

# Cation-Exchange Kinetics and Electrical Conductivity Studies of An 'Organic-Inorganic' Composite Cation-Exchanger: Polypyrrole Th(IV) Phosphate

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**ABSTRACT:** Polypyrrole Th(IV) phosphate, an electrically conducting 'organic-inorganic' cation-exchange composite material was prepared by the incorporation of an electrically conducting polymer, i.e., polypyrrole, into the matrix of a fibrous type inorganic cation-exchanger thorium(IV) phosphate. The composite cation-exchanger has been of interest because of its good ion-exchange capacity, higher chemical and thermal stability, and high selectivity for heavy metal ions. The temperature dependence of electrical conductivity of this composite system with increasing temperatures was measured on compressed pellets by using four-in-line-probe dc electrical conductivity measuring instrument. The conductivity values lie in the semiconducting region, i.e., in the

order of  $10^{-6}$  to  $10^{-4}$  S  $\text{cm}^{-1}$  that follow the Arrhenius equation. Nernst-Planck equation has been applied to determine some kinetic parameters such as self-diffusion coefficient ( $D_0$ ), energy of activation ( $E_a$ ), and entropy of activation ( $\Delta S^*$ ) for Mg(II), Ca(II), Sr(II), Ba(II), Ni(II), Cu(II), Mn(II), and Zn(II) exchange with  $\text{H}^+$  at different temperatures on this composite material. These results are useful for predicting the ion-exchange process occurring on the surface of this cation-exchanger. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 2806–2815, 2007

**Key words:** organic-inorganic composite material; cation-exchanger; electrical conductivity; ion-exchange kinetics

## INTRODUCTION

The possibility of combining the properties of organic and inorganic compounds in a unique material is an old challenge. Actually, research on hybrid organic/inorganic materials is an expanding area in the material science.<sup>1–10</sup> Therefore, organic-inorganic composite materials are of intensive interest in the field of contemporary materials chemistry as these materials can exhibit synergetic extraordinary properties such as electrical, magnetic, and optical properties,<sup>11</sup> which arise from the synergism between the properties of the organic and inorganic components. Thus, these materials have gained much interest because of their remarkable change in properties such as mechanical,<sup>12</sup> thermal,<sup>13–16</sup> electrical,<sup>17</sup> and magnetic<sup>18</sup> when compared with pure organic polymers. Additionally, the properties of the composite materials depend upon the morphology of the phases, *viz.* organic and/or inorganic network, which has to be controlled over several length scales. Therefore, the development of such materials is a 'land of multidisciplinary,'<sup>1</sup> where chem-

ists, physicists, material scientists, and engineers have to work closely together to fully exploit this technical opportunity for creating new materials and devices.

One important class of hybrid materials is that in which the inorganic fraction is composed of conducting polymers, in which new inorganic lattice structures are formed, resulting from cooperative interactions between the organic and inorganic components. In all cases, there is possibility of developing new materials with properties not seen in purely organic or purely inorganic solids. In recent past, such materials have shown excellent ion-exchange properties.<sup>19–21</sup> Composite materials consisting of conducting polymers have an additional advantage in making ion-selective membrane electrodes.<sup>22,23</sup>

Kinetic studies are helpful in understanding the ion-exchange mechanism undergoing in a particular system on the basis of rate of exchange<sup>24–28</sup> using Nernst-Planck equation<sup>29–31</sup> with some additional assumptions. In the present research work, kinetic study of some divalent metal ions on polypyrrole Th(IV) phosphate has been performed to understand its ion-exchange mechanism. As a result, some useful physical parameters such as self-diffusion coefficient ( $D_0$ ), energy of activation ( $E_a$ ), and entropy of activation ( $\Delta S^*$ ) have been determined. Electrical conductivity properties have also been studied in the present work.

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## EXPERIMENTAL

### Reagents and instruments

The reagents used for the synthesis of material were obtained from CDH, E- Merck and Qualigens (India). All other reagents and chemicals were of analytical reagent grade. A four-in-line probe dc electrical conductivity-measuring instrument, Scientific Equipment (India), was used for measuring dc electrical conductivity. A hydraulic pressure instrument was used for making pellets of sample materials. A water bath incubator shaker having a temperature variation of  $\pm 0.5^\circ\text{C}$  was used for all equilibrium studies.

### Preparation of polypyrrole Th(IV) phosphate

The 'organic-inorganic' electrically conducting composite cation-exchanger was synthesized as reported earlier,<sup>32</sup> in which inorganic precipitate was prepared by mixing a solution of 0.1M  $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$  prepared in 1M  $\text{HNO}_3$  at the flow rate of  $0.5 \text{ mL min}^{-1}$  to a solution of 2M  $\text{H}_3\text{PO}_4$  prepared in DMW (demineralized water) at a temperature of  $85 \pm 5^\circ\text{C}$ . Constant stirring was done during mixing using a magnetic stirrer and a white gel type slurry was obtained. After digestion of the mixture for several hours, it was cooled to room temperature. In the digested slurry of inorganic precipitate of Th(IV)

phosphate, 0.1M  $\text{FeCl}_3$  solution prepared in DMW was mixed thoroughly, to which  $\sim 33.33\%$  (v/v, in toluene) solution of pyrrole was added dropwise and mixed thoroughly, continuous stirring was done during the addition of pyrrole solution. The white inorganic precipitate gel slowly turned first to green and then to black. The reaction mixture was kept for 24 h under ambient condition ( $25 \pm 2^\circ\text{C}$ ). Now the polypyrrole based composite gel was filtered off, washed thoroughly with DMW to remove excess acid and any adhering trace of ferric chloride. The washed gel was then dried over  $\text{P}_4\text{O}_{10}$  at  $30^\circ\text{C}$  in an oven. The dried product was immersed in DMW to obtain small granules. These were converted to the  $\text{H}^+$ - form by placing them in 1M  $\text{HNO}_3$  for 24 h with occasional shaking intermittently, replacing the supernatant liquid with a fresh acid. The excess acid was removed after several washings with DMW and again the material was dried at  $40^\circ\text{C}$  and sieved to obtain particles of particular size range ( $\sim 125 \mu\text{m}$ ). The sample (S-1) prepared with  $\sim 33.33\%$  pyrrole solution showed high stability and maximum ion-exchange capacity (1.56 meq dry/g for  $\text{Na}^+$ ), was chosen for detailed studies of electrical conductivity and ion exchange kinetics. Conditions of preparation and the ion-exchange capacity of polypyrrole Th(IV) phosphate composite cation-exchange material (sample S-1) are given below:

Sample	Mixing volume ration (v/v)			0.1 M $\text{FeCl}_3$	Pyrrole in toluence (33.33%)	Appearance of the beads after drying	$\text{Na}^+$ Ion-exchange capacity (meq dryg <sup>-1</sup> )
	0.1 M $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ in 1 M $\text{HNO}_3$	2 M $\text{H}_3\text{PO}_4$	Digestion time (h)				
S-1	5	2	5	2	0.30	Blackish granular	1.56

### Electrical conductivity measurements

The composite samples were treated with 0.5M aqueous solution of HCl and washed repeatedly with DMW to remove excess HCl until the filtrates gave a negative test for hydrogen ions. The sample materials were dried completely at  $50^\circ\text{C}$  in the oven. Then  $\sim 0.5 \text{ g}$  material from each sample was finely grounded in a mortar pastel and pellets were made at room temperature with the help of a hydraulic pressure instrument at 25 kN pressure for 20 min. The thickness of each pellet was measured by a micrometer.

Four-probe electrical conductivity measurements with increasing temperatures (between  $30$  and  $140^\circ\text{C}$ ) for the composite cation-exchanger 'polypyrrole Th(IV) phosphate' samples were performed on pressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring technique. The sample to be tested was placed on the base plate of the four-probe arrangement

and the probes were allowed to rest in the middle of the sample. A very gentle pressure was applied on the probes and then it was tightened in this position so as to avoid piercing the samples by the probes. The arrangement was placed in the oven. The current was passed through the two outer probes and the floating potential across the inner pair of probes was measured. The oven supply was then switched on, the temperature was allowed to increase gradually, and the current and voltage were recorded with rise in temperature.

The current-voltage data so generated by a 4-in-line probe dc electrical conductivity measuring instrument was processed for calculation of resistivity ( $\rho_o$ ), using the following equation:

$$\rho_o = (V/I) \times 2\pi S \quad (1)$$

where  $V$  is the voltage (V) and  $I$  is the current (A).

Because the thickness of the sample is small when compared with the probe distance and so a correc-

tion factor has to be applied for it and the corrected resistivity may be calculated as:

$$\rho = \rho_0 / G_7(W/S) \quad (2)$$

where  $\rho$  is the corrected resistivity in  $\Omega$  cm,  $G_7(W/S)$  is the correction factor used in the case of nonconducting bottom surface and it is a function of  $W$ , thickness of the sample under test (cm) and  $S$ , probe spacing (cm); i.e.,

$$G_7(W/S) = (2S/W) \log_e 2 \quad (3)$$

Thus, the electrical conductivity ( $\sigma$ ) was calculated using the following equation:

$$\sigma = 1/\rho \quad (4)$$

where  $\sigma$  is the electrical conductivity in  $S \text{ cm}^{-1}$ .

This composite material was also treated with 0.5M NaCl, KCl, LiCl, CaCl<sub>2</sub>, Pb(NO<sub>3</sub>)<sub>2</sub>, MnCl<sub>2</sub>, and Cu(NO<sub>3</sub>)<sub>2</sub> solutions, and electrical conductivity measurements were carried out on different forms (Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Mn<sup>2+</sup>, and Cu<sup>2+</sup>) of composite cation-exchanger.

The isothermal stability of polypyrrole Th(IV) phosphate composite in terms of dc electrical conductivity retention was carried out on the selected samples (treated with 0.5M HCl) at 50, 70, 90, 110, and 130°C in an air oven. The electrical conductivity measurements were carried out at an interval of 15 min. The thermal stability of the composite material in terms of dc electrical conductivity retention was also studied by a cyclic measurement of the dc electrical conductivity on pressed pallets with increasing temperature from 30 to 200°C. The measurements were repeated on the same sample in this temperature range for five times at intervals of 45 min.

### Kinetic measurements

The composite cation-exchange material was treated with 0.5M HNO<sub>3</sub> for 24 h at room temperature with occasional shaking; intermittently replacing the supernatant liquid with a fresh acid to ensure the complete conversion to H<sup>+</sup>-form and the excess acid was

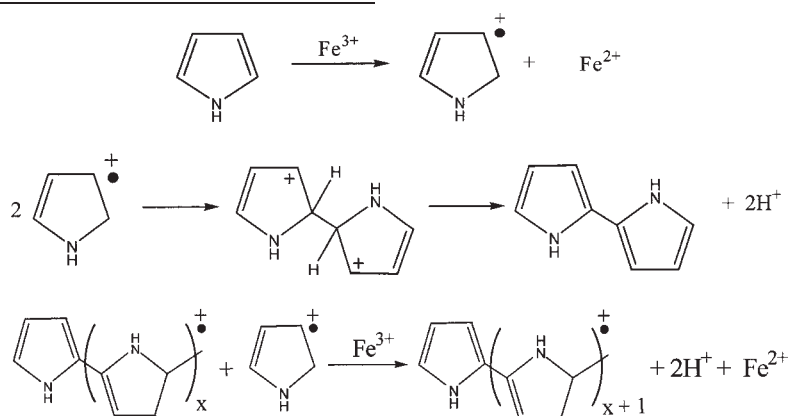
removed after several washing with DMW. Now the dried ion-exchanger sample in the H<sup>+</sup>-form was grounded and then sieved to obtain particles of definite mesh sizes (25–50, 50–70, 70–100, and 100–125  $\mu\text{m}$ ). Out of them, the particles of mean radii  $\sim 125 \mu\text{m}$  (50–70 mesh) were used to evaluate various kinetic parameters. The rate of exchange was determined by limited bath technique as follows:

Twenty milliliter fractions of the 0.02M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn, and Zn) were shaken with 200 mg of the cation-exchanger in H<sup>+</sup>-form in several stoppered conical flasks at desired temperatures [25, 33, 50, and 65 ( $\pm 0.5$ )°C] for different time intervals (0.5, 1.0, 2.0, 3.0, and 4.0 min). The supernatant liquid was removed immediately and determinations were made usually by EDTA titrations.<sup>33</sup> Each set was repeated four times and the mean values were taken for calculations.

