

## Chromogenic polyaniline picrate- A novel sorbent for selectivity of anions in potassium and sodium salts

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A novel chromogenic, polymeric sorbent material Polyaniline picrate (PANIPi) has been synthesized by chemical oxidative polymerization and characterized using various spectral techniques. Cyclic voltammetry and four probe conductivity measurements have revealed that the polymer is highly electroactive. Surface morphology is analyzed using SEM and TEM micrographs. Potassium halides, potassium sulphate and potassium thiocyanate are used as sorbate materials for ion exchange on PANIPi. Five types of sorption isotherms namely Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Redlich-Peterson are applied to the sorption process. Among these isotherms Langmuir, Freundlich and Temkin models fitted well for the sorption of potassium salts on PANIPi. The maximum adsorption capacity ( $q_m$ ) follows the size order of anions. The intensity of FT-IR stretching vibration for  $SCN^-$  at  $2066\text{ cm}^{-1}$  varies linearly with concentration, making PANIPi an effective sensor material for the quantitative determination of  $SCN^-$ . The potassium to sodium selectivity of 2:1 is observed at both low and high sorbate concentrations.

**Keywords:** Polyaniline picrate, Potassium salts, Sorption, Thiocyanate sensor

Sodium, potassium and chloride ions are the most common electrolytes essential for living organisms. Potassium is the primary cation in the intercellular fluids while sodium and chloride are abundant ions in the extracellular fluids. These ions are necessary for regulating the muscle and nerve excitability across the cell membranes. The electrolyte balance is maintained by the "sodium-potassium" pump leading to cell turgidity and normal functioning of the cells<sup>1</sup>. Halide, thiocyanate and sulphate ions are generally present in the food. Iodide and thiocyanate ions are important for thyroid hormone regulation. Thiocyanate ions are potent competitive inhibitor of the sodium-iodide symporter<sup>2</sup>. Optimal concentrations of these ions are required for the normal functioning of human host defence system. High concentration of sulphate ions are known to inhibit certain microbial activities<sup>3</sup>. Hence it is essential to regulate the concentrations of these ions in solutions. In recent years, sorption<sup>4</sup> is suggested as a highly efficient method to study the nature of ion transport process.

Sorption process is mainly dependent on the nature of the adsorbents. In the last three decades, organic conducting polymers<sup>5</sup> have emerged as an important class of materials due to the wide variety of applications in the field of adsorption<sup>6-8</sup>, ion

exchange<sup>9</sup> and catalysis<sup>10</sup>. Polyaniline (PANI) is a conducting polymer widely used for its unique electrical conductivity and electroactivity<sup>11</sup> but currently it is used as an adsorbent material for sorption of ions and organic molecules due to its high specific surface area and excellent exchange capacity<sup>12</sup>. In continuation of our previous studies<sup>13,14</sup>, the sorption capacity of polyaniline picrate (PANIPi) for the adsorption of potassium salts is explored. The sensitivity of PANIPi for discriminating between potassium and sodium salts and sensing property of the PANIPi for  $SCN^-$  are also investigated.

Various sorption isotherms and spectral techniques are employed for understanding the possible ion transport mechanism and structural modifications taking place during the sorption process. The presence of chromogenic dopant picric acid in PANI matrix, imparts colour to the solutions containing colourless potassium salts so that the sorption process can be monitored easily by UV-Visible spectroscopy.

### Experimental Section

Aniline was vacuum distilled before polymerisation and all other chemicals were of analytical grade and used as received. Double distilled water was used for the preparation of potassium salt solutions for the sorption process.

**Sorbent****Chemical oxidative polymerization and characterization of PANIPI**

The sorbent PANIPI was prepared<sup>15</sup> using aniline (0.1 M) as monomer, ammonium peroxydisulphate (0.1 M) as oxidant and picric acid (0.05 M) as dopant in aqueous solution. This synthesis yielded green coloured polymeric solid. This polymer on repeated washings with distilled water, alcohol, acetone, diethyl ether and hexane resulted in a free flowing powder. The pristine polymer was stored in a vacuum desiccator for further characterization and sorption experiments.

The UV-Visible spectra of PANIPI (1 mg/ 25 mL) in DMF was recorded in the region of 300-1000 nm using Perkin-Elmer Lambda 25 spectrophotometer. FT-IR spectra were recorded as KBr pellets on a Perkin-Elmer RXI FT-IR spectrophotometer. Cyclic Voltammetric studies were performed on a Princeton applied research electrochemical analyser (PAR-VSP) using a conventional three-electrode system with the glassy carbon electrode as the working electrode, a platinum wire as the counter electrode and silver/silver chloride (Ag/AgCl) as reference electrode. The polymer was ground to a fine powder, 1 mg of PANIPI was suspended in 10 mL DMF, 1 M Tetrabutylammonium perchlorate (TBAP) was used as the supporting electrolyte and the cyclic voltammograms were recorded at different scan rates (20, 40, 60, 80, 100, 200 mV/s). The DC conductivity of PANIPI was measured using a four probe meter (Model: DFP-03).

The stock solution of PANIPI (4 mg/dL) in DMF was serially diluted to required concentrations by adding DMF for density and viscosity measurements. Densities of the respective solutions were determined using specific gravity bottles (10 mL) and flow times were measured using a Cannon Fenske glass viscometer at 30±1°C. The morphology of PANIPI

were analysed using SEM and TEM. SEM image of PANIPI was obtained using Scanning Electron Microscope (Jeol JSM-5610LV). TEM analysis was performed on a Transmission electron Microscope (Jeol JEM-2100F) using a dilute dispersion of PANIPI. This dispersion was placed on a carbon film coated on a copper grid. The copper grid was fixed into the sample holder and placed in a vacuum chamber of the transmission electron microscope and TEM images were observed under low vacuum at 8 KV.

