

## ELECTROCHEMICAL BEHAVIOUR OF PRUSSIAN BLUE DEPOSITS IN PRESENCE OF SOME NON-AQUEOUS BACKGROUND SOLUTIONS

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The redox surface film of Prussian Blue (PB) is studied for its electrochemical properties in contact with non-aqueous solutions in acetonitrile (ACN), dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO). The Cyclic Voltammetric (CV) results are quite interesting as they tend to be irreversible in contrast to the behaviour in aqueous medium. Surface coverage from CV data showed an increase in the order of  $H_2O > ACN > DMF > DMSO$ . A similar trend is reflected in the facile intercalation/deintercalation processes of hydrated and solvated potassium ion computed from double potential step chronoamperometric studies. Diffusion coefficients and heterogeneous electron transfer rate constants are elucidated by processing I-t transients.

**Keywords:** Prussian blue films, non-aqueous electrolytes, kinetic parameters and current-time transients.

### INTRODUCTION

A vast literature is available on the electrochemistry of PB films in aqueous solutions [1-4]. The significance of the electrochemistry of PB films in non-aqueous electrolytes has been outlined in our earlier communications [5-7]. The strategies adopted by us earlier in the characterisation of PB films in non-aqueous electrolytes included the preparation of PB films by two distinct experimental approaches, one of them being conventional and the other involving the preparation from a modifying mixture which contained only  $H^+$  ions in the supporting electrolyte during surface modification. This study had led to the identification of partially protonated  $[K_{1-x}H_xFe^{III}Fe^{II}(CN)_6]$  or cation substituted  $[K_{1-x}M_xFe^{III}Fe^{II}(CN)_6]$ ;  $M = Na^+$  or  $Li^+$  species for the first time. Likewise, elucidation of diffusion coefficients and calculation of surface excess has been made possible from chronoamperometric and chronocoulometric studies performed on PB films in acetonitrile containing  $K^+$  or  $Na^+$  or  $Li^+$  ions. The coexistence of both hydrated and solvated unlike cations  $Na^+/K^+$  in the film has been formulated in yet another work by us.

The studies in aqueous medium offer wealth of information on the kinetics of chemical and electrochemical reactions [8]. However, altered interfaces are inevitable under several

circumstances from specified application point of view [9-11]. Such an altered interface for PB films (formed in aqueous solution), in addition to adding to the complexity offers scope for elucidation of kinetic parameters for the first time in the said media. Present communication pertains to the electrochemical experiments performed and methodologies adopted towards the elucidation of kinetic parameters for PB films in non-aqueous electrolytes such as ACN, DMF and DMSO and presentation of a comparative account along with the data obtained in aqueous electrolytes.

### EXPERIMENTAL

All chemicals used are of analytical grade and aqueous solutions are prepared from double-distilled water. CV and chronoamperometric experiments are carried out using BAS-100A (Bioanalytical System, USA). A three electrode cell assembly with glassy carbon (area  $0.07 \text{ cm}^2$ ) working electrode, platinum auxiliary electrode and  $Ag/AgCl/KCl$  reference electrode is employed.

Modification of GC electrode with iron hexacyanoferrate (i.e. PB) is achieved by cycling these electrodes between -100 to +100 mV at  $100 \text{ mVs}^{-1}$  in a clear solution containing 2 mM  $FeCl_3$ ,  $K_3Fe(CN)_6$  and 0.1 M KCl. The pH of the solution is adjusted with Analar HCl between 2-3. In order to maintain constant coverage throughout the experiments, film

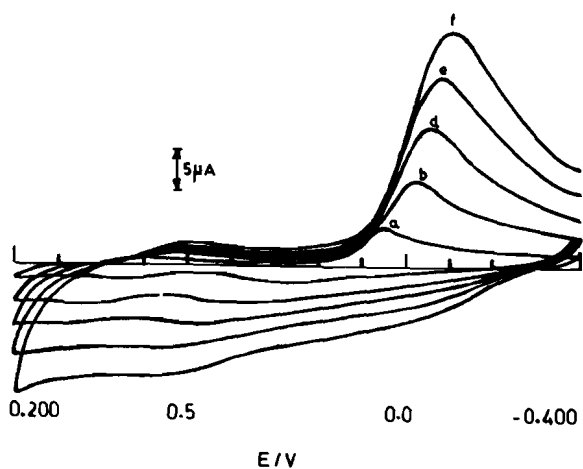


Fig. 1: CVs of PB coated GC electrode in DMSO + 0.1 M KClO<sub>4</sub> at scan rates (a) 10 (b) 20 (c) 40 (d) 75 and (e) 100 mVs<sup>-1</sup>

