

DOPING BEHAVIOUR OF IONS ON POLYPYRROLE-COATED PLATINUM IN BINARY SOLVENTS - INFLUENCE OF TEMPERATURE AND COMPOSITION

M ARUNPRASAD, V ARAVIND AND M V SANGARANARAYANAN

Department of Chemistry, Indian Institute of Technology, Madras - 600 036 (India)

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The cyclic voltammetric study pertaining to the doping behaviour of chloride ions onto the polypyrrole-coated Pt electrode in water-dimethylsulphoxide system shows an un-usual dependence of the peak current on temperature and composition of the system indicating a transition from semiconductor to metallic behaviour.

Key Words : Conducting Polymers; Polypyrrole; Cyclic Voltammetry; Doping Behaviour; Binary Solvents; Dimethyl Sulphoxide; Peak Current; Conductivity

1 Introduction

The field of conducting polymers continues to be a frontier area of research in view of its potential applications as materials with good mechanical properties¹, functional electrodes² and electronic devices³. While the extent of doping is estimated from the magnitude of current, the influence of binary solvents at various temperatures has not hitherto been studied in this context.

In this article, we report a study pertaining to polypyrrole (Ppy) coated Pt when water-dimethylsulphoxide (DMSO) is employed as the medium for the doping of anions. It is demonstrated that at a particular composition of this system and at ambient temperatures, an unusual current response analogous to the 'semiconductor to metallic' transition is inferred from extensive cyclic voltammetric studies. Interestingly, such a temperature-dependent transition has till now been observed only in metal composites such as manganese pervoskites. While diverse combinations of binary solvents can be envisaged, water-DMSO system is especially attractive on account of its pronounced deviations from ideal behaviour. At low mole fractions, water-DMSO system behaves as a compound indicating the existence of a very stable trihydrate of DMSO⁴. It is of interest to mention that by fine-tuning the system parameters such as film thickness, solvent characteristics, nature of the dopant ions, polymer morphology etc, conducting

polymers can be endowed with properties customarily associated with metal oxides and metallic composites.

2 Experimental

The electrochemical studies were carried out using a platinum disc of 3mm diameter (Bioanalytical Systems BAS, USA) as the working electrode, while a platinum plate (2cm² area) served as the counter-electrode, the reference electrode being silver/silver chloride in a conventional one-compartment three-electrode cell assembly. All the solutions were de-aerated using nitrogen before use. The films were grown by electro oxidation of 0.1M pyrrole (Sisco Research Laboratories Ltd, India) in 0.1M potassium chloride (Sisco Research Laboratories Ltd, India) solutions by potentiostatic electropolymerisation as well as continuous cycling between 1000 mV to -1000 mV vs. Ag/AgCl using BAS 100A workstation. The film thickness was controlled and evaluated in the former method by the amount of charge passed and in the latter, from the number of potential cycles. The film thickness was estimated to be ca.400 nm using the procedure advocated by Diaz *et al*⁵. After the film was formed, it was rinsed thrice with 0.1M KCl in various compositions of water-DMSO mixtures. The experiments were carried out with thermostated (*Lauda ultra-kryostat*) and non-thermostated reference electrodes in order to verify whether the temperature dependence of the reference electrode potential affected the features of the cyclic voltammograms. In the case of thermostated reference electrode, the variation in its potential was corrected⁶ and was in

agreement with the experimental results in which reference electrode has not been thermostated. All the cyclic voltammetric studies were performed at 60-80% iR compensation. The first reduction scan was different from the subsequent re-oxidation – reduction cycles as is well known⁷ and the current reached saturation after 3-4 cycles. The peak current (i_p) and the corresponding potential (E_p) values were noted as follows: a) at constant compositions and varying temperatures (T) and b) at constant temperatures with different compositions. In both methods, the respective peak current and peak potentials differed by ca. 1 to 5%. While the current increased with scan rate till 1000mV/s, further increase led to broad and featureless waves and hence the scan rate was fixed at 1000mV/sec in order to obtain a significant magnitude of current.

3 Results and Discussion

The cyclic voltammograms of Pt/Ppy at various water-DMSO compositions containing 0.1 M KCl were recorded at a scan rate of 1000mV/sec. Interestingly, the anodic and cathodic peak currents which are a measure of the doping and de-doping of anions exhibits an unexpected dependence on the composition of DMSO by volume. (In the subsequent sections, the composition denotes the volume % of DMSO in the total volume). The anodic peak current ($i_{p,a}$) as a function of composition is shown in Fig. 1.