**Preparation of sorbate solutions**

All the potassium salts (KCl, KBr, KI, K<sub>2</sub>SO<sub>4</sub> and KSCN) were weighed accurately in an electronic balance and stock solutions were prepared in double distilled water and suitably diluted to required concentrations (2 M, 10<sup>-1</sup>-10<sup>-6</sup> M) for the sorption experiments.

**Batch sorption experiments**

Sorption experiments of potassium salts on PANIPI resin were carried out by the batch process at 30 ± 1°C. The experiments were performed by mixing 1 mg of PANIPI with 25 mL of a given initial concentration of potassium salt solutions (10<sup>-1</sup>-10<sup>-6</sup> M) in a 50 mL conical flask. This solution was ultrasonically stirred (Ultrasonic cleaning bath 50 KHz, Ultrasonic Ney) for 30 min, centrifuged and the concentration of picrate ion released (C<sub>e</sub>) in the centrifugate was ascertained from the calibration curves at 360 nm. The concentration of picrate ion released (C<sub>0</sub>) in water was considered as the standard.

Five types of sorption isotherms such as Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Redlich-Peterson isotherms were applied using the C<sub>0</sub> and C<sub>e</sub> values. All the experiments were performed thrice and the mean of the three values were presented in Tables 1 and 2. Graphs were constructed with Origin 8.6 software and the slopes and intercepts were calculated using linear regression analysis.

Table 1 — Langmuir and Freundlich isothermal parameters for sorption of potassium salts on PANIPI

Potassium salts (KX)	Langmuir constants					Freundlich constants				-ΔG° (kJ/mol)	anionic radius r (Å <sup>0</sup> )
	q <sub>m</sub> (mg/g)	K <sub>L</sub> (L/mg)	R <sup>2</sup>	<sup>a</sup> S.D	R <sub>L</sub>	K <sub>F</sub> (L/mg)	n	R <sup>2</sup>	S.D		
KCl	7.15	0.013	0.965	0.019	0.939	0.013	0.242	0.988	0.010	5.279	1.67
KBr	31.55	0.084	0.968	0.005	0.703	0.148	0.339	0.989	0.013	6.230	1.82
KI	98.72	0.127	0.903	0.020	0.610	0.030	0.296	0.975	0.070	5.198	2.16
K <sub>2</sub> SO <sub>4</sub>	3.57	0.131	0.967	0.019	0.603	0.034	0.295	0.981	0.072	1.596	3.38
KSCN	103.15	0.011	0.887	0.019	0.947	0.008	0.229	0.978	0.068	11.407	2.20

<sup>a</sup>Standard deviation

Table 2 — Dubinin-Radushkevich, Temkin and Redlich-Peterson isothermal parameters for sorption of potassium salts on PANIPI

KX	Dubinin-Radushkevich constants				Temkin constants				Redlich- Peterson constants ( $\beta=1$ )			
	$q_s$ (mg/g)	E (kJ/mol)	$R^2$	S.D.	$K_T$ (L/mg)	$b_T$ (kJ/mol)	$R^2$	S.D.	$K_{RP}$ (L/mg)	$\alpha_{RP}$ (L/mmol)	$R^2$	S.D.
KCl	0.264	5.829	0.989	0.10	5.429	0.014	0.998	0.089	1.653	0.103	0.923	0.023
KBr	0.031	6.743	0.985	0.076	5.619	0.013	0.997	0.021	2.811	0.083	0.903	0.029
KI	0.228	6.578	0.932	0.100	5.701	0.017	0.993	0.025	1.540	0.126	0.800	0.121
$K_2SO_4$	0.010	7.181	0.949	0.038	3.805	0.084	0.995	0.085	0.305	0.158	0.944	0.002
KSCN	0.414	5.671	0.979	0.123	5.369	0.014	0.998	0.024	1.169	0.109	0.839	0.100

### Sorption experiments at high concentrations (2 M)

The sorption experiments were also conducted at high concentrations (2 M) of potassium salts by adding 10 mg of PANIPI to 25 mL of the potassium salt solutions. The sorption process was monitored by following the pH changes (Digital pH meter EQ 160, Equiptronics) at regular time intervals. The midpoints of the pH curves were taken for determining the  $K_{PI}^{X-}$  values.

Flame Photometric analyses (Flame Photometer Elico 360 A) were performed on the solutions of potassium salts after the sorption experiments. From the concentration of ions present before and after the sorption process  $\alpha$  values were calculated. The FT-IR spectral results before and after sorption were used to determine the structural changes on PANIPI resin.

## Results and Discussion

Ion transport across polymeric membranes is an important physiological process in living cells. Sorption is a widely used method to understand such ion-transport processes. Doped PANI salts exhibit excellent anion exchanging characteristics<sup>8,12,13</sup>. PANIPI is a superior novel sorbent for such processes, since the dopant picric acid absorbs at 360 nm in the visible region and is highly acidic. PANIPI being chromogenic, in the sorption experiments the picric acid is released into the aqueous solutions and the concentration changes are monitored at 360 nm. Ion exchanges at high concentrations are followed by measuring the pH changes of the solutions. Hence it is of interest to explore the ion exchange behaviour of PANIPI with potassium salts.