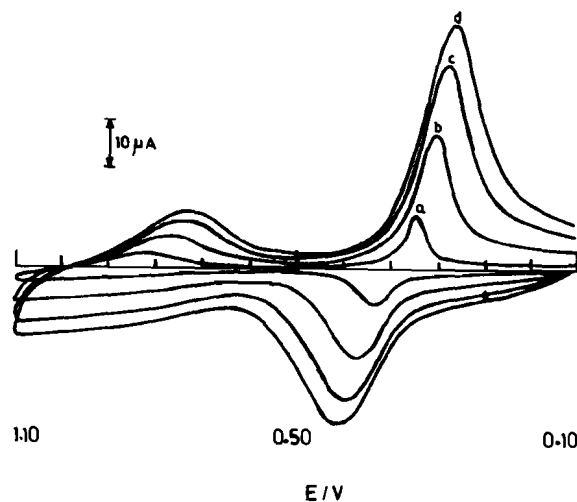


Fig. 3: CVs of PB coated GC electrode in ACN + sat. KClO<sub>4</sub> solution, at scan rates (a) 10 (b) 40 (c) 75 and (d) 100 mVs<sup>-1</sup>

growth is restricted to 20 cycles in all cases. The modified substrate is air dried at room temperature and kept immersed in non-aqueous electrolytes till use. The supporting electrolyte is 0.1 M KClO<sub>4</sub> in all the solvents except in ACN where saturated KClO<sub>4</sub> is taken due to solubility restrictions.

The solvents used in this study are water, ACN, DMF and DMSO. Highly pure spectroscopic grade solvents are used as received without further purification.

## RESULTS AND DISCUSSION

### Cyclic voltammetric studies

The CVs for PB film in DMSO + 0.1 M KClO<sub>4</sub>, DMF + 0.1 M KClO<sub>4</sub> and ACN + sat. KClO<sub>4</sub> solutions obtained at different scan rates are shown in Figs. 1, 2 and 3 respectively. The voltammetric behaviour of PB film in non-aqueous solvents differ from that in aqueous KClO<sub>4</sub> (cf. Fig. 4), with regard to peak current values and peak potentials and their separation ( $\Delta E_p$ ). The highly reversible nature of the redox film in aqueous medium is transformed into quasi-reversible response in the non-aqueous electrolytes studies. A detailed comparison is made in the following pages.

In DMSO (Fig. 1), the PB film shows electrochemical inactivity at the low spin iron centre as noticed by the

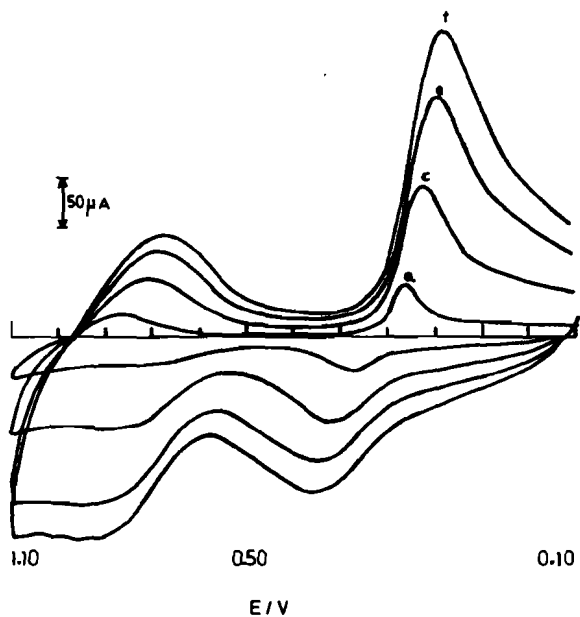


Fig. 2: CVs of PB coated GC electrode in DMF + 0.1 M KClO<sub>4</sub> solution, at scan rates (a) 10 (b) 40 (c) 75 and (d) 100 mVs<sup>-1</sup>