## RESULTS AND DISCUSSION

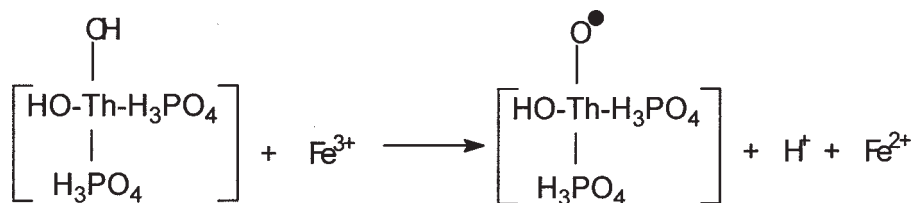
### Preparation and electrical conductivity measurement studies of polypyrrole Th(IV) phosphate

For this study, sample of polypyrrole Th(IV) phosphate, an electrically conducting composite cation-exchanger was chemically prepared by incorporation of polypyrrole, a conducting polymer into inorganic matrices of fibrous type Th(IV) phosphate. The sample prepared with  $\sim 33.33\%$  pyrrole solution showed high chemical, mechanical, and thermal stability<sup>32</sup> and maximum ion-exchange capacity (1.56 meq dry/g for Na<sup>+</sup>),<sup>32</sup> was selected for detailed studies of electrical conductivity and ion-exchange kinetics. The polymerization reaction for the synthesis of polypyrrole is a very complicated one. The initial oxidation step, in which a radical cation is formed is followed by a coupling reaction, deprotonation, and one-electron oxidation to regenerate the aromatic system,<sup>34</sup> using FeCl<sub>3</sub> in aqueous medium at room temperature ( $25 \pm 2^\circ\text{C}$ ) as given in the following reactions:

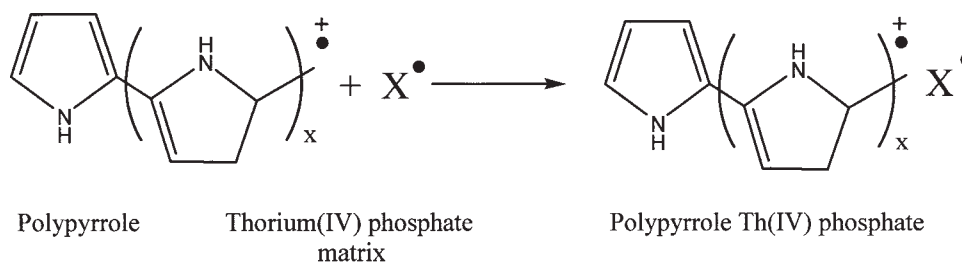


When aqueous solution of  $\text{FeCl}_3$  was added with the inorganic precipitate of thorium(IV) phosphate,  $\text{Fe}^{3+}$

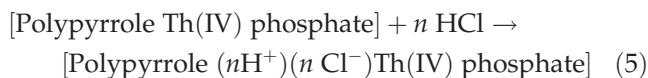
may convert thorium phosphate into a radical that can be shown as:



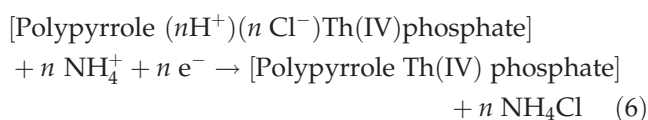
Hence, the binding of polypyrrole into the matrix of thorium(IV) phosphate can be shown as:



This composite material contains two components, *viz.* inorganic and organic. The inorganic component is an efficient ion-exchange material whereas organic component, polypyrrole, is a good electrically conducting polymer. The dc electrical conductivity of composite is because of the presence of sufficient amount of the conducting polymer and basically, it is electronic conduction contributed by the conducting component, i.e., polypyrrole by the charge-transfer reaction between polypyrrole component of the composites and doping agents, HCl.



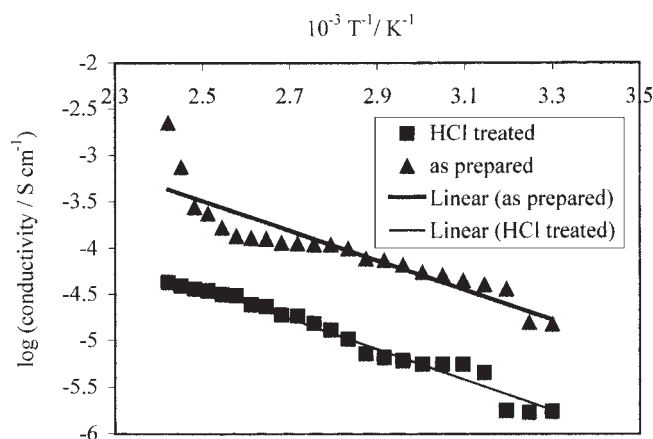
Controlling the doping process, the electrical conductivity of these materials could be varied from insulator, through semiconductor to metal range. A redox reaction for ammonia and amine intercalation into layered chalcogenides has been reported by Schöllhorn and Zagefka<sup>35</sup> and further supported by the work of Foot and Shake.<sup>36</sup> Thus, the neutralization reactions to undope polypyrrole within polypyrrole Th(IV) phosphate composite cation-exchange material by ammonia may be suggested as given below:



In the present study, the variations of electrical conductivity ( $\sigma$ ) of the polypyrrole Th(IV) phosphate composite samples (as prepared and doped with HCl and prepared with 33.33% pyrrole concentration, vol %) by

raising temperatures (between 30 and 140°C) are carried out. On examination, it was observed that the electrical conductivity of the samples increase with the increase in temperature and the values lie in the order of  $10^{-6}$  to  $10^{-4} \text{ S cm}^{-1}$ , i.e., in the semiconductor region. To determine the nature of dependence of electrical conductivity on temperature, plots of  $\log \sigma$  versus  $10^3 T^{-1} (\text{K}^{-1})$  were drawn (Fig. 1) and they followed Arrhenius equation similar to other semiconductors.<sup>37</sup>

The dependence of the electrical conductivity through the bi-phasic systems (polypyrrole Th(IV) phosphate composites; prepared with different concentrations of pyrrole monomer) on the concentration of conducting phase, i.e., polypyrrole was also examined (Table I). A slight increase in electrical conductivity for the composite is followed at a certain pyrrole concentration by a sudden jump, which is again followed by moderate



**Figure 1** Arrhenius plots for polypyrrole Th(IV) phosphate composite material.

**TABLE I**  
**Values of dc Electrical Conductivity for the Polypyrrole and Polypyrrole Th(IV) Phosphate Composites with Different Concentrations of Pyrrole Monomer**

Sample No.	Polypyrrole (prepared with 33.33% pyrrole in toluene)	Polypyrrole Th(IV) phosphate	
	Ambient temperature dc electrical conductivity ( $S\text{ cm}^{-1}$ )	Pyrrole monomer concentration (vol %)	Ambient temperature dc electrical conductivity ( $S\text{ cm}^{-1}$ )
1	$3.28 \times 10^{-5}$	3.33	$4.13 \times 10^{-8}$
2	–	6.66	$5.19 \times 10^{-8}$
3	–	10	$2.82 \times 10^{-8}$
4	–	13.33	$3.84 \times 10^{-8}$
5	–	16.66	$5.92 \times 10^{-8}$
6	–	20	$6.15 \times 10^{-8}$
7	–	23.33	$2.53 \times 10^{-5}$
8	–	26.66	$3.47 \times 10^{-5}$
9	–	30	$3.54 \times 10^{-5}$
10	–	33.33	$3.82 \times 10^{-4}$
11	–	36.66	$4.90 \times 10^{-4}$
12	–	40	$5.16 \times 10^{-4}$

increase (Table I). At about 23.33% pyrrole concentration (critical concentration of conducting phase), this sharp rise in electrical conductivity is observed, which could possibly be explained on the basis of percolation theory.<sup>38</sup> It was also observed that the ambient temperature conductivities of the composite for some concentrations of pyrrole monomers are greater than that of polypyrrole as shown in Table I. The effect on electrical conductivity of the different forms ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Cu}^{2+}$ ), of composite cation-exchanger was also examined (Table II). It was observed that the electrical conductivity was affected negligibly when treated with the metal nitrate solutions of ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ , and  $\text{Ca}^{2+}$ ), while the electrical conductivity of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Mn}^{2+}$  forms were decreased to  $10^{-8}\text{ S cm}^{-1}$  beyond the semiconducting region (Table II).

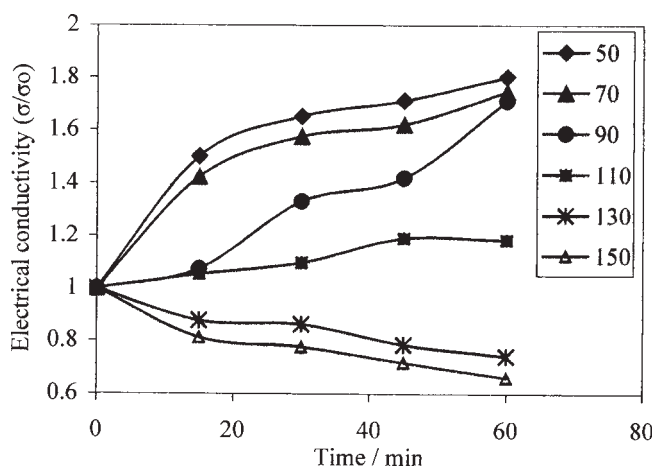
The thermal stability of the composite material (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal condition (at 50, 70, 90, 110, 130, and 150°C) by measuring four-probe-in-line dc electrical conductivity at an interval of 15 min. The

**TABLE II**  
**Four-Probe dc Electrical Conductivity of Different Forms of Polypyrrole Th(IV) Phosphate Composite System at Ambient Temperature (Prepared with 33.33% Pyrrole Monomers)**

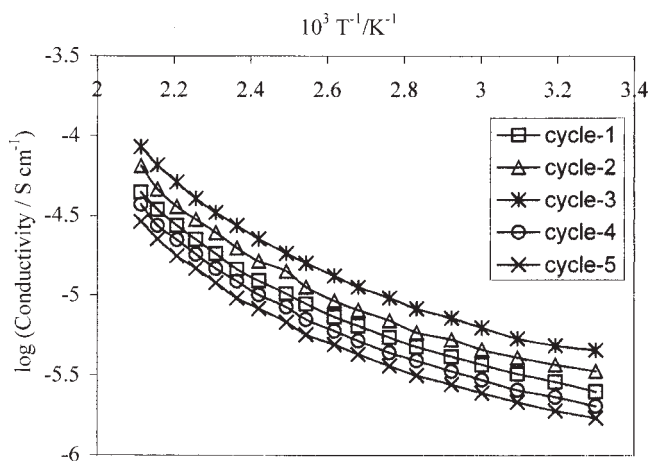
Sample No.	Polypyrrole Th(IV) phosphate composite	Conductivity ( $S\text{ cm}^{-1}$ )
1	As prepared	$1.68 \times 10^{-6}$
2	HCl treated	$1.46 \times 10^{-4}$
3	NaCl treated	$2.27 \times 10^{-5}$
4	KCl treated	$1.25 \times 10^{-5}$
5	LiCl treated	$1.84 \times 10^{-5}$
6	$\text{CaCl}_2$ treated	$1.74 \times 10^{-5}$
7	$\text{Pb}(\text{NO}_3)_2$ treated	$2.04 \times 10^{-8}$
8	$\text{MnCl}_2$ treated	$1.26 \times 10^{-8}$
9	$\text{Cu}(\text{NO}_3)_2$ treated	$2.02 \times 10^{-8}$

