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SOLVATION VS HYDRATION OF INTERCALATED POTASSIUM AND SODIUM IONS IN PRUSSIAN BLUE FILMS

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The complexity at the PB film/solution interface in aqueous and non-aqueous electrolytes is analysed. Evidence for the co-existence of two dissimilar cations in the PB film which again differ in their hydration and solvation characteristics is illustrated with cyclic voltammetric experiments.

Keywords: PB films and cyclic voltammetry

INTRODUCTION

The facile intercalation/deintercalation of supporting electrolyte cation decides the utility of surface prussian blue (PB) films for various applications such as in electrochromic devices [1-2], in solid state batteries [3-4], as ion selective electrodes [5-6], as signal enhancing devices [7-9] and in electrocatalysis [10]. In our earlier work, we have reported the intercalation of two unlike cations co-existing in the PB film by manipulating the film preparation conditions [11]. Both potassium and sodium ions as well as potassium and lithium ions are found to co-exist in the PB film of composition $K_{1-x} M[Fe^{III} Fe^{II} (CN)_6]$ (where $M = H^+, Na^+, Li^+$), which is proved by intercomparison of cyclic voltammograms recorded in aqueous and acetonitrile media. In yet another work done by us, the intercalation/deintercalation charges and diffusion coefficients for solvated and hydrated potassium, sodium and lithium ions were reported [12]. We found that in acetonitrile, the $Fe^{2+/3+}$ redox reaction in presence of potassium is quasireversible which was quite contrary to the high reversibility observed in aqueous medium. In continuation of the above projected work, in the present study, our observations in acetonitrile medium under carefully selected experimental conditions, help to propose the co-existence of hydrated and solvated cations in the PB film for the first time. The concept of Donnan membrane equilibrium as reported for PB film/solution interface [6] is used as a tool to understand the present work.

EXPERIMENTAL

All chemicals used are of analytical grade. Doubly distilled water is used for preparation of aqueous solutions.

Cyclic voltammetric experiments are carried out in Electrochemical Analyser, Model BAS 100 A. A conventional three electrode assembly comprising a glassy carbon (GC) disc (0.07 cm) working electrode platinum counter electrode and Ag/AgCl reference electrode is employed.

Modification of GC electrodes with iron hexacyanoferrate (i.e., PB) is done by cycling the electrodes in a clear solution containing 2 mM $FeCl_3$, 2 mM $K_3Fe(CN)_6$ and 0.1 *M* KCl. The *p*H of the solution is adjusted with analar HCl to be between 2 to 3. In order to maintain constant coverage throughout the experiments, film growth is restricted to 20 cycles in all cases.

The modified substrate is air dried at room temperature and kept immersed in acetonitrile till use. Cyclic voltammetric experiments are carried

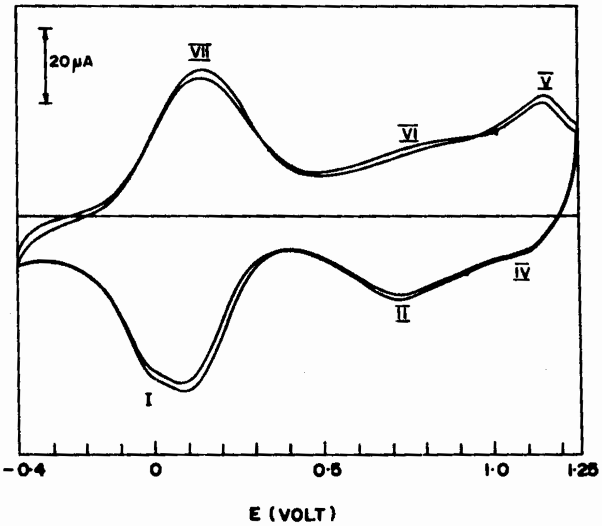

Fig. 1: Cyclic voltammograms for PB film in 0.1 *M* $NaClO_4$ + ACN solution V = 100 mVs^{-1}

out in 0.1 *M* $NaClO_4$ supporting electrolyte in acetonitrile. Various percentage addition of water to the ACN electrolyte solution is performed to study the effect of added water in mixed solvents.