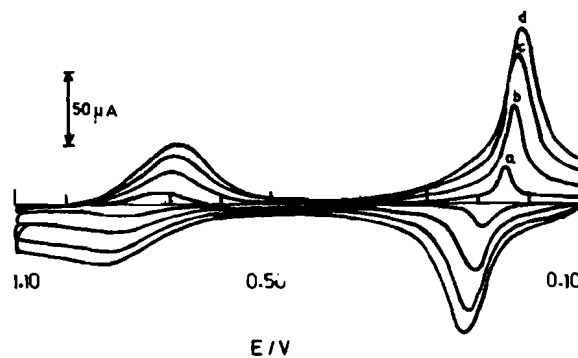
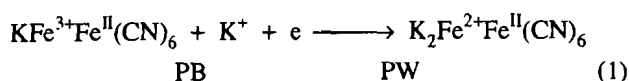


Fig. 4: CVs of PB coated GC electrode in aq. KClO<sub>4</sub> solution, at scan rates (a) 10 (b) 40 (c) 75 and (d) 100 mVs<sup>-1</sup>

absence of redox peaks for the PB  $\rightleftharpoons$  PG reaction. As against the excellent reversibility reported PB  $\rightleftharpoons$  PW redox transition in aqueous medium, a special trait responsible for the application of PB films in electrochemical devices and other related areas [4], this irreversibility of PB  $\rightleftharpoons$  PW transition in DMSO, shown by the absence of anodic peak, is quite interesting and unexpected. The cathodic peak at -104 mV at 100 mVs<sup>-1</sup> is due to the following reaction.



The appearance of peak for this reaction confirms the supposition that the solvated K<sup>+</sup> ion enters into the PB lattice via reduction. The reverse is not observed. During oxidation of PW  $\rightleftharpoons$  PB, the deintercalation of K<sup>+</sup> ions does not take place, indicating that the solvated cations are trapped inside the PB channel. The electrostatic interaction between the negatively charged PB film and the solvated ions may be stronger so that the ions are withheld within the PB lattice leading to irreversible redox reaction. This phenomenon is new in non-aqueous electrochemistry of PB films but it is well studied for Li<sup>+</sup> ion on aqueous medium [12-14].

The shape of cathodic peak at all scan rates shows a diffusion tail with increasing potential. As the potential is swept from 200 to -400 mV, the forward half-wave (before the mid-peak potential) obtained due to the increase in concentration gradient at the PB film solution interface, shows a sharp rise in current indicating that the forward step is an activation and diffusion controlled process. However, the backward half-wave (after the mid-peak potential) is not a mirror image of the forward one, which results due to the decrease in concentration gradient at the PB film interface i.e. diffusion of solvated K<sup>+</sup> ions from the solution to the film surface. Due to the high viscosity of DMSO, the diffusion of solvated K<sup>+</sup> ions may not be fast enough thus leading to the formation of diffusion tail.

As shown in Fig. 2, the CVs obtained for the PB film in DMF are different from that of DMSO as well as that of water (cf. Fig. 4). In contrast to the behaviour in DMSO + 0.1 M KClO<sub>4</sub> solution, PB film shows electrochemical activity at both the iron centres in DMF + 0.1 M KClO<sub>4</sub> solution. The redox peaks due to PB  $\rightleftharpoons$  BG reaction occurred at E<sub>av</sub> = 700 mV to 100 mVs<sup>-1</sup>. The redox peaks due to PB  $\rightleftharpoons$  PW reaction are well defined and quasi-reversible with a ΔE<sub>p</sub> value of 110 mV at the slowest

scan rate of 10 mVs<sup>-1</sup>. Based on the earlier deductions that the compatibility between the channel diameter and hydrated radius decides the electrochemical reversibility [12]. The CV obtained for PB film in DMF should be reversible. But it is not observed to be so. However, solvated K<sup>+</sup> ions in DMF do not get trapped as in the case of DMSO but exhibit ion transport behaviour to and from the PB film. The plausible reason for the departure of reversibility of PB film in DMF may be attributed to the flux of solvated K<sup>+</sup> ions in DMF being different from that of the flux of hydrated K<sup>+</sup> ion. This factor is reflected in the peak current values (Figs. 2 and 4) which remain in the same order for the cathodic peak and different order for the anodic peak in DMF and water respectively. Intercalation of solvated K<sup>+</sup> ions occurs more effectively than deintercalation of the same.

