–electric field characteristics of the PVP film at 25°C.

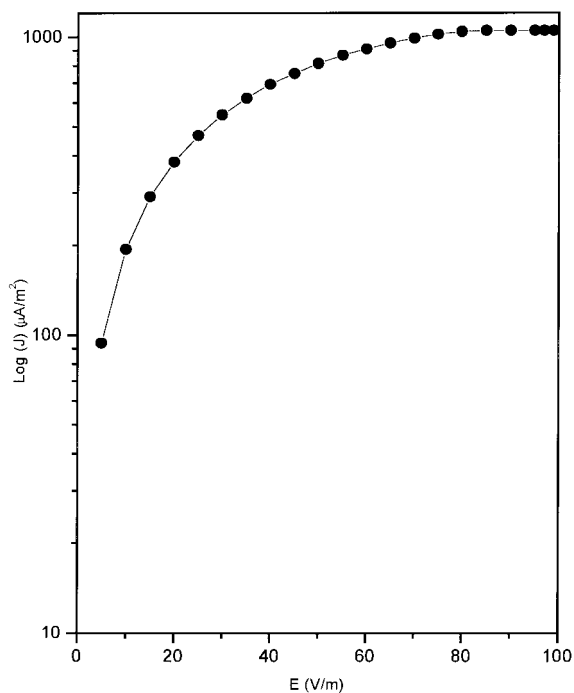


Figure 13. The current density–electric field characteristics of the PVP–Co film at 25°C.

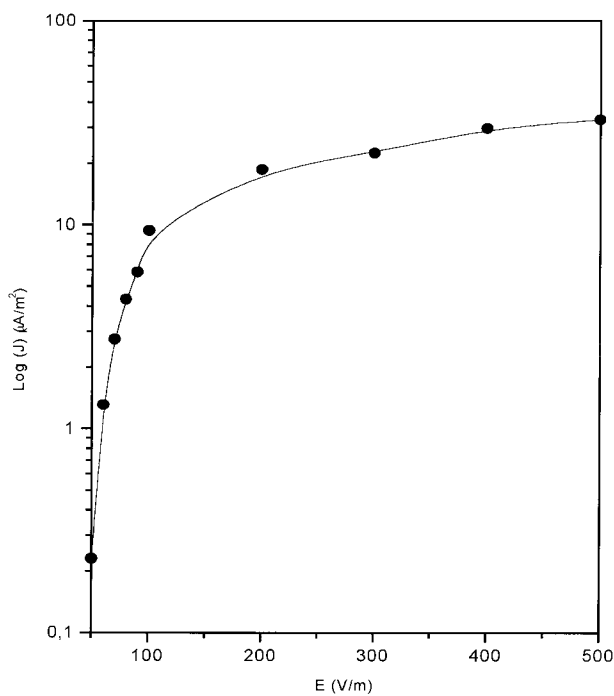


Figure 12. The current density–electric field characteristics of the PVP–I₂ film at 25°C.

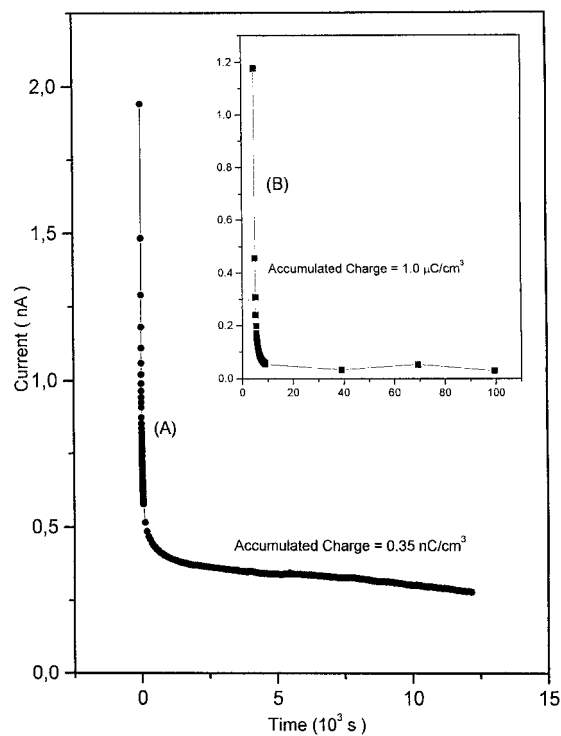


Figure 14. Discharge current characteristics for PVP–I₂ (A) and PVP–Co (B) complexes at 25°C.

charge storage capacity of the sample will increase.^{56,57}

The polymeric complexes PVP-I₂ and PVP-Co were found to possess electric properties (Fig. 14). The estimation of the value of the bulk charge of the samples from the discharge current on a series of standard resistances give values on the order of 0.35 nC/cm³ and 1.0 μC/cm³ for PVP-I₂ and PVP-Co, respectively.