The fact that a maximum in current is observed at a specific composition (30% DMSO by volume) indicates the non-trivial role of DMSO. In view of this, the effect of temperature pertaining to 30% DMSO by volume was analyzed and a maximum in the anodic peak current (representing the doping process) is observed for the above composition at a temperature of 70°C (Fig. 2).

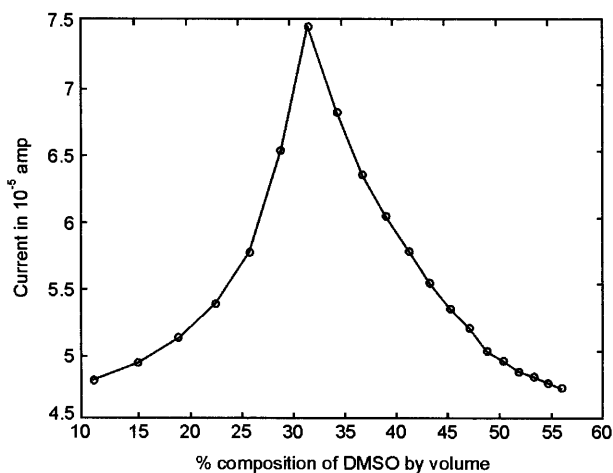


Fig. 1 The dependence of the anodic peak current ($i_{p,a}$) on the composition of DMSO at 27°C.

However, for all other compositions employed the anodic peak current increases with temperature monotonically as anticipated (cf. Fig. 3).

Fig. 4a depicts the voltammograms pertaining to 30% DMSO (by volume) at 70°C and 85°C. In comparison, Fig. 4b shows the cyclic voltammogram of Pt/Ppy in the presence of aqueous 0.1M KCl at 27°C wherein the magnitude of anodic peak current ($i_{p,a}$) is nearly four times smaller than that for 30% DMSO by volume at 70°C.

The anodic peak currents ($i_{p,a}$) for various temperatures pertaining to 30% DMSO by volume and the corresponding peak potentials ($E_{p,a}$) were noted so as to define the integral conductivity of the composite system as $K_p = i_{p,a}/E_{p,a}$. The above defined conductivity K_p represents the entire system and not the conductivity of the polymer matrix. A plot of K_p vs T is shown in Fig. 5 and a maximum in conductivity occurs with

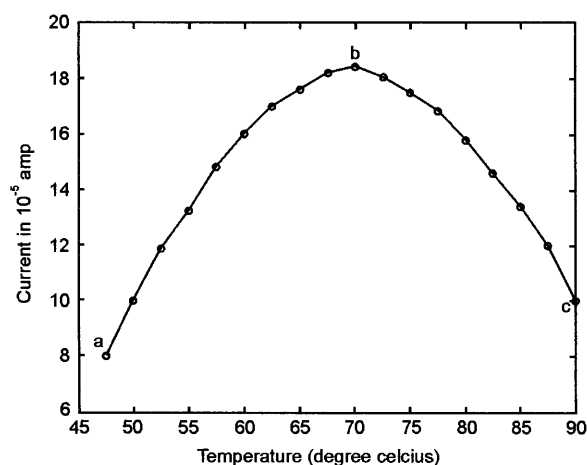


Fig. 2 The dependence of the anodic doping current ($i_{p,a}$) on temperature for 30% DMSO by volume

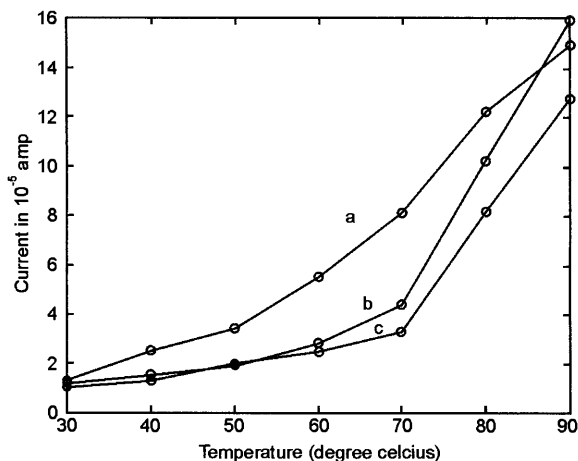


Fig. 3 The variation of the doping current with temperature for a) 50% b) 40% and c) 20% composition of DMSO by volume