### Characterisation of PANIPI resin

#### UV-Visible Spectrum

In the UV-Visible spectrum of PANIPI in DMF two peaks appear at 360 nm and 621 nm (Table 3) characteristic of the benzenoid and quinoid<sup>16,17</sup> absorptions of the PANI skeleton. At 360 nm,  $\Pi-\Pi^*$

Table 3 — UV-Visible spectral results and equilibrium constants for ion exchange of potassium salts on PANIPI resin

KX	$\lambda_{max}$ (nm)		y	$^a1-y$	$b_{KPI}^{X-}$
	Benzenoid (B)	Quinoid (Q)			
PANIPI	360	621	0.70	0.30	-
KCl	365	619	0.63	0.36	$4.89 \times 10^{-7}$
KBr	366	620	0.65	0.34	$8.71 \times 10^{-8}$
KI	374	605	0.68	0.31	$4.87 \times 10^{-7}$
$K_2SO_4$	362	619	0.59	0.40	$3.16 \times 10^{-7}$
KSCN	362	619	0.65	0.34	$9.12 \times 10^{-8}$

$$^a1-y = \frac{OD_Q}{OD_B}; [KX] = b_{2M}$$

absorptions of the benzenoid ring of the PANI chain and the dopant picrate ion have merged together as an intense peak.

#### FT-IR Spectrum

In the FT-IR spectrum of PANIPI, N-H stretching vibrations are observed at 3425, 3246  $cm^{-1}$ . The absorptions around 3080, 2984, 2847 and 2827  $cm^{-1}$  correspond to C-H stretching vibrations. Peaks in the region 3400-2800  $cm^{-1}$  are partly masked by the extended absorption tail of the protonated PANI.<sup>18</sup> Quinoid (N=Q=N) and benzenoid (N=B=N) vibrations<sup>19</sup> are observed at 1588 and 1491  $cm^{-1}$ . The C-N and  $NO_2$  stretching vibrations are merged around 1300  $cm^{-1}$  (Table 4). The absorption at 1137  $cm^{-1}$  is due to charge delocalisation on the polymer backbone. The three distinct bands at 797, 699 and 504  $cm^{-1}$  are characteristic of bending vibrations of PANIPI<sup>20</sup>.

#### Electroactivity of PANIPI

PANIPI exhibits two redox couples at -0.8 and -1.2 V in solution phase containing TBAP in DMF solvent (Fig. 1a). The redox couples are centred at  $E_{1/2} = 0.7, 1.3$  V with a peak separation of 0.1 V. The sharp, symmetrical anodic peak at -0.8 V and a small ill-defined peak at -1.2 V suggest the transfer of two electrons at the two imine sites in

Table 4 — FTIR spectral data of PANIPI before and after sorption of potassium salts on PANIPI

Vibrational assignment	N-H str	Ar C-H str / NH <sub>2</sub>	C=N <sup>+</sup>	SCN stretching	N=Q=N	N=B=N	CN str	Ar C-N-C bending	C-H bending	C-H ring deformation	C-X stretching	C-N- C torsion
PANIPI	3425, 3246	3080, 2984, 2827	2800-2400	-	1588	1491	1300 (NO <sub>2</sub> ) <sub>PI</sub>	1137	797	699	-	505
KCl	3430	2808	2483, 2361	-	1588	1491	1300	1135	795	699	612,sh (Cl)	503
KBr	3441, 3205	3021, 2827	2359	-	1593	1490	1300	1136	787	698	586,sh (Br)	503
KI	3480, 3412	3180, 2940	2473, 2324	-	1578	1488	1286	1133	800	701	595,sh (I)	501
K <sub>2</sub> SO <sub>4</sub>	3437	2821	2360	-	1594	1492	1300 (SO <sub>4</sub> )	1133	787	692 619	-	506
KSCN	3462	2816	2362	2066 (SCN)	1593	1492	1338	1142	794, 744 (SCN)	699	585,sh (SCN)	504