In ACN + sat. KClO<sub>4</sub> solution, PB film response is similar to that in DMF. The redox peaks for PB  $\rightleftharpoons$  PW reaction are quasi-reversible with a ΔE<sub>p</sub> values of 92 mV at 10 mVs<sup>-1</sup>. The low spin centre is also electroactive as shown by the presence of cathodic peaks. The peaks for the PB  $\rightleftharpoons$  PW redox reaction are well defined and there is no diffusion tail as observed in the case of DMSO and DMF, indicating that the flux of solvated cation is not affected by the viscosity of the non-aqueous solvent. The density of the non-aqueous solvents has a role in deciding the ionic movement [15] and the increasing order of donor property for these solvents in DMSO > DMF > ACN. Since ACN has the lower donor property among the solvents, the solvated K<sup>+</sup> ion in ACN may have liable and fast ionic movement compared to the other two, as revealed by the CVs.

In all these solvents, peak potentials for PB  $\rightleftharpoons$  PW reaction are shifted towards positive direction with respect to water as DMSO > DMF > ACN. Again the magnitude of

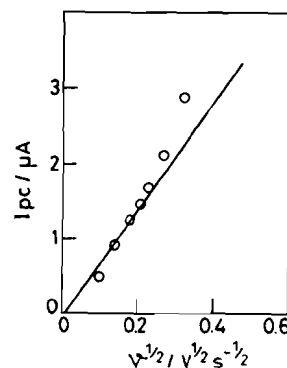


Fig. 5: Plots of  $I_{pc}$  vs  $\sqrt{v}$  for PB  $\rightleftharpoons$  PW redox reaction in DMSO + 0.1 M KClO<sub>4</sub> solution

peak currents are comparatively lesser than the retained in water (Figs. 1-4).

The plots of  $I_{pc}$  vs  $\sqrt{v}$  for PB  $\rightleftharpoons$  PW reaction in all the three non-aqueous solvents and in water (Typical plot for DMSO + 1 M KClO<sub>4</sub> is shown in Fig. 5) show noticeable similarity in all the solvents as the peak currents are linear with  $v$  as well as with  $\sqrt{v}$ , suggesting that both the movement of K<sup>+</sup> ions, within the film as well as the ion transport to and from the film, takes place simultaneously.  $I_p$  vs  $v$  plot, deviates from linearity at fast scan rates in all the solvents and so the figures are not included.

Such behaviour of PB film switching between two processes had been reported earlier [16] in aqueous medium. At slow sweep rates  $I_p$  varies linearly with scan rate and in the range between 5 and 20 mVs<sup>-1</sup>, a cross-over occurs while the peak current varies linearly with  $\sqrt{v}$ . The kinetics of this mixed process is not yet clearly understood.

### Surface coverage

Under Nernstian conditions, in cyclic voltammetry, where both the oxidized and reduced species are adsorbed and electroactive, the surface coverage can be calculated from the peak current values by using the following equation [17,18].

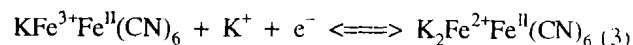
$$I_p = \frac{(n^2 F^2)}{4RT} v A \Gamma_0 \quad (2)$$

From CV response obtained at different scan rates the half peak width is found to be  $\geq 0.09$  V which indicates that the system is non-interacting ( $nVF/RTk_s = 0$ ) [19]. The above equation can be readily applied for computing surface coverage, based on the assumption that concentrations in solution tend towards zero, which is true in the case of irreversibly adsorbed surface redox systems. Moreover value of  $k_s$  can be obtained at several coverages, including extrapolation to zero coverage where the interaction between molecules becomes negligible, provided the molecules do not form aggregates.

**TABLE I: Surface coverage of redox species of PB film in various supporting electrolytes**

Solvent	$10^{11} \Gamma_0 / \text{mol.cm}^{-2}$	$10^{11} \Gamma_R / \text{mol.cm}^{-2}$
H <sub>2</sub> O	1.72	3.07
ACN	0.95	1.79
DMF	0.33	0.86
DMSO	0.04	0.06

The surface coverage values obtained for all the solvents is tabulated (Table I). It is interesting to note that  $\Gamma_R$  is greater than that of  $\Gamma_0$  in all the solvents studied. This reflects on the cation transport behaviour or in other words the rate of deintercalation of a cation appears to be faster than that of its intercalation. The redox reaction of interest is,



in which during reduction K<sup>+</sup> ions are consumed and during oxidation, K<sup>+</sup> ions are released. So, one would expect an increase in surface coverage for oxidation rather than reduction. The results obtained are confirmative suggesting that the surface coverage values prove the adsorption/desorption of potassium ions on the PB film. This situation is analogous to that observed during the passivation of iron by carbonate ions in alkaline carbonate solutions [20].