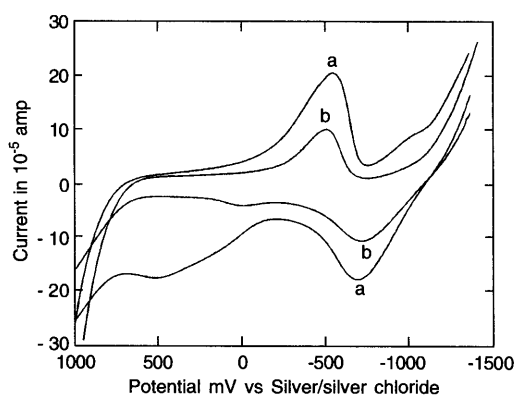


Fig. 4a Cyclic voltammogram of Ppy/Pt in water-DMSO system at 30% composition of DMSO by volume a) 70°C and (b) 85°C at the scan rate of 1000 mV/s

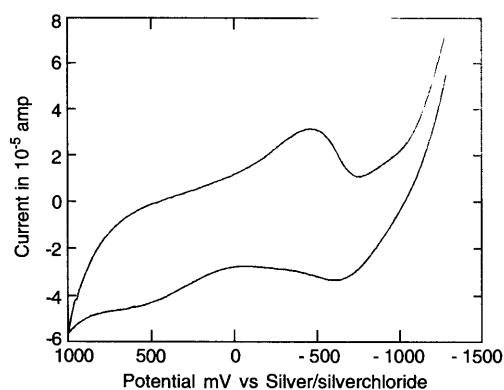


Fig. 4b Cyclic voltammogram of Ppy/Pt in aq 0.1 M KCl at the scan rate of 1000 mV/s at 27°C.

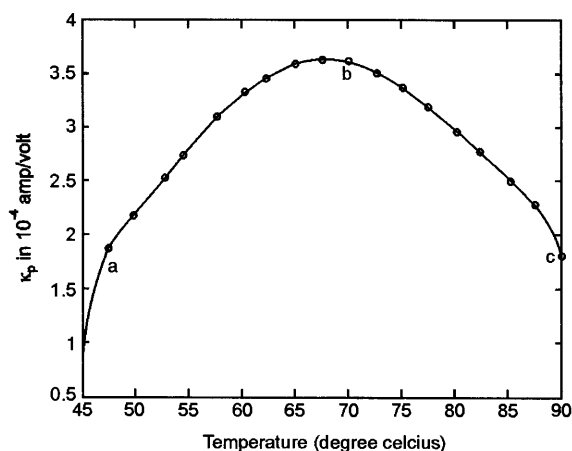


Fig. 5 Influence of temperature on the doping conductivity K_p at the peak potential for 30% DMSO by volume. Segment a-b represents a semiconductor-like behaviour, while b-c denotes the metallic nature, b being the temperature at which the transition occurs

positive and negative temperature coefficients on its either side. The anodic peak potentials shifted to less negative values with increase in temperatures while the cathodic potentials became more negative. However, in both cases, the magnitude of the change is ca. 50-100 mV hence the equivalence between current and conductivity is inferred and consequently, the location of the maximum in current may be identified with that pertaining to the conductivity!

Since the sign of the slope of the conductivity vs temperature plot is indicative of semiconducting and metallic properties, the doping behaviour in the system Pt/Ppy in water-DMSO containing KCl as the electrolyte may be considered as exhibiting a semiconductor-like behavior between 45°C - 70°C and metallic nature between 70°C - 90°C (denoted as the regions a-b and c-d in Fig. 5). The temperature at which this transition occurs (T_{smt}) is ca. 70°C.

The foregoing observations indicate that the peak current pertaining to a specific composition exhibits a maximum at $T_{smt} = 70^\circ\text{C}$. Before we investigate the origin and consequences of the behaviour, it is imperative to decipher the influence of factors such as film thickness, potential drop, dielectric effects etc as well as discount several other factors such as resistances and capacitances associated with various components of the system which might have caused the observed phenomenon.