sh-shoulder

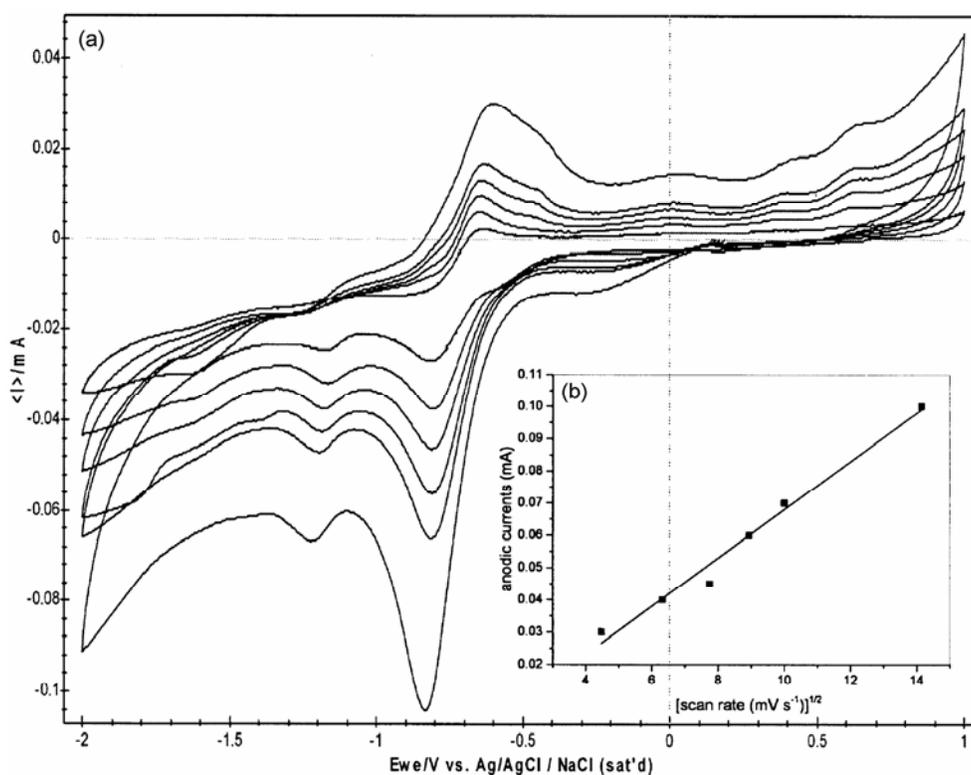


Fig. 1 — (a) Cyclic voltammograms of PANIPI in DMF at different scan rates (20, 40, 60, 80, 100, 200 mV/s) (b) Plot of anodic currents vs square root of scan rate

PANIPI<sup>21</sup>. As the scan rate is increased both the anodic and cathodic peak currents increase, thereby suggesting the reversibility of the redox couple<sup>22,23</sup>. The transport characteristics of PANIPI are investigated by plotting anodic currents (mA) at -0.8V vs square root of the scan rate in the range of 20- 200 mV/s (Fig. 1binset). The voltammetric peak currents of PANIPI in DMF are found to be

proportional to the square root of the scan rates as evinced from the linear plot with  $R^2 = 0.979$ . This indicates that the electrode reaction is a controlled diffusion process which is the characteristic feature of PANI<sup>11</sup>. The conductivity<sup>15</sup> of the solid PANIPI measured by four probe method exhibits ohmic behaviour and falls in the “metallic regime” ( $\sigma = 1.5 \text{ S cm}^{-1}$ ).

### Structural morphology

The conformation and structural morphology of the PANIPI resin are ascertained from viscosity, SEM and TEM analysis.

### Viscosity

Generally, the viscosity of PANI solutions is influenced by the nature of the solvent, polymer concentrations, pH and conformational changes in the polymer<sup>24</sup>. In the present work, the reduced viscosity  $\eta_{sp}/C$  (Fig. 2) is plotted against different concentrations of PANIPI ( $0.4 - 4.0 \times 10^{-3}$  g/dL) in DMF.  $\eta_{sp}/C$  decreases steeply with increasing concentration indicating the presence of random coil conformation<sup>25</sup> in PANIPI. Conformational changes from random coil to compact coil occur on dilution as evidenced from the break in the viscosity plot. The molecular weight of PANIPI calculated using Mark-Houwink equation  $[\eta] = 1.2 \times 10^{-2} M_w$  is  $33,925 \text{ g mol}^{-1}$  assuming  $\alpha = 1$  for spherical entities. This result is consistent with the molecular weights reported in literatures<sup>25,26</sup>.

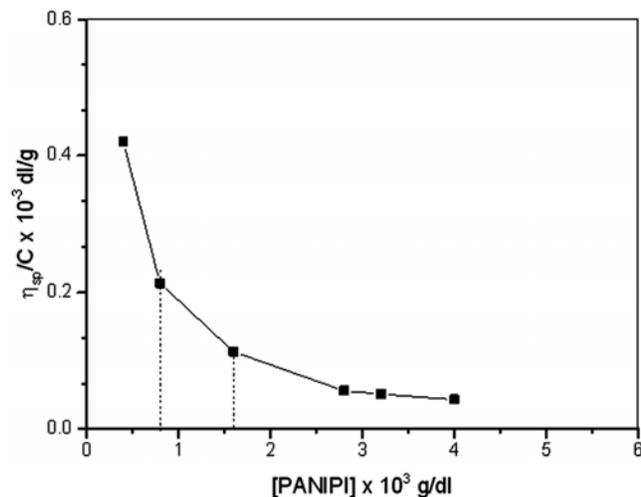


Fig. 2 — Viscosity plot for PANIPI in DMF

### SEM

The SEM micrograph (Fig. 3a) shows aggregation<sup>27</sup> with granular morphology probably due to the amphiphilic nature of PANIPI resulting in spherical entities similar to micelles.

### TEM

The morphological changes, aggregation state and size of PANIPI are analysed using TEM. The TEM images reveal the size of the PANIPI  $< 100 \text{ nm}$ . The TEM micrograph (Fig. 3b) reveals that PANIPI exist as aggregates. Generally, aggregation result in dense packing of disordered spheres with fractal geometry<sup>28</sup>. It has also been reported by Wu *et al.*<sup>29</sup> and Jin *et al.*<sup>30</sup> that fractal structures are present in the TEM images of polyaniline dispersions. Fractal structures are loose structures which are scale invariant at different scales. Polymers with these structures have been known to exhibit superior properties for adsorption, ion exchange of substances, filtration and membrane separation of compound<sup>31</sup>. The presence of such loose structures (fractal) in PANIPI may be the reason for the observed conformational changes in viscosity measurements. Further, the dopant picrate ion renders hydrophilicity to the PANI matrix resulting in spatial flexibility and transport character similar to micelles. Hence PANIPI should be a novel sorbent material for the sorption of potassium and sodium salts.

### Sorption Isotherms

A novel sorbent needs to establish equilibrium with sorbate for the prediction of sorption parameters. Generally, sorption isotherms describe the mechanistic pathways involved in this equilibrium.