Further both  $\Gamma_0$  and  $\Gamma_r$  values are maximum in water and minimum in DMSO. The increasing order of surface coverage is H<sub>2</sub>O > ACN > DMF > DMSO which reflect the kinetics of electrochemical redox transition under study.

### Chronoamperometric studies

The CV behaviour of PB film in non-aqueous solvents does not follow a uniform trend. Hence, I-t transients of PB film in these solvents in different time scales are obtained in order to evaluate the intercalation vs deintercalation charges. Further, analysis of the observed results with the help of I vs  $t^{1/2}$  plot leads us to calculate the diffusion coefficients from the gradient and heterogeneous electron transfer rate constant from the intercept. The details are given below.

**TABLE II: Intercalation/deintercalation charges from I-t transients of PB film for potassium iron transport in various supporting electrolytes**

Step time (ms)	H <sub>2</sub> O		ACN		DMF		DMSO	
	X	Y	X	Y	X	Y	X	Y
50	0.31	0.52	0.09	0.16	0.14	0.19	0.05	0.09
250	0.69	0.96	0.38	0.45	0.25	0.32	0.09	0.10
500	1.15	1.19	0.58	0.77	0.43	0.50	0.08	0.09
1000	1.00	1.00	0.78	0.98	0.56	0.60	0.19	0.19
2500	1.65	1.20	1.01	1.06	0.59	0.63	0.26	0.14
5000	1.12	0.96	1.22	1.23	0.64	0.72	0.33	0.17
10000	1.11	0.86	0.86	0.95	0.48	0.55	0.20	0.16

$$X = Q_{in}/mC \text{ (cm}^{-2}\text{)}; \quad Y = Q_{dc}/mC \text{ (cm}^{-2}\text{)}$$

**Intercalation vs deintercalation of potassium ions**

From I-t transients, intercalation and deintercalation charges of ions are evaluated by integrating the area under these I-t transients intercalation/deintercalation processes are usually investigated for potential battery related applications [7,21]. On the other hand, these studies may also help in understanding the solvent effects since the ion is assumed to move along with its primary solvation sheath. Another parameter obtained is the ratio  $Q_{dc}/Q_{in}$  which can provide quantitative information on the reversibility of the intercalation/deintercalation processes.

Table II shows the intercalation/deintercalation charges obtained for PB  $\rightleftharpoons$  PW reaction in water, ACN, DMF and DMSO solvents at different pulse width values. Both  $Q_{in}$  and  $Q_{dc}$  increase with increase in step time in all the solvents. But at 10 s, the values start decreasing suggesting that the process is time-dependent. This behaviour is expected for a Cottrell experiment [17]. On applying the potential step from -100 to +500 mV, oxidation of PW to PB takes place, which would create a concentration gradient that produces in turn, a net flux of potassium ions to the electrode surface. At 500 mV, the process is reversed by applying the reverse potential step from 500 to - 100 mV. Hence, the flux of potassium ions as well as the current is directly proportional to the concentration gradient at the modified surface. Therefore, with increase in time scales, the continued flux of potassium ions causes the zone of potassium ion depletion to thicken, causing a decline in concentration profile with time.

Table III shows the  $Q_{in}, Q_{dc}$  ratio obtained for all the solvents. At shorter time profiles (50- 500 ms) larger  $Q_{dc}$  suggests that the number of cations deintercalated from the

film is greater than the cations intercalated. However, the process approaches equilibrium at 1000 ms in water, DMF and DMSO while in ACN, the equilibrium is attained only at 2500 ms.

In longer time scales, the process of intercalation/deintercalation of potassium ions is not uniform in all the solvents. For e.g. in the oxygen coordinating solvents of water and DMSO,  $Q_{in}/Q_{dc}$  ratio in the range of -2500 to 1000 ms time scales, indicate that the intercalation dominates over that of deintercalation of potassium ions which is contrary to the behaviour at shorter time scales. However, in ACN and DMF, the behaviour is uniform at all time scales as evident from the  $Q_{in}/Q_{dc}$  ratios.