Figure 15 shows how the conductivity varies with the humidity for the PVP-I₂ and PVP-Co complexes at room temperature (25 °C). An abrupt increase in the conductivity is observed for the PVP-I₂ and PVP-Co complexes, compared to the PVP matrix, at higher relative humidity of the environment. This result indicates that the conductivity of the PVP-I₂ and PVP-Co sensors can be classified as ionic, in which the charge carriers are formed during electrolytic dissociation of the iodine or cobalt present in the PVP matrix.⁵⁸

Figure 16 exhibits the impedance of PVP-I₂ and PVP-Co sensors in the humidity region of 10–100%. It may be noted that the impedance of the sensors changes from 10⁶–10¹⁰ over the whole

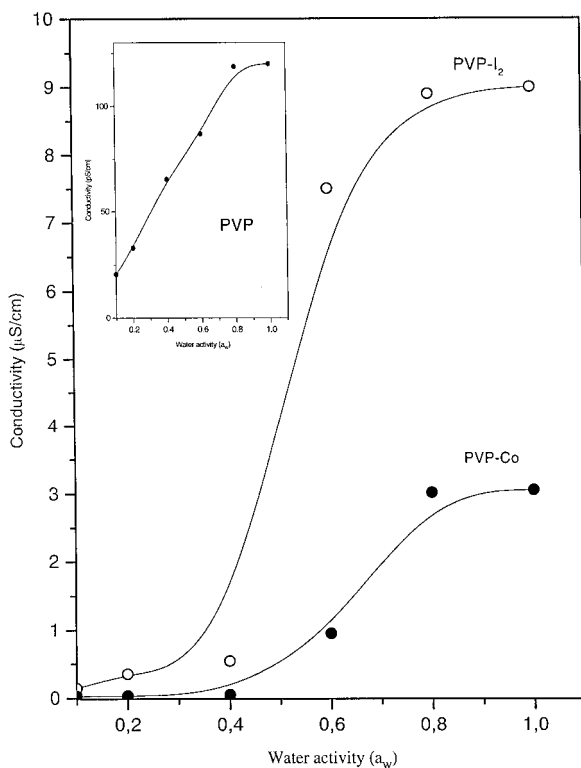


Figure 15. Dependence of the electrical conductivity of PVP-I₂ and PVP-Co complexes on the relative humidity at 24°C.

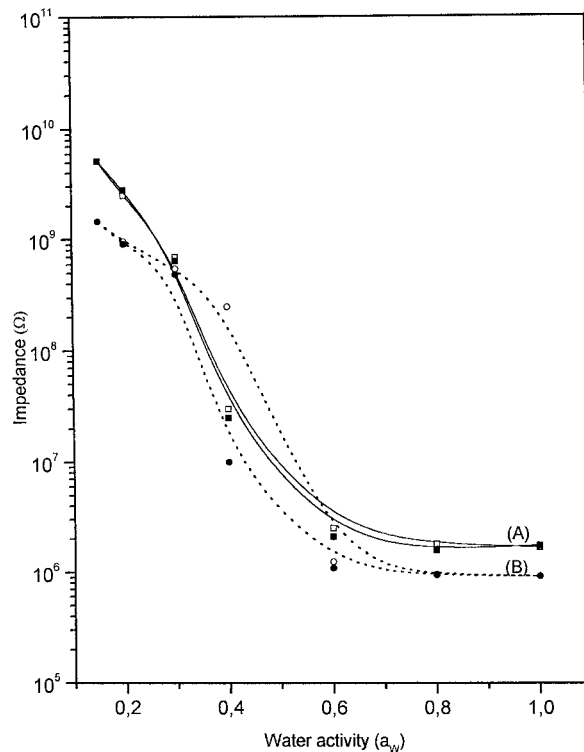


Figure 16. Impedance response to humidity of PVP-I₂ (A) and PVP-Co (B) based sensors at 27°C. (□/○) Adsorption, and (■/●) desorption.

humidity region and the hysteresis recorded is between 3–8% for the PVP-I₂ and PVP-Co complexes, respectively. These results indicate that PVP-I₂ sensor gives the best response to the environment humidities. However, the unexpected high hysteresis observed for the PVP-Co films is difficult to understand. The hydrophilic structure of PVP enables it to absorb water, and no high conductivity will be achieved from dissociated hydrogen protons of the lactam groups. It is supposed that the lactam structure of PVP plays an important role in achieving the low impedance after metal doping, which may be concerned with the formation of superconjugated orbitals or with charge transfer along ionic species formed by absorbed moisture.

CONCLUSIONS

Poly(vinylpyrrolidone) form charge transfer complexes with iodine and cobalt by the association of the lactam groups with the dopant metals. The conductivity of PVP-I₂ and PVP-Co complexes was found to increase with relative

humidity of the environment. The electrical properties of PVP-I₂ and PVP-Co complexes are sufficiently reproducible, and their sensitivity and response times measured with respect to water vapor meet the requirements for humidity sensor elements.

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