When PANIPI is equilibrated with potassium salts of different concentrations for sufficient time, a state of dynamic equilibrium is established thereby clearly depicting that both sorption and desorption process (Scheme 1) are facilitated on the PANIPI resin.

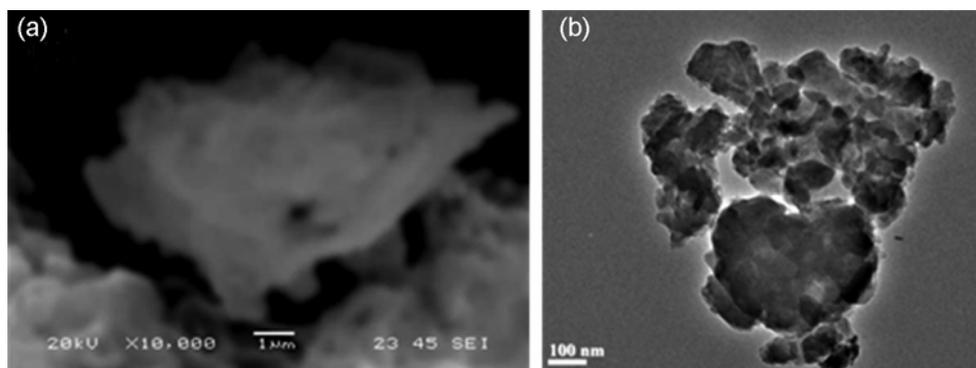
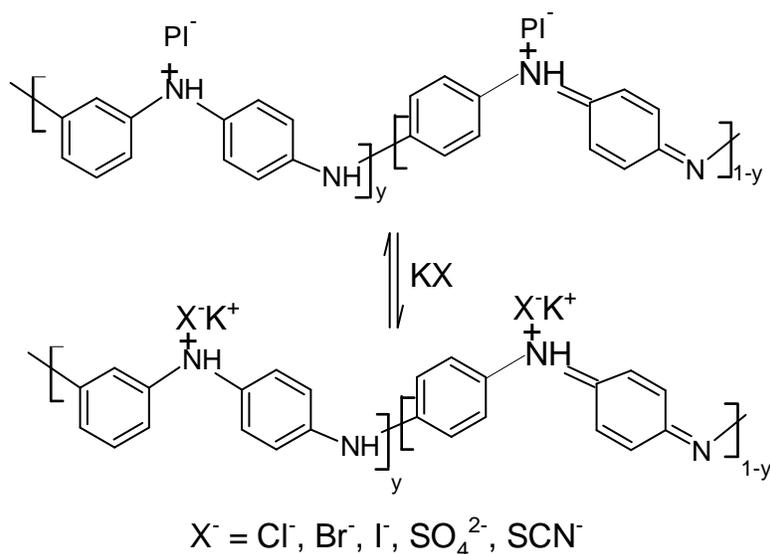


Fig. 3 — (a) SEM and (b) TEM images of PANIPI



Scheme 1 — Sorption process of potassium salts on PANIPI

Langmuir, Freundlich, Dubinin-Radushkevich, Temkin and Redlich Peterson isotherm models are used to evaluate the sorption process of PANIPI on potassium salts.

#### Langmuir Isotherm

This isotherm describes the quantitative formation of a homogenous monolayer adsorption onto a surface containing a finite number of identical sites<sup>32</sup> and the equilibrium distribution of ions between solid and liquid phases. The model also assumes uniform energies of sorption onto the surface and no transmigration of sorbate in the plane of the surface. The mathematical expression in its linear form is given in eqn (1)

$$\frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \quad \dots (1)$$

The Langmuir constants such as  $K_L$  (L/mg) and  $q_m$  (mg/g) are calculated from the slope and intercept of the plot,  $1/q_e$  vs  $1/C_e$  and presented in Table 1. The relative affinity of anions is in the order  $\text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{SO}_4^{2-}$  based on the maximum adsorption capacity ( $q_m$ ) for the sorption process. The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter referred as separation factor ( $R_L$ )<sup>33</sup> a dimensionless constant, calculated using eqn (2)

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots (2)$$

The  $R_L$  values for sorption of potassium salts on PANIPI is in the range of 0.603-0.939 fulfilling the Langmuir isotherm condition of  $0 < R_L < 1$  (Table 1). Hence, monolayer formation of anions is envisaged to take place on the surface of PANIPI.

#### Thermodynamic Studies

The Gibbs free energy of adsorption<sup>34</sup> ( $\Delta G^\circ$ ) of potassium salts on PANIPI is calculated from Langmuir constant ' $K_L$ ' using eqn (3)

$$\Delta G^\circ = -RT \ln K \quad \dots (3)$$

where  $R$  is the universal gas constant,  $T$  is the absolute temperature in Kelvin and  $K$  is the reciprocal of Langmuir constant  $K_L$ . The negative values of  $\Delta G^\circ$  (Table 1) indicate that the sorption process is spontaneous.

#### Freundlich Isotherm

Freundlich adsorption isotherm<sup>35</sup>, describes the non-ideal and reversible adsorption on heterogeneous surfaces. The main advantage of this isotherm is that the sorption process can follow both monolayer and multilayer adsorption.<sup>36</sup> A linear form of this isotherm is expressed as in eqn (4),

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \dots (4)$$

The slope and intercept of the Freundlich plot of  $\log q_e$  vs  $\log C_e$  namely  $n$  and  $K_F$  (Table 1), show that this model is also obeyed for the sorption of

potassium salts on PANIPI since ion pairing may occur at varying concentrations. It may be concluded that initially monolayer facilitates sorption followed by multilayer sorption of potassium salts on the surface of PANIPI. Further sorption isotherm models such as Dubinin-Radushkevich, Temkin and Redlich Peterson isotherms are also tested for the sorption process.