Comparison of magnitude of charge of hydrated potassium ions with that of solvated potassium ions reveals the fact that the cations are preferably hydrated rather than solvated. It is reported earlier [6,21] that the potassium ions have a difficulty in getting solvated due to its polarizability as compared to that of lithium ions. Based on the magnitude of charges, the order of preference for the solvation of potassium ion in these solvents is  $H_2O > ACN > DMF > DMSO$ .

**Diffusion coefficients**

By double potential step chronoamperometry, diffusion coefficients for both oxidation and reduction processes are computed in all the solvents. From the I-t transient obtained at 50 ms pulse width, the current values are taken for the calculation of diffusion co-efficient from the I vs  $t^{1/2}$  plot using the Cottrell equation as [17]

$$|I| = \frac{nFAc^0D^{1/2}}{\pi^{1/2}t^{1/2}} \tag{4}$$

where the symbols have their usual meaning. From the gradient of I vs  $t^{1/2}$  plot, diffusion co-efficients can be

**TABLE III: Charge ratio for the intercalation/deintercalation process of potassium ion transport through PB films in various supporting electrolytes**

Step time (ms)	$Q_{in}/Q_{dc}$			
	H <sub>2</sub> O	ACN	DMF	DMSO
50	0.60	0.59	0.69	0.56
250	0.71	0.63	0.78	0.87
500	0.97	0.75	0.87	0.88
1000	1.00	0.80	0.92	1.00
2500	1.39	1.00	0.94	1.89
5000	1.17	0.99	0.89	1.98
10000	1.29	0.90	0.86	1.30

**TABLE IV: Diffusion co-efficient values and heterogeneous rate constants for potassium ion transport through PB film in various supporting electrolytes**

Solvent	$10^9 D_{ox} / \text{cm}^2 \text{s}^{-1}$	$10^9 D_R / \text{cm}^2 \text{s}^{-1}$	$10^6 K_h / \text{cm s}^{-1}$	$10^6 K_h / \text{cm s}^{-1}$
H <sub>2</sub> O	3.01	4.37	29	15
ACN	1.18	2.36	87	73
DMF	6.83	9.50	14	13
DMSO	1.91	1.67	69	51

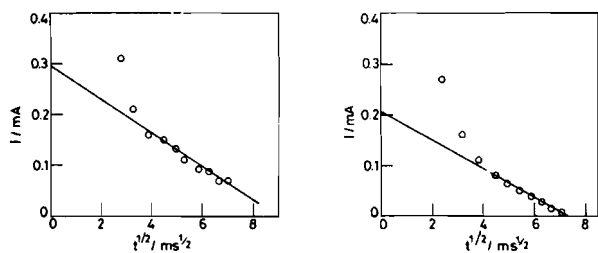


Fig. 6:  $I$  vs  $t^{1/2}$  plots derived from  $I$ - $t$  transients, obtained at 50 ms pulse width for the PB  $\leftrightarrow$  PW redox reaction in DMSO (a) during oxidation and (b) during reduction

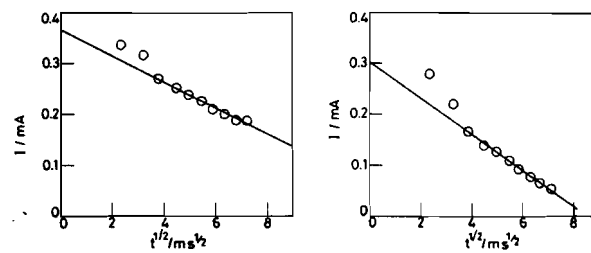


Fig. 8:  $I$  vs  $t^{1/2}$  plots derived from  $I$ - $t$  transients, obtained at 50 ms pulse width for the PB  $\leftrightarrow$  PW redox reaction in ACN (a) during oxidation and (b) during reduction

evaluated. The  $c^0$  value used in the calculation is  $6.26 \times 10^{-3} \text{ mol/cm}^3$  assuming the face centered cubic crystal cell in PB [9]. The diffusion coefficient is an apparent value indicating the net movement of both ionic and electronic species.