electrical conductivity measured with respect to the time of accelerated ageing is presented in Figure 2. It was observed that the electrical conductivity for polypyrrole Th(IV) phosphate composite material is quite stable at 50, 70, 90, and 110°C that supports the fact that the dc electrical conductivity of the composites is sufficiently stable under ambient temperature conditions. The electrical conductivity decreases with time at 130 and 150°C that may be attributed to the loss of dopant and the chemical reaction of dopant with the material.

The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles by repeatedly measuring linear four-probe dc electrical conductivity with increase in temperature at an interval of 45 min and the dc conductivity for each heating cycle was plotted as  $\log \sigma$  versus  $10^3 T^{-1}$  ( $\text{K}^{-1}$ ) as shown in Figure 3. It was observed



**Figure 2** Isothermal stability of polypyrrole Th(IV) phosphate composite (HCl treated) in terms of retention of dc electrical conductivity with respect to time at 50, 70, 90, 110, 130, and 150°C.

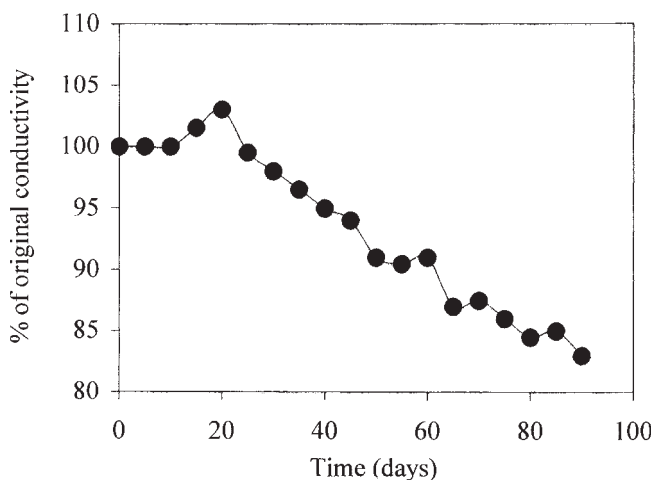


**Figure 3** Arrhenius plots of retention of dc electrical conductivity for polypyrrole Th(IV) phosphate composite (HCl treated) during heating-cooling cycles up to 200°C.

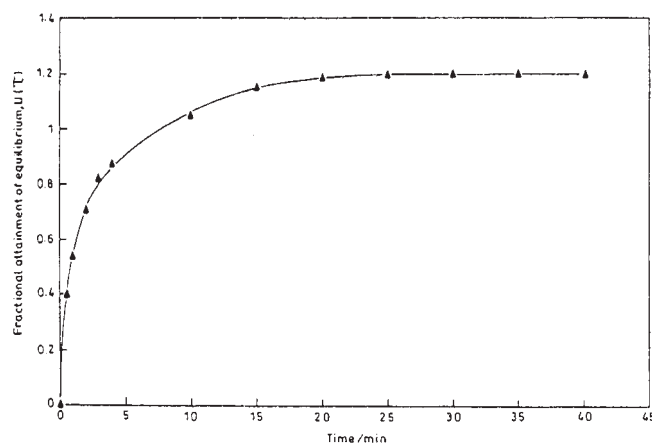
that each plot followed the Arrhenius equation for its temperature dependence similar to other semiconductors.<sup>37</sup> There was minor difference in their electrical conductivity even after repeating the experiment for five times which showed the good stability of the material during heating-cooling cycles under severe oxidizing conditions up to 200°C. This composite material was also observed to be a stable material, i.e., the room temperature conductivity is negligibly affected by short-term exposure to laboratory air as evident from Figure 4.

#### Ion-exchange kinetics of polypyrrole Th(IV) phosphate composite cation-exchanger

Kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchange of Mg(II)-H(I), Ca(II)-H(I), Sr(II)-H(I), Ba(II)-H(I), Ni(II)-H(I), Cu(II)-H(I),



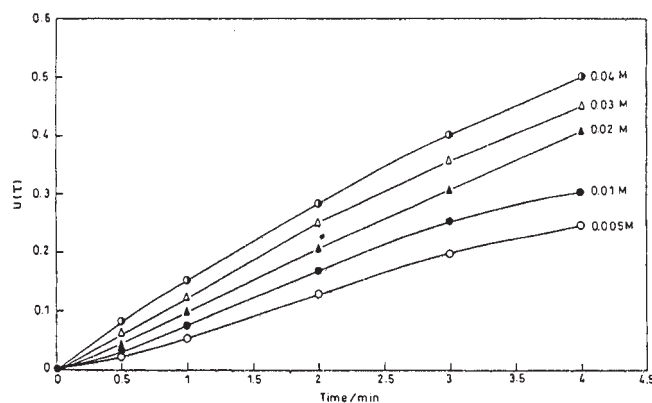
**Figure 4** Conductivity versus time of exposure to laboratory air for polypyrrole Th(IV) phosphate composite material (HCl) treated.