RESULTS AND DISCUSSION

Fig. 1 shows the cyclic voltammetric response of PB film in acetonitrile (ACN) with 0.1 *M* $NaClO_4$ supporting electrolyte. The CV is marked with broad redox peaks at about 60 mV and 150 mV in the anodic and cathodic cycle for PB <==> PW reaction. The potentials corresponding to the other peaks and CVs are tabulated (Table I). In conformity with our earlier work [11], the PB <==> PW redox reaction can be written as

$$K_{1-x}Na_x[Fe^{III}Fe^{II}(CN)_6] + Na^+ + e^- \longrightarrow K_{1-x}Na_y[Fe^{II}Fe^{II}(CN)_6] \qquad (1)$$

The presence of two dissimilar alkali metal cations in the PB film is much more evident from the ferrocyanide/ferricyanide redox response. such mixed transition metal cations response has been reported earlier [13-14]. The intermittant peaks II and VII at 730 mV and 750 mV are attributed to PB <==> PY involving hydrated K^+ ions as,

$$K_H[Fe^{III}Fe^{II}(CN)_6] \longrightarrow [Fe^{III}Fe^{II}(CN)_6] + K_H^+ + e \qquad (2)$$

Since the ACN solution does not contain K^+ ions, it is reasonable to presuppose that interstitially occupied K^+ ions during the film preparation in aqueous medium participate in this reaction. It is well known that the PB film prepared in aqueous medium contains interstitial K^+ ions and water molecules in abundance which are essential for ion transport within the film [15-16]. Moreover the presence of three kinds of water molecules in PB, characterized as zeolitic (338 K), lattice (368 K) and coordinated (398 K) has been reported [17] based on differential thermal analysis. Quartz-crystal microbalance measurements [18] for potentiostatic PB electrodeposition onto gold also revealed that the PB films are highly hydrated. Similar studies on nickel hexa cyanoferrate give additional support for this proposition in which the potassium ion is reported to enter the film with 0.23 water molecules [19]. Quantitatively, the level of hydration in PB film is enumerated from

TABLE I: Redox peak potentials from the CVs ofPB in absence and presence of water in ACN medium

Supporting electrolyte	Anodic peak potentials (mV)				Cathodic peak potentials (mV)			
	I	II	III	IV	V	VI	VII	VIII
0.1 *M* $NaClO_4$ in ACN (A)	60	730	—	1100	1150	—	750	150
A + 10% H_2O	-8	700	830	1028	1068	890	600	96
A + 30% H_2O	-112	670	780	940	996	765	560	55
A + 70% H_2O	-200	590	—	830	945	770	550	30

ellipsometric measurements [20][as around 32 water molecules per PB unit cell.

Peaks IV and V at 1100 mV and 1150 mV are due to PB <==> PY reaction involving solvated