3.1 System Parameters and Equivalent Circuit Representation

The role of the film thickness, potential drop between the working and reference electrodes and the pre-treatment of the electrode find importance in the analysis. In the experimental protocol employed here, the film thickness was controlled by the number of potential cycles and T_{smt} pertains to the film thickness of ca 400 nm. While the thickness of the film influences the location of the current maximum, its occurrence *per se* is not altered; further, the surface-bound and the diffusion-controlled behaviour of the cyclic voltammograms is also affected by the film thickness⁸. The potential drop within the film is assumed to be linear, since the occurrence of T_{smt} refers to a specific composition of the system and the peak potentials are effectively constant and independent of temperature. The experiments were performed with 60-80% iR compensation, thus minimizing the ohmic overpotential and till 80% iR compensation, the circuit remained stable (BAS 100A workstation with the positive feed-back circuit). The dielectric permittivity depends upon concentration *vis a vis* composition; since the observed phenomenon refers to 30% DMSO by volume, the dielectric permittivity is constant. (In the case of water-DMSO, the excess static dielectric permittivity shows

a maximum at 0.33 mole fraction of DMSO in contrast to the observed behaviour here viz. 0.099 mole fraction of DMSO). The quantum chemical methods⁹ indicate that trihydrate and tetrahydrate 'supermolecules' of water-DMSO clusters form at 0.25 and 0.33 mole fractions of DMSO. Hence the electrolyte KCl seems to alter the composition at which these clusters are formed.

The equivalent circuit shown in Fig. 6 indicates that Pt electrode is in series with Ppy which in turn is in series with the appropriate binary system having 0.1M KCl as the electrolyte, while the counter-electrode terminates the other end. R_1 is the resistance associated with the working electrode while R_4 denotes that of the counter electrode. Since R_1 and R_4 are pure resistances, they can affect neither the occurrence nor the location of the T_{smt} . R_2 denotes the charge transfer resistance and the sign pertaining to its slope can neither reverse with respect to the temperature nor is there any literature evidence for this. The solution resistance R_3 depends upon the composition of the binary system; however it is constant at a given composition. Further, the capacitance term C_1 is associated with the adsorption of ions/dipoles which penetrate into the polymer film and its magnitude is negligible since these species entering the polymer matrix essentially aid in neutralizing the oxidized polymer (Ppy^+) along with partial adsorption on the platinum surface. Finally, the part of the circuit on which the current response of system can be attributed is as given in Fig. 6b.

The composition of the binary solvent and the temperature represent the two important variables of the system. In the present context, the current at various scanning potentials is a measure of the extent of doping and being a composite parameter, can not be partitioned

into individual contributions. Nevertheless, the observed pattern of variations can be interpreted taking into account, various operational factors in the system. For example, any mechanistic analysis substantiating the observations should incorporate the specificity associated with Cl⁻ and DMSO. Within the series, Cl⁻, Br⁻ and I⁻, the structure-breaking role of Cl⁻ upon water dipoles is more pronounced and is sensitive to temperature. However, the specificity of mole fractions and the effect of scan rate still need to be accounted for.

3.2 Influence of Scan Rate

The range of scan rates (v) leads to significant differences in the nature of the cyclic voltammograms. (viz diffusion controlled vs surface bound). A plot of $\log i_{p,a}/\log v$ is linear and yields a slope of 1 till 1000mV/sec and 0.6 at higher scan rates indicating that at scan rates lower than 1000mV/sec surface-bound voltammogram is noticed while diffusion-controlled voltammogram results at scan rates higher than 1000mV/sec. Scheme 1 depicts a plausible frame-work by which the influence of scan rates may be interpreted.

The doping of anions is visualized as a two-step process consisting of (a) transport of Cl⁻ ions from the bulk to the electrode/polymer interface and (b) its ingress into the film during the electro-oxidation of Ppy so as to maintain electroneutrality. At scan rates lower than 1000 mV/sec the steps (a) and (b) occur sequentially yielding a surface bound cyclic voltammogram. On the other hand, at scan rates between 1000-1500mV/sec, the transport of Cl⁻ ions is accelerated and the rate of adsorption on the polymer surface is slower which leads to the diffusion controlled

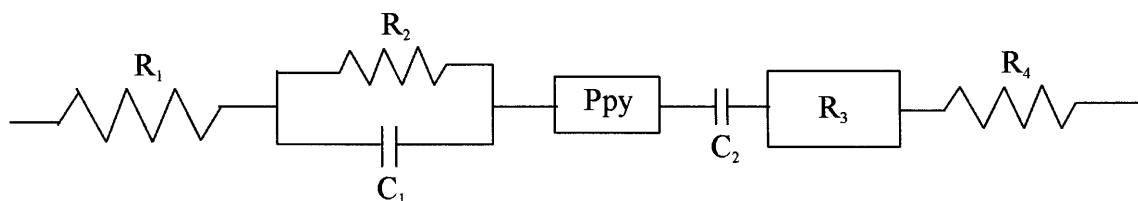


Fig. 6a Equivalent circuit representation of the system. R_1 denotes the resistance of the working electrode and R_2 the charge transfer resistance. R_3 is the solution resistance. R_4 is the resistance of the counter electrode. C_1 refers to interfacial capacitance. C_2 is the capacitance due to adsorption of ions/dipolar species at the polymer surface.