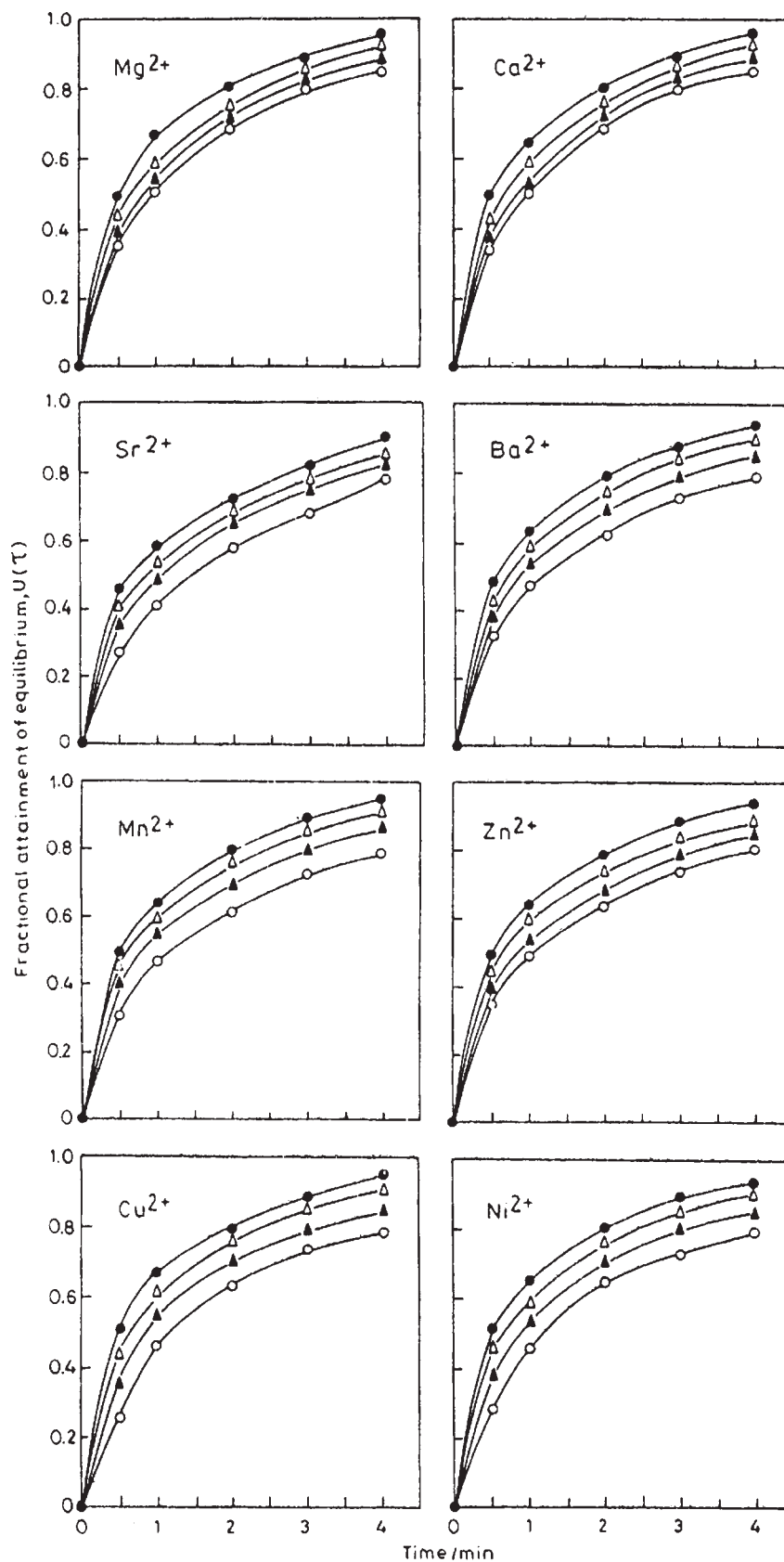
**Figure 5** A plot of  $U(\tau)$  versus  $t$  (time) for M(II)-H(I) exchanges at 33°C on polypyrrole Th(IV) phosphate composite cation-exchanger for the determination of infinite time.

Mn(II)-H(I), and Zn(II)-H(I). The particle diffusion-controlled phenomenon is favored by a high metal ion concentration, a relatively large particle size of the exchanger, and vigorous shaking of the exchanging mixture.