#### Dubinin-Radushkevich Isotherm

This isotherm<sup>37</sup> is an empirical model expressed as in eqn (5) is applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogenous surface.

$$\log q_e = \log q_s - (B_{DR} \varepsilon^2) \quad \dots (5)$$

This model is applied to distinguish the physical and chemical adsorption of ions<sup>38</sup>. When logarithm of amount adsorbed ( $q_e$ ) are plotted vs the square of the potential energy ( $\varepsilon^2$ ), all the suitable data should lie on the same curve, named as the characteristic curve. The constants such as  $B_{DR}$  and  $q_s$ , the amount adsorbed (mg/g), are calculated from the slope and intercept of the plot (Table 2). The mean free energy  $E$  per molecule of adsorbate for removing a molecule from its location in the sorption space to the infinity can be computed by using the eqn (6)

$$E = \left[ \frac{1}{\sqrt{2B_{DR}}} \right] \quad \dots (6)$$

The mean free energies for the sorption of all the potassium salts on PANIPI using eqn (6) are less than 8 kJ mol<sup>-1</sup> (Table 2) indicating that physisorption play a significant role in the sorption process.

#### Temkin Isotherm

This isotherm takes into account the sorbent-sorbate interactions<sup>39</sup>. This model eqn (7) assumes that the heat of adsorption of all the molecules in the adsorbed layer would decrease linearly with coverage<sup>40</sup>.  $K_T$  the equilibrium binding constant (L/mg) and  $b_T$  the Temkin constant related to energy of adsorption (kJ/mol) are calculated from the slope and intercept of the plot,  $q_e$  vs  $\log C_e$ . The low  $b_T$  values obtained in the present study (Table 2) are indicative of physisorption. The  $K_T$  values are all in the range of 5 L/mg except for potassium sulphate which is 3.805 L/mg. The low value of sulphate may be due to its hydrophilicity. The low values of  $b_T$  suggest weak interactions between sorbate and

sorbent supporting ion exchange mechanism<sup>41</sup> for the present study. The sorption process fits well for Temkin isotherm model as inferred from  $R^2$  and S.D. values (Table 2).

$$q_e = \frac{RT}{b_T} \ln K_T + \frac{RT}{b_T} \ln C_e \quad \dots (7)$$

#### Redlich-Peterson Isotherm

Redlich-Peterson isotherm<sup>42</sup> is a hybrid isotherm featuring Langmuir and Freundlich models, which incorporate three parameters into an empirical equation. The linear dependence of this model over a wide concentration range can be applied either in homogenous or heterogeneous system due to its versatility. The linear form of this equation is expressed in eqn (8)

$$\frac{C_e}{q_e} = \frac{1}{K_{RP}} + \frac{\alpha_{RP}}{K_{RP}} C_e^\beta \quad \dots (8)$$

where  $K_{RP}$ ,  $\alpha_{RP}$  and  $\beta$  are Redlich constants. These constants can be predicted from the plot between  $C_e/q_e$  vs  $C_e^\beta$ . In order to relate the three unknown parameters  $K_{RP}$ ,  $\alpha_{RP}$  and  $\beta$  a minimization procedure is adopted to maximize the coefficient of determination,  $R^2$ . However, the low value of  $R^2$  (Table 2) indicate that this model is not suitable for the potassium salt exchange on PANIPI.

#### Sorption at high concentration

Langmuir isotherm indicates that the sorption process should be complete at high concentration of sorbate. In order to explore this phenomenon, the ion exchange between potassium salts on PANIPI is attempted at a high salt concentration (2 M). At this concentration, the pH of the potassium salt solutions changed with a rapid fall in pH. The  $K_{PI}^{X-}$  values determined from the midpoints of the pH variation curves are presented in Table 3. It is interesting to note that the equilibrium constants for the sorption process at high concentration for all the potassium salts are lower ( $K_F = 10^{-7} - 10^{-8}$ ) compared to the Freundlich constants ( $\sim 10^{-3}$ ). This may be due to the adsorption of potassium salts as ion-pairs. The separation factor  $\alpha$  calculated from Eqn (9) are presented in Table 5.

$$\alpha = \frac{\text{concentration of ions in the resin phase}}{\text{concentration of ions in the solution phase}} \quad \dots (9)$$

The  $\alpha$  values observed in the range of 0.7-5.97 indicate that PANIPI is able to discriminate the

various anions and act as an effective sorbent for potassium salts even at high concentrations.

#### Sorption mechanism

Based on the above results a tentative mechanism is proposed for the sorption process. The sorption process is accompanied by the release of picrate ions due to the entry of potassium salts as ion-pairs (Scheme 1). The relation<sup>43</sup> between the equilibrium concentrations and hydrogen ion concentrations in the ion exchange phenomenon is represented by Eqn (10).  $[N^+]$  is used to designate the concentration of quinoid forms and  $[-N=]$  represents the concentration of the benzenoid forms in PANI resins.

$$\frac{[N^+]}{[-N=]} = K[H^+]^2 \quad \dots (10)$$

The ratio of intensities (Q/B) of the UV-Visible spectral bands (Table 3) of the PANIPI resin in DMF after ion exchange is used to get  $\frac{[N^+]}{[-N=]}$  ratio. The

presence of picrate ion on the surface of PANI renders hydrophilicity to PANIPI resin and the ions are attracted towards the PANI surface. The anions bind to the imine sites and the hydrogen atoms on the NH groups present in between the benzenoid units, while the potassium ions move towards the picrate ions released into the solution. This phenomenon can be inferred from changes in the stretching frequencies of the NH group at  $3200\text{ cm}^{-1}$  and C-N-C bending vibrations in the IR spectra of the PANIPI after sorption. The sorption of ions initially occurs as a monolayer as inferred from the results of Langmuir isotherm model. Multilayer formation on PANI surface may take place subsequently due to ion pairing. Further, Temkin isotherm model ( $R^2=0.99$ ) indicates that ion exchange is the favoured mechanism in the sorption process.