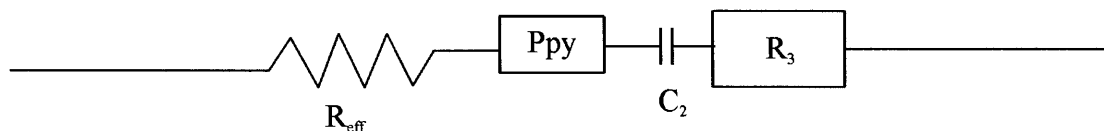
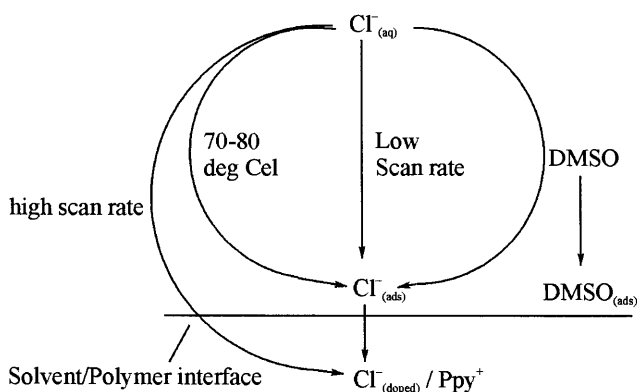


Fig. 6b Simplified equivalent circuit of the system. R_{eff} is the effective resistance comprising all the other components.



Scheme 1

Schematic representation of the doping process of polypyrrole-coated Platinum in the water-DMSO system containing KCl as the electrolyte

cyclic voltammogram. Thus, it is anticipated that two different types of cyclic voltammograms should arise depending upon whether the doping process is diffusion-controlled or surface-bound as illustrated in Scheme 1.

3.3 Role of Composition of the System

As mentioned earlier, water-DMSO system is especially interesting in view of the formation of clusters. Several characterization techniques such as iR spectroscopy, X-ray and small angle neutron scattering, differential scanning calorimetry¹⁰ indicate that strong hydrogen bonds are formed between water and DMSO, commencing from a mole fraction of 0.1 DMSO. Consequently, one may invoke the DMSO induced de-hydration of chloride ions. In this context, a recent study concerning the DMSO induced dehydration of intermembrane space pertaining to phospholipids deserves mention¹⁰.

The observed maximum in current vs. composition plot may be semi-quantitatively interpreted using considerations based upon adsorption of the species involved. It is well known that, at a given temperature, the magnitude of current (*i*) is proportional to the current function χ_{Cl^-} and is given by¹¹

$$i = \{n^2 F N v / RT\} \chi_{Cl^-} \quad \dots(1)$$

in the case of surface-bound Cl^- ions. In eq. (1), *n* is the number of electrons involved, *F* denotes the Faraday, *N*, the amount of surface bound species present, *v* being the scan rate. χ_{Cl^-} may also be represented as¹¹

$$\chi_{Cl^-} = \theta_{Cl^-} (1 - \theta_{Cl^-}) \quad \dots(2)$$

where θ_{Cl^-} refers to the surface coverage of chloride ions. At lower compositions of DMSO in the binary system albeit in the absence of KCl, χ_{DMSO} may be defined as

$$\chi_{DMSO} = \theta_{DMSO} (1 - \theta_{DMSO}) \quad \dots(3)$$

where χ_{DMSO} is the surface coverage of DMSO. Analogously, in the ternary system involving KCl, water and DMSO, χ_{Cl^-} is involved in the competitive adsorption and the current function $\chi_{Cl^-}^{ter}$ of the system is given by

$$\chi_{Cl^-}^{ter} = \theta_{Cl^-}^{ter} (1 - \theta_{Cl^-}^{ter})$$

where $\theta_{Cl^-}^{ter}$ is the surface coverage of Cl^- in the ternary system and $\chi_{Cl^-}^{ter}$ is given as

$$\chi_{Cl^-}^{ter} = \chi_{Cl^-} X_{Cl^-} \quad \dots(4)$$

wherein X_{Cl^-} the mole fraction of Cl^- ions and χ_{Cl^-} is given by eq. (2). Consequently, current becomes

$$i_{(ads, Cl^-)} \propto n_{Cl^-} / (n_{Cl^-} + n_{DMSO}) \quad \dots(5)$$

where *n* denotes the number of moles of the concerned species. We infer that an increase in the DMSO composition leads to a decrease in current according to the above equation.