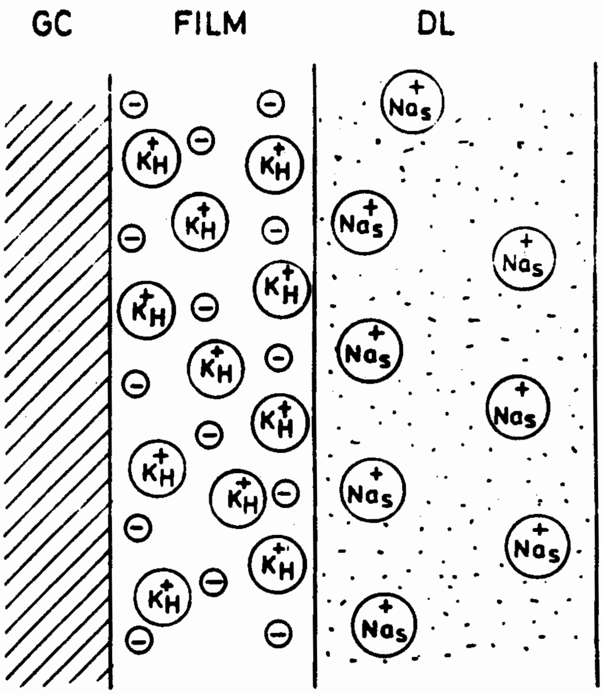

Fig. 2a

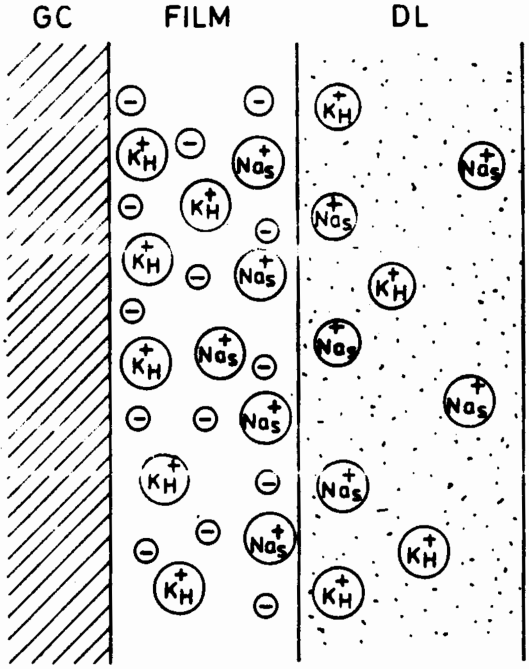

Fig. 2(a): PB film/solution interface before attaining the ion exchange equilibrium
(b): PB film/solution interface after attaining the ion-exchange equilibrium

Na^+ ion as it is known that solvent molecules enter into the film during redox reactions [21].

$$Na_S[Fe^{III}Fe^{II}(CN)_6] \longrightarrow [Fe^{III}Fe^{III}(CN)_6] + Na_S^+ + e \quad (3)$$

The appearance of a single broad peak for ferrous/ferric transition as against two surface waves for ferrocyanide/ferricyanide transformation may result due to the non-equivalent nature of two iron centres. The columbic interaction between the alkali metal cations and the two iron centres may be different from one another, which leads to substantial difference in the ion exchange property of PB films at both centres [22].

Water is more basic than acetonitrile and so, alkali metal cations are preferably hydrated than solvated [23]. The equilibrium constants for the replacement of solvent molecules from acetonitrile by the preferred water, around various cations has been reported [24]. It is found that Na^+ ion and K^+ ion have log K values as 0.40 and 0.11 respectively, suggesting that these cations prefer to be hydrated in a solvent mixture. Another measure of the affinity of solvents in a mixture towards ions is the average residence times (as determined from NMR band widths) in the co-ordination sphere of the ion. For Na^+ ion, the average life time 't' of water and acetonitrile molecules in a mixture is reported to be 3.30 and 0.60 ns respectively.

In view of these inferences, it is assumed in the present work that both cations would prefer to remain hydrated provided the experimental conditions are favourable. Thus for redox reaction (2), the K^+ counter cation is assumed to be hydrated state, since the film is modified in aqueous solutions.

According to Doblhofer [6], the Donnan membrane equilibrium between the PB film and the solution is dominated mainly by the interfacial potential drop. In colloidal chemistry [25], Donnan membrane equilibrium is defined as an interexchange of the ions of an electrolyte and that of fixed matrix or adsorbent, which will lead to equilibrium where some of the ions from the film may diffuse outward into the solution and the external cations will have passed inside. The process is similar to interfacial diffusion observed in passivation of metals [26] where the diffusion layer may become anion or cation selective to form passive film depending on the experimental conditions.

Figs. 2a and 2b schematically show the PB film/solution interface before and after attaining the equilibrium. Fig. 2a conceptually shows the presence of hydrated K^+ ions in the film and solvated Na^+ ions in the diffusion layer. For clarity, sorption effects are ignored. Fig. 2b shows the interexchange of cations between the film and solution, revealing the coexistence of both cations in the film, which is evident from the cyclic voltammetric response as in Fig. 1.

Cyclic voltammetric response of the PB film in ACN + 10% H_2O (% as to the total volume of ACN taken) with 0.1 *M* $NaClO_4$ supporting electrolyte is shown in Fig. 3. There are four sets of redox peaks (Table I) and the extra set of redox peaks at E_{av} = 860 mV appears after the addition of water to the electrolyte solution. These peaks may be assigned as follows: The redox peaks III and VI at 830 mV and 890 mV in the anodic and cathodic cycles, may be assigned to the ferrocyanide/ferricyanide redox reaction involving solvated Na^+ ions as per the equation (3). Similarly, peaks II and VII appear due to the redox reaction of ferrocyanide/ferricyanide involving hydrated K^+ ions as per the equation