Table IV shows the diffusion coefficients obtained for both oxidation and reduction of PW  $\rightleftharpoons$  PB reaction in aqueous and non-aqueous solvents. It can be seen that except in DMSO, the  $D_R$  is greater than that of  $D_{ox}$  in all other solvents. It is known that  $D$  value depends qualitatively on the ionic charge which in turn is related to the extent of solvation [22]. In a case of monovalent potassium ion, the charge on the ion remains invariably the same but the extent of hydration/solvation may vary depending on the nature of ion solvent intercalation. Increase in solvated ionic size

would lead to decrease in diffusion coefficient as in the case of DMF while the reverse is true in ACN and DMSO.

### Kinetics of charge transfer

From  $I$ - $t$  transients, heterogeneous electron transfer rate constant for the PB  $\rightleftharpoons$  PW redox reaction in all the solvents under study may be determined using the following expression derived based on Fick's laws [23].

$$I_{t=0} = nFk_h c_0 s p b \quad (5)$$

This simplified expression is obtained from the following equation,

$$I = nFAk_h c_0^b [1 - 2k_h t^{1/2} (\pi^{1/2} D_0^{1/2})] \quad (6)$$

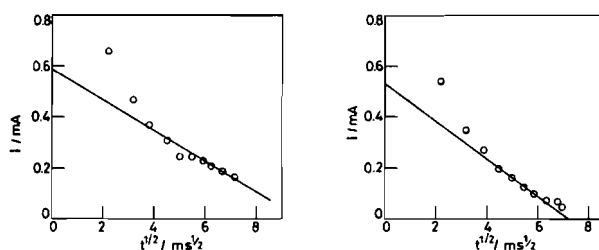


Fig. 7:  $I$  vs  $t^{1/2}$  plots derived from  $I$ - $t$  transients, obtained at 50 ms pulse width for the PB  $\leftrightarrow$  PW redox reaction in DMF (a) during oxidation and (b) during reduction

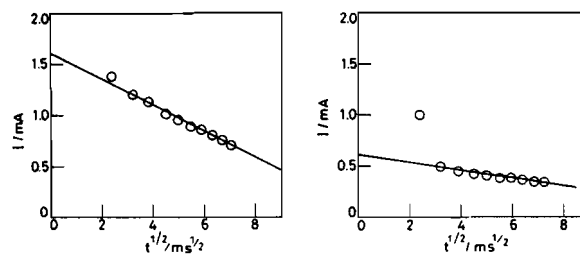


Fig. 9:  $I$  vs  $t^{1/2}$  plots derived from  $I$ - $t$  transients, obtained at 50 ms pulse width for the PB  $\leftrightarrow$  PW redox reaction in aqueous medium (a) during oxidation and (b) during reduction

Which is valid at shorter time scales of chronoamperometric experiments. In general, this equation predicts that the current varies linearly with square root of time. However, for the reversible case  $I \rightarrow x$  as  $t \rightarrow 0$  and for the irreversible case,  $I \rightarrow nFAk_h c_0^b$  as  $t \rightarrow 0$  i.e. in the limit of  $t = 0$ , the current is equal to that which would result in the absence of diffusion. Thus extrapolation to zero time effectively separates the effects of charge transfer and diffusion upon the kinetics of the overall process and the rate constant, can then be evaluated.

It is known that  $I_{t=0}$  cannot be evaluated directly due to instrumental limitations [24]. By extrapolating  $I$  vs  $t^{1/2}$  plot obtained at 50 ms pulse width (Figs. 6-9a and b) in all the solvents, one can arrive at the value of  $I_{t=0}$ . Substituting this known quantity in eq. (5)  $k_h$  can be evaluated. Table IV shows the rate constant values obtained in the cases. In water and DMF,  $k_h$  values are of the order of  $10^{-5}$  cm while in ACN and DMSO, they are of the order  $10^{-6}$  cm. The redox reaction is facile in water and DMF than the other two solvents. It is also to be noticed that in accordance with the greater value reported earlier, the rate of deintercalation is uniformly higher in all the solvents used (cf. Table IV).

### CONCLUSION

The hitherto reversible PB  $\rightleftharpoons$  PW redox reaction in aqueous medium serves as a model system to elucidate kinetic parameters in some non-aqueous electrolytes such as ACN, DMF and DMSO and a meaningful comparison is provided for the performance in aqueous electrolyte.

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