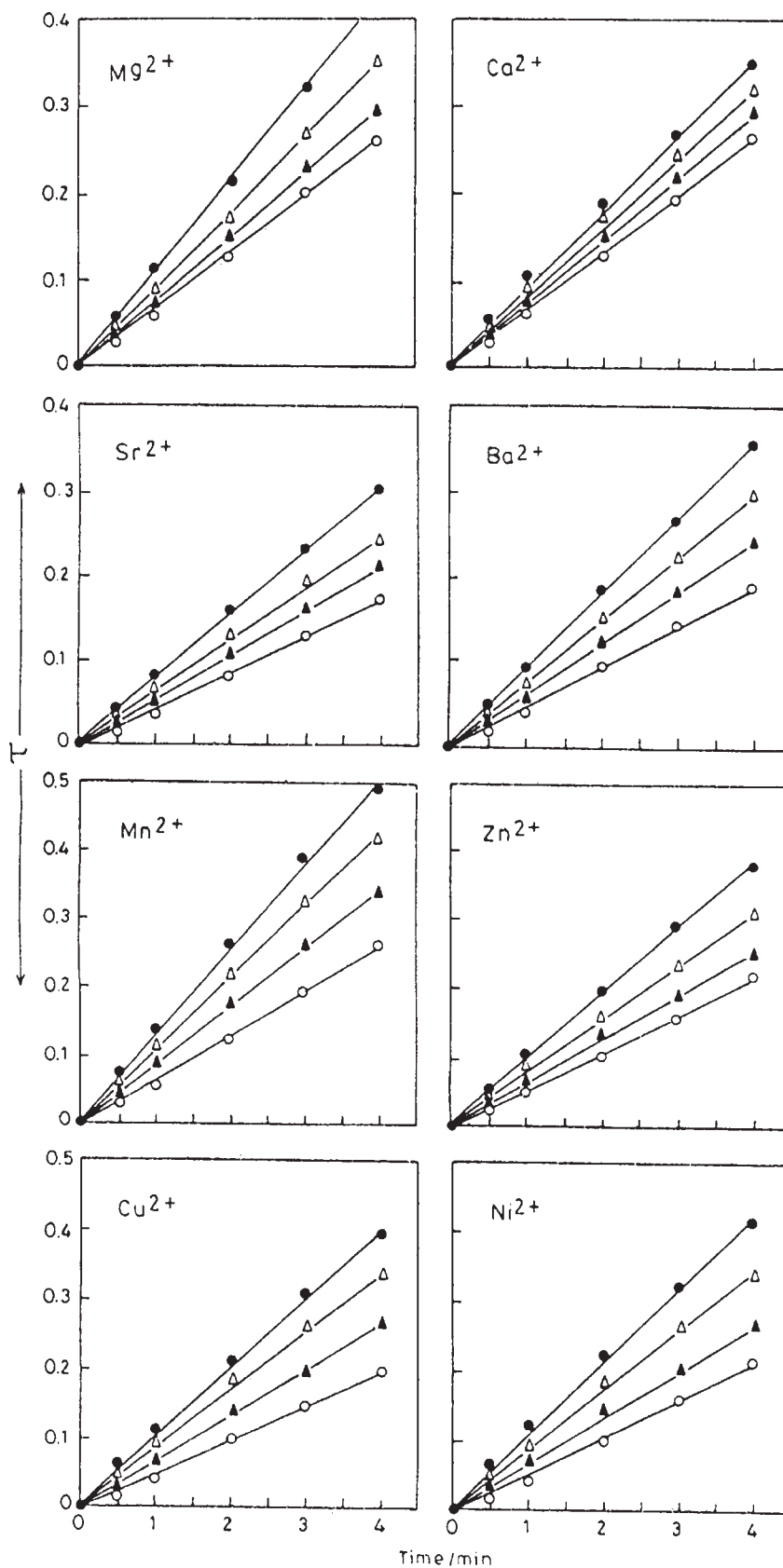
The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. The ion-exchange rate becomes independent of time after this interval. Figure 5 shows that 20 min were required for the establishment of equilibrium at 33°C for  $Mg^{2+}$ - $H^+$  exchange. Similar behavior was observed for  $Ca^{2+}$ - $H^+$ ,  $Sr^{2+}$ - $H^+$ ,  $Ba^{2+}$ - $H^+$ ,  $Ni^{2+}$ - $H^+$ ,  $Cu^{2+}$ - $H^+$ ,  $Mn^{2+}$ - $H^+$ , and  $Zn^{2+}$ - $H^+$  exchanges. Therefore, 20 min was assumed to be the infinite time of exchange for the system. A study of the concentration effect on the rate of exchange at 33°C showed that the initial rate of exchange was proportional to the metal ion concentration at and above 0.02M (Fig. 6). Below 0.02M concentration, film diffusion control was more prominent.



**Figure 6** Plots of  $U(\tau)$  versus  $t$  (time) for M(II)-H(I) exchanges using different metal solution concentrations at 33°C on polypyrrole Th(IV) phosphate composite cation-exchanger.



**Figure 7** Plots of  $U(\tau)$  versus  $t$  (time) for different M(II)-H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: ( $\square$ ) 25°C, ( $\blacktriangle$ ) 33°C, ( $\triangle$ ) 50°C, and ( $\bullet$ ) 65°C.



**Figure 8** Plots of  $\tau$  versus  $t$  (time) for different M(II)-H(I) exchanges at different temperatures on polypyrrole Th(IV) phosphate composite cation-exchanger: ( $\square$ ) 25°C, ( $\blacktriangle$ ) 33°C, ( $\triangle$ ) 50°C, and ( $\bullet$ ) 65°C.



**TABLE III**  
Slopes of Various  $\tau$  Versus Time ( $t$ ) Plots  
on Polypyrrole Th(IV) Phosphate Cation-Exchanger  
at Different Temperatures

Migrating ions	Slope ( $10^2 \text{ s}^{-1}$ )			
	25°C	33°C	50°C	65°C
Mg(II)	6.48	7.38	8.73	10.61
Ca(II)	6.48	7.27	8.06	8.88
Sr(II)	4.21	5.24	6.19	7.62
Ba(II)	4.70	6.08	7.45	8.93
Cu(II)	4.85	6.59	8.46	10.10
Ni(II)	5.23	6.68	8.58	10.62
Zn(II)	5.36	6.41	7.74	9.68
Mn(II)	6.35	8.53	10.52	12.73

The results are expressed in terms of the fractional attainment of equilibrium,  $U(\tau)$  with time according to the equation:

$$U(\tau) = \frac{\text{The amount of exchange at time "t"}}{\text{The amount of exchange at infinite time}} \quad (7)$$