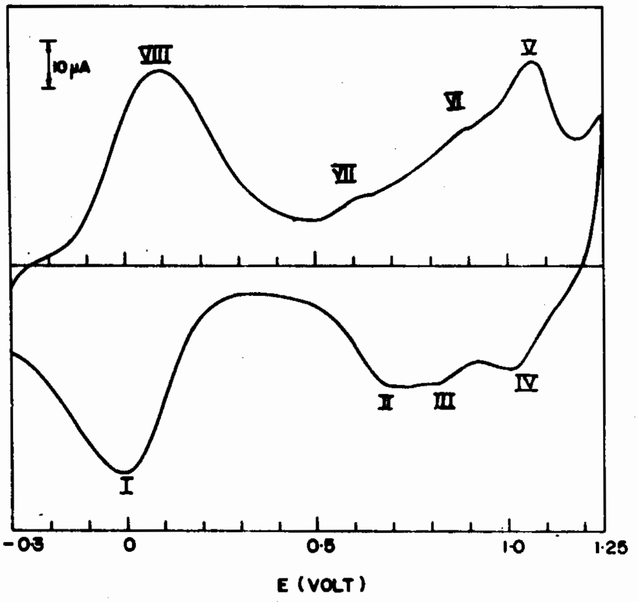

Fig. 3: Cyclic voltammogram for PB film in 0.1 *M* $NaClO_4$ with ACN + 10% H_2O addition V = 100 mVs^{-1}

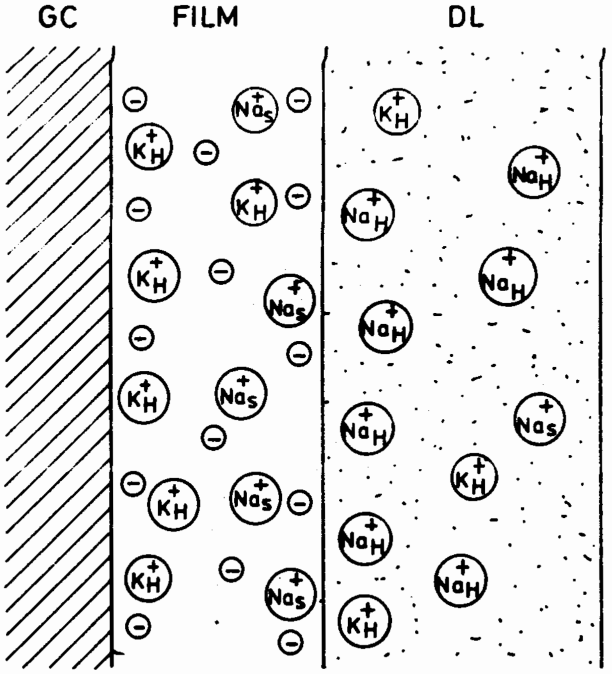

Fig. 4a

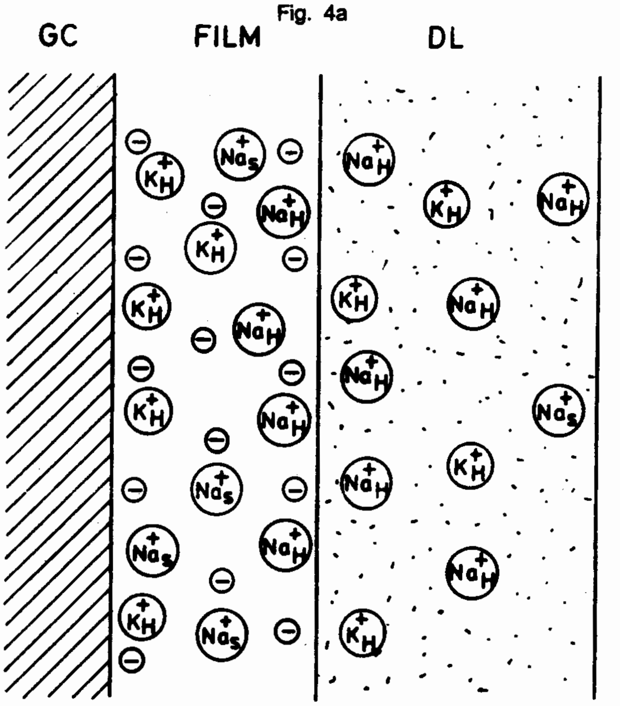

Fig. 4(a): PB film/solution interface after the addition of water to ACN solution; before attaining the ion exchange equilibrium (b): PB film/solution interface after the addition of water to ACN solution; after attaining the ion exchange equilibrium