While the above semi-quantitative approach incorporates adsorption and doping processes, the specificity associated with DMSO has not been taken into account. As pointed out earlier, DMSO induces de-hydration of chloride ions in the water-DMSO system. Thus, when the % composition of DMSO increases, the extent of de-hydration of chloride ions is enhanced since more Cl^- ions get rid of their solvation sheath thus yielding a higher current. Hence, a synergistic effect arises comprising (a) the extent of de-solvation dictated by the composition of DMSO wherein the current is directly proportional to the amount of DMSO and (b) competitive adsorption of chloride ions in which current is inversely proportional to the % composition of DMSO i.e. $i_{(ads, Cl^-)} \propto n_{Cl^-} / (n_{Cl^-} + n_{DMSO})$ [cf eq. (5) above].

The net effect is the occurrence of a current maximum observed at 30% DMSO in the present study. At lower DMSO compositions the ratio $n_{Cl^-} / (n_{Cl^-} + n_{DMSO})$ is nearly unity and the current is directly proportional to DMSO composition, giving rise to the ascending branch (Fig. 1). When the % composition of DMSO is higher, the maximum dehydration of Cl^- occurs and hence the net current is inversely proportional to the composition of DMSO leading to the decreasing region in the current. As a result of this interplay between the two processes, a maximum current is observed at a composition wherein the rate of de-solvation of chloride ions balances the rate of adsorption of DMSO. Such a composition-dependence can not be attributed to the variation in

excess static dielectric property of the medium since the maximum excess static dielectric constant occurs at a mole fraction 0.33 of DMSO¹².

3.4 Effect of Temperature

The de-solvation of Cl⁻ ion is a pre-requisite for its adsorption onto the polymer moiety and is a temperature-dependent phenomenon. It was observed that for all compositions excluding 30% DMSO, the increase of current with T was minor till ca 70° C and exhibited a sharper increase at higher temperatures. Fig. 3 depicts the effect of temperature for 50 %, 40% and 20% compositions as illustrative cases. This positive temperature coefficient is indicative of a semiconductor like¹³ behaviour (since the sign of $d i_{p,a} / dT$ is identical with $d K_p / dT$). However, at 30% DMSO composition, a negative temperature coefficient is noticed at T > 70 deg C (Fig. 4). Consequently, the temperature characterizing the semiconductor - metallic transition may be considered as occurring at ca 70°C in this study. It is of interest to note that a wide range of T_{smt} values has been reported for metal oxides and perovskites; for example T_{smt} in the case of $La_{1.5}Ca_{1.5}Mn_2O_7$ is -178°C¹⁴ while that pertaining to $Ce_2Mo_3O_9$ is 250°C¹⁵. In metal oxides, T_{smt} usually coincides with T_c , the ferromagnetic transition¹⁶. On the other hand, the present study provides the first example of a *composite system* (polymer modified electrode in binary solvents) exhibiting a semiconductor-metallic transition at ambient temperatures, which can be controlled by the method of preparation, thickness of the film etc.

The entire set of experiments was carried out using KBr and KI as the electrolytes which did not show the

above dependence on temperature thus indicating the specificity of Cl⁻. The solvation free energy of the halide ions becomes more and more negative in the order of I⁻ > Br⁻ > Cl⁻. The standard free energy of activation also becomes more negative from I⁻ to Br⁻ to Cl⁻, while a monotonic decrease of current with increase in the composition of DMSO is noticed in contrast to the behaviour shown by KCl.

Since a binary solvent containing a specific electrolyte has accomplished the interesting variation of current, it is a pointer to the role, thermodynamics of solution chemistry may play in the development of polymer modified electrodes and similar binary systems have immense potentialities in polymer modified batteries wherein the reduction of internal resistances is a central objective. Further, it is preferable to investigate diverse combinations of solvents and/or electrolytes rather than employing derivatives of pyrrole, since interesting properties of conducting polymers in general, get suppressed¹⁷ due to the incorporation of substituents. Further experiments employing electrogravimetry¹⁸ along with elemental analysis are in progress for obtaining more insights into the mechanism of the doping process.

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