Plots of  $U(\tau)$  versus time ( $t$ ) (min), for all metal ions (Fig. 7) indicated that the fractional attainment of equilibrium was faster at a higher temperature suggesting that the mobility of the ions increased with an increase in temperature and the uptake decreased with time. Each value of  $U(\tau)$  will have a corresponding value of  $\tau$ , a dimensionless time parameter. On the basis of the Nernst-Planck equation, the numerical results can be expressed by explicit approximation:<sup>39-41</sup>

$$U(\tau) = \{1 - \exp[\pi^2(f_1(\alpha)\tau + f_2(\alpha)\tau^2 + f_3(\alpha)\tau^3)]\}^{1/2} \quad (8)$$

where  $\tau$  is the half-time of exchange =  $\bar{D}_{H^+}t/r_o^2$ ,  $\alpha$  is the mobility ratio =  $\bar{D}_{H^+}/\bar{D}_{M^{2+}}$ ,  $r_o$  is the particle radius,  $\bar{D}_{H^+}$  and  $\bar{D}_{M^{2+}}$  are the inter diffusion coefficients of counter ions  $H^+$  and  $M^{2+}$  in the exchanger phase, respectively. The three functions  $f_1(\alpha)$ ,  $f_2(\alpha)$ , and  $f_3(\alpha)$  depend upon the mobility ratio ( $\alpha$ ) and the charge ratio ( $Z_{H^+}/Z_{M^{2+}}$ ) of the exchanging ions. Thus, they have different expressions as given below. When the exchanger is taken in the  $H^+$ -form and the exchanging ion is  $M^{2+}$ , for  $1 \leq \alpha \leq 20$ , as in the present case, the three functions have the values:

$$f_1(\alpha) = -\frac{1}{0.64 + 0.36 \alpha^{0.668}}$$

$$f_2(\alpha) = -\frac{1}{0.96 - 2.0 \alpha^{0.4635}}$$

$$f_3(\alpha) = -\frac{1}{0.27 + 0.09 \alpha^{1.140}}$$

The value of  $\tau$  was obtained on solving eq. (10) using a computer. The plots of  $\tau$  versus time ( $t$ ) at the four

temperatures, as shown in Figure 8, are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M(II)-H(I) exchanges at a metal ion concentration of 0.02M.

The slopes ( $S$  values) of various  $\tau$  versus time ( $t$ ) plots are given in Table III. The  $S$  values are related to  $\bar{D}_{H^+}$  as follows:

$$S = \bar{D}_{H^+}/r_o^2 \quad (9)$$

The values of  $-\log \bar{D}_{H^+}$  obtained by using eq. (9) plotted against  $1/T$  are straight lines as shown in Figure 9, thus verifying the validity of the Arrhenius relation:

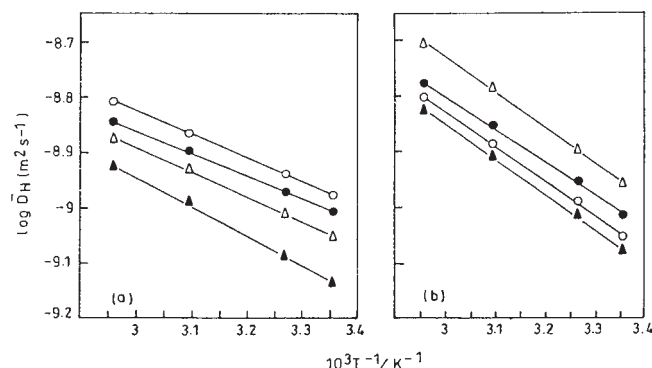
$$\bar{D}_{H^+} = D_0 \exp(-E_a/RT) \quad (10)$$

$D_0$  is obtained by extrapolating these lines and using the intercepts at the origin. The activation energy ( $E_a$ ) is then calculated with the help of the eq. (10), by substituting the value of  $\bar{D}_{H^+}$  at 273 K. The entropy of activation ( $\Delta S^*$ ) was then calculated by substituting  $D_0$  in eq. (11).

$$D_0 = 2.72d^2 (kT/h) \exp(\Delta S^*/R) \quad (11)$$

where  $d$  is the ionic jump distance taken as  $5 \times 10^{-10}$  m,<sup>26</sup>  $k$  is the Boltzmann constant,  $R$  is the gas constant,  $h$  is Planck's constant and  $T$  is taken as 273 K. The values of the diffusion coefficient ( $D_0$ ), energy of activation ( $E_a$ ), and entropy of activation ( $\Delta S^*$ ), thus obtained are summarized in Table IV.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Fig. 6), probably because of a higher diffusion rate of ions through the thermally enlarged interstitial positions of the ion-exchange matrix. The particle diffusion phenomenon is evident from the straight lines passing through the origin for the  $\tau$  versus time ( $t$ ) plots, as shown in Figure 8. The values of activation energy indicate the



**Figure 9** Plots of  $-\log \bar{D}_H$  versus  $10^3 T^{-1}$  ( $K^{-1}$ ) for: (a) ( $\square$ ) Mg (II), ( $\bullet$ ) Ca(II), ( $\Delta$ ) Ba(II), ( $\blacktriangle$ ) Sr(II), and (b) ( $\Delta$ ) Mn(II), ( $\bullet$ ) Ni(II), ( $\square$ ) Cu(II), ( $\blacktriangle$ ) Zn(II), on polypyrrole Th(IV) phosphate composite cation-exchanger.

TABLE IV  
Values of  $D_0$ ,  $E_a$ , and  $\Delta S^*$  for the Exchange of H(I) with Some Metal Ions on Polypyrrole Th(IV) Phosphate Composite Cation-Exchange Material

Metal ion exchange with H(I)	Ionic mobility ( $10^9 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	Ionic radii ( $10^2 \text{ nm}$ )	$D_0$ ( $10^8 \text{ m}^2 \text{ s}^{-1}$ )	$E_a$ ( $10^2 \text{ kJ mol}^{-1}$ )	$\Delta S^*$ ( $\text{J K}^{-1} \text{ mol}^{-1}$ )
Mg(II)	55	7.8	2.86	42.71	-1.21
Ca(II)	62	10.6	2.39	41.29	-1.29
Sr(II)	62	12.7	4.61	53.85	-1.00
Ba(II)	66	14.3	2.83	44.80	-1.22
Cu(II)	57	7.0	11.34	62.70	-0.61
Ni(II)	52	7.8	9.80	59.67	-0.68
Zn(II)	56	8.3	12.00	64.16	-0.59
Mn(II)	55	9.1	16.26	64.56	-0.46

minimum energy required for [M(II)-H(I)] ion-exchange process. Negative values of the entropy of activation suggest a greater degree of order achieved during the forward ion-exchange [M(II)-H(I)] process.

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