(2). Interestingly, this peak current increases slightly after further addition of water (30%). The fourth set of peaks IV and V at 1028 mV and 1068 mV are again due to ferrocyanide/ ferricyanide redox reaction involving hydrated Na^+ ions as,

$$Na_H[Fe^{III}Fe^{II}(CN)_6] \longrightarrow [Fe^{III}Fe^{III}(CN)_6] + Na_H^+ + e \quad (4)$$

Addition of water to the electrolyte solution may lead to the preferential hydration of some Na^+ ions as shown schematically in Fig. 4a. Now, the ion transport to and from the PB film would involve both hydrated and solvated Na^+ ions. Thus we expect a mixed response in cyclic voltammograms due to hydrated K^+ ions, hydrated Na^+ ions and solvated Na^+ ions, after attaining the ion exchange equilibrium. Fig. 3 reveals the same with four sets of redox peaks. The complexity at the interface and in the film may be better understood if one look into the Fig. 4b, where the scheme is visualised.

Further, addition of water to the electrolyte solution (30% and 70%) in addition to causing increase in peak current shift the redox peak potentials towards active direction indicating the gradual increase in proportion of hydrated cations in the film and solution. Further, the peaks at ferrous/ ferric centre change in shape from typical thin layer behaviour [27] as in Fig. 1 to diffusion like behaviour (Figs. 5 and 6) suggesting a change in kinetic control from film/solution interface to solution alone.

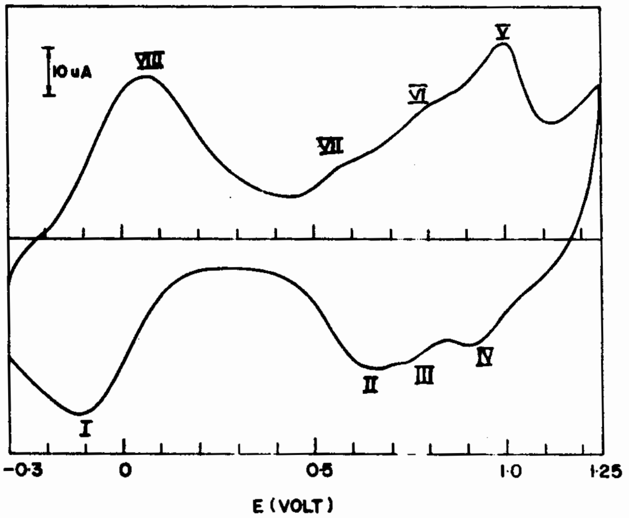

Fig. 5: Cyclic voltammogram for PB film in 0.1 *M* $NaClO_4$ + 30% H_2O addition V = 100 mVs^{-1}

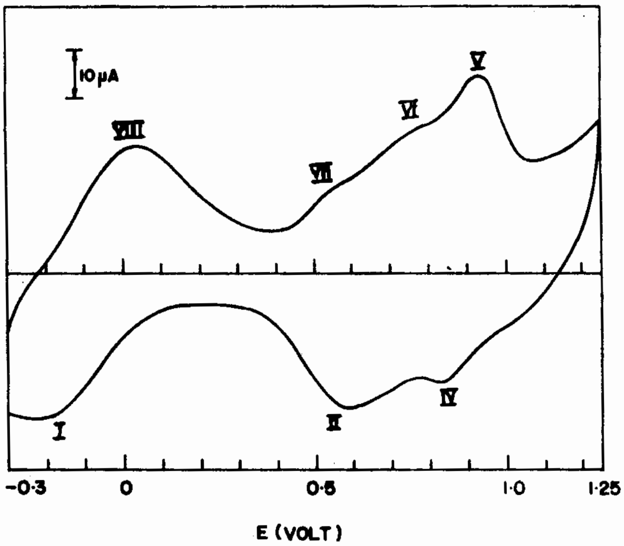

Fig. 6: Cyclic voltammogram for PB film in 0.1 *M* $NaClO_4$ + 70% H_2O addition V = 100 mVs^{-1}

It is quite interesting to observe that cations involved in the ferrocyanide/ferricyanide redox reaction manifest themselves as different set of peaks due to their hydration/solvation characteristics. This fact is understandable since cation transport within the film is limiting and rate determining [28] provided the film contains water/solvent molecules in it as against the solid state electrochemistry where the electronic transport is proved to be rate determining.

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