#### Structural characterization after sorption

##### UV-Visible spectra

The ionochromic effects are unprecedented in polyaniline chemistry. The shifts in  $\lambda_{\text{max}}$  values are

dependent upon both the metal ions and the associated anions<sup>24</sup>. The spectra obtained after exchange of potassium ions exhibit slight bathochromic shifts of benzenoid and hypsochromic shifts of quinoid bands due to the changes in the PANIPI structure. PANIPI is found to possess 70% benzenoid forms and 30% quinoid forms (Table 3). After sorption process the PANI resins obtained contain lower percentages of benzenoid and slightly higher percentages of quinoid moieties.

##### FT-IR spectra

The changes in the IR spectral bands of PANIPI after sorption process (Table 4) confirm the presence of respective ions on the PANI matrix. The ion sensitive bands at  $3425$  and  $3246\text{ cm}^{-1}$  corresponding N-H stretching vibrations undergo red and blue shifts respectively, depending on the type of ions used. The absorption patterns around  $3000-2900\text{ cm}^{-1}$  are much affected due to sorption of ions. The bands around  $2400\text{ cm}^{-1}$  confirm the existence of emeraldine salt structure. The peaks at  $1588$  and  $1491\text{ cm}^{-1}$  corresponding to quinoid and benzenoid rings are not much affected due to sorption. The C-N stretching vibrations at  $1300\text{ cm}^{-1}$  are only slightly shifted due to ion exchange. The bending vibrations at  $1137\text{ cm}^{-1}$  and around  $800-500\text{ cm}^{-1}$  are greatly affected due to the incorporation of anions. The presence of anion stretching vibrations in their respective wave numbers confirm the existence of anions in the PANI matrix; particularly the emergence of a new intense band at  $2066\text{ cm}^{-1}$  and around  $744\text{ cm}^{-1}$  are assigned to SCN and CS stretching vibrations<sup>44</sup>. The shifts in the bending vibrations around  $585$  and  $504\text{ cm}^{-1}$  in PANIPI-KSCN sorption process clearly depicts the presence of SCN<sup>-</sup> (Fig. 4a) on PANI skeleton making PANIPI a suitable material to detect SCN<sup>-</sup> quantitatively.

##### Detection of SCN<sup>-</sup>

Sensing is accomplished by monitoring the intensities of the SCN<sup>-</sup> ion at  $2066\text{ cm}^{-1}$  (Fig. 4a). This SCN<sup>-</sup> stretching vibration is not very much disturbed by the PANIPI backbone and other anionic vibrations.

Table 5 — A comparison of ion exchange characteristics of sodium and potassium salts on PANIPI

Sorption parameters	#Sodium salts				Potassium salts				
	NaF	NaCl	NaBr	Na <sub>2</sub> SO <sub>4</sub>	KCl	KBr	KI	K <sub>2</sub> SO <sub>4</sub>	KSCN
q <sub>m</sub> (mg/g)	12.48	26.74	15.34	1.80	7.15	31.55	98.72	3.57	103.15
*IEC (meq/g)	2.00	2.71	2.23	1.96	1.99	2.04	1.71	1.64	2.13
α	3.52	0.74	1.82	3.38	0.70	3.78	1.11	5.97	5.11

\*  $IEC = \frac{C_0 - C_e}{W} V$  (meq/g)

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This behaviour helps in facilitating the use of PANIPI for quantitative determination of  $\text{SCN}^-$  in aqueous solution. The intensity of the vibration is directly proportional to the concentration of  $\text{SCN}^-$  ions (Fig. 4b inset) adsorbed by the PANIPI resin with a good linearity of the calibration curve for five different concentrations ( $R^2 = 0.997$ ) with a detection limit of 0.1 - 2 M for  $\text{SCN}^-$  concentration.

#### Potassium to sodium selectivity

The cation adsorption selectivity of PANIPI is investigated in detail for potassium and sodium salts using anions as control. In order to study the selectivity of PANIPI towards sodium and potassium salts, the maximum amount adsorbed ( $q_m$ ) is plotted against charge to anion radius ratio ( $r/nq$ ) at low concentrations (Fig. 5). A linear trend is observed for potassium salts in contrast to sodium salts<sup>14</sup> where a curvature is obtained. The preferential selectivity of the potassium salts rather than sodium salts is well differentiated from the slopes of the plots which are  $\sim 200$  and  $\sim 100$  respectively. Similarly at high concentrations also, the plot of  $\log Q/B$  vs  $pH$  (Fig. 6) is found to be linear for potassium salts (slope = 0.13) while for sodium salts a curvature is obtained (slope = 0.081). The observed K-Na selectivity of two is due to the relatively small hydrated radius of potassium ions (3.31 Å) compared to sodium ions (3.58 Å). Due to the differences in the sizes the cations  $\text{K}^+$  and  $\text{Na}^+$  are adsorbed to the PANIPI with different strengths. The relatively small hydrated potassium ions are strongly adsorbed to the PANIPI than the hydrated sodium

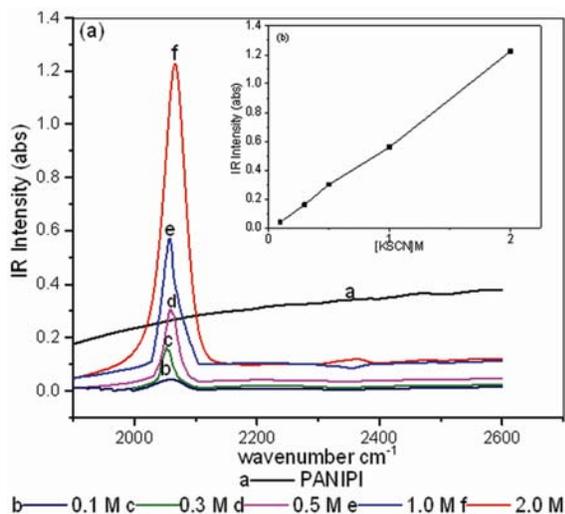


Fig.4 — (a) A typical FT-IR spectra of  $\text{SCN}^-$  adsorbed on PANIPI at  $\nu = 2066 \text{ cm}^{-1}$  (b- inset) Linear response of IR intensity with  $\text{SCN}^-$  concentration

ions which preferentially tend to remain in solution. A similar trend is observed at high concentrations also for the separation factors ( $\alpha$ ), particularly for bromide and sulphate salts (Table 5). Thus PANIPI is a novel sorbent for alkali metal salts and may find potential application as a sensor.

The dopant picric acid makes PANIPI chromogenic, electroactive and hydrophilic while the released picric acid after ion exchange is colored, acidic and soluble in aqueous solution. The polymer matrix renders insolubility and binds to anions and cations through the imine and amine sites. All the results point towards ion exchange mechanism operating during the sorption of potassium and sodium salts on PANIPI resin

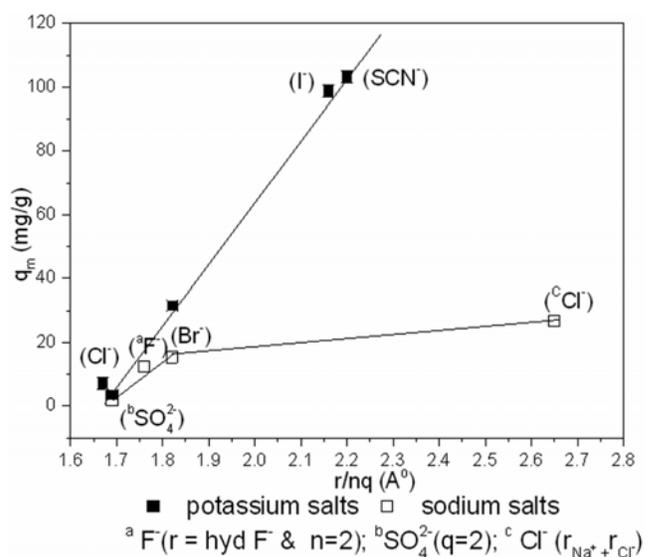


Fig. 5 — Dependence of sorption potential ( $q_m$ ) vs charge to radius ratio ( $nq/r$ ) for potassium and sodium salts

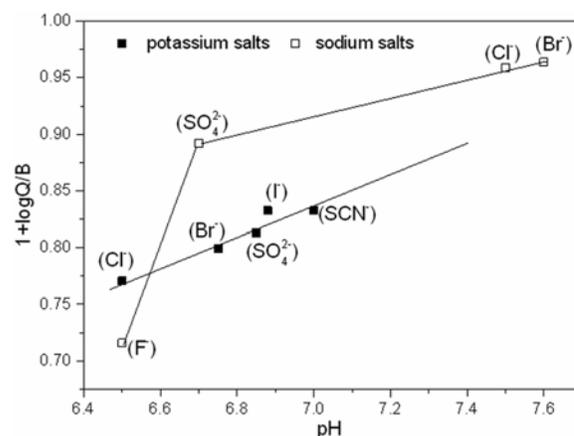


Fig. 6 —  $\log Q/B$  vs  $pH$  of PANIPI resin after exchange for potassium and sodium salts

## Conclusion

Anion exchange is the predominant phenomenon during sorption. Anions of potassium salts are exchanged for the picrate ion present as dopant on the PANI matrix. PANIPI prepared by chemical oxidative polymerisation has been characterized by several techniques such as UV-Visible, FT-IR, SEM, TEM, cyclic voltammetry, conductivity, viscosity and flame photometry. The exchange process is followed by measuring the concentrations of the anions and cations in the solution and resin phase by suitable spectral studies. Among the five isotherm models tested, Langmuir, Freundlich and Temkin models fitted well for the sorption process. The maximum amount adsorbed ( $q_m$ ) depends on the size of the anions. The remarkable ability of PANIPI to sense potassium salts rather than sodium salts (2:1) may be due to the presence of the dopant picrate ion. This dopant makes PANIPI an electroactive and hydrophilic resin. Picric acid released into the solution after ion exchange is acidic and soluble in aqueous solutions. The polymer matrix is insoluble and the amine and imine sites on PANI skeleton binds to the ions causing structural changes on the polymer. Thus PANIPI can be considered as a novel sorbent for alkali metal salts and possess potential application as a sensor for these electrolytes.

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