

Research Article

Thermodynamic Sorption Studies of Metal Ions on Polyaniline-Sn(IV) Tungstophosphate: Hybrid Cation Exchanger

A. Akhtar^{1*}, G. Nizami¹, Haroon²

¹Analytical Research Laboratory, Department of Chemistry,

²Physics Laboratory (Electronics), Department of Physics,

Sir Syed Faculty of Science, Mohammad Ali Jauhar University Rampur, India-244901.

*Corresponding author's e-mail: arshia.chem@gmail.com

Abstract

A novel polymer based organic-inorganic cation exchanger (polyaniline-Sn(IV) tungstophosphate) has been synthesized using a sol-gel method by the incorporation of precipitates of Sn(IV) tungstophosphate into the matrices of polyaniline. It exhibits good cation exchange capacity as well as thermodynamic properties suitable for ion exchange process and ion exchange equilibria of bivalent [Mg(II), Ba(II)], trivalent [Y(III), Nd(III), Gd(III)] and tetravalent metal ions [Th(IV), Zr(IV)] with the hydrogen form of sorbent have been evaluated at different temperatures 30, 40, 50 and 60°C. Equilibrium constant (K°) and thermodynamic parameters like standard free energy (ΔG°), entropy (ΔS°) and enthalpy (ΔH°) were also determined during the exchange reactions on this ion-exchange material. A correlation has been made for these parameters with the ion exchange characteristics of the exchanger. The variation of selectivity coefficients (log scale) with the equivalent fraction (\bar{X}_M) of metal ions in the exchanger at constant ionic strength (0.03 M), gives a non-linear function against \bar{X}_M .

Keywords: Exchanger; Ion exchange equilibria; Thermodynamic parameters; Selectivity coefficient.

Introduction

In last few decades organic-inorganic type hybrid ion exchanger have become a field of wide interest in different laboratories for various applications. Owing to further improved properties of hybrid ion exchanger, researchers are prompted to synthesis and investigate various types of "organic-inorganic" hybrid ion-exchangers [1-4]. Tin based hybrid ion-exchangers have got wide attention because of their excellent ion-exchange behavior, chemical and thermal stabilities, reproducibility as well as other important applications in the field of environmental pollution control, particularly in the removal of contagious ions from waste effluents [5].

The various applications of hybrid materials have been explored in the fields of heterogeneous catalysis [6,7], solid polymer electrolyte membrane fuel cells [8], and ion selective membrane electrodes [9], separation and sensor technologies, gas perm-selectivity [10], ion transport [11] and ion exchange. The ion-exchangers have gained popularity for being more selective and less expensive as compared

to other methods. In most of these fields, information related to the ion exchange equilibrium and the mobility of counter ions in the lattice structure is needed. Equilibrium analysis is fundamental for the assessment of the affinity or capacity of the exchanger. A sorption isotherm described by the attainment of equilibrium at the surface and is characterized by certain constants whose values indicate surface properties and affinity of the exchanger. The surface of the exchanger in contact with a solution has a tendency of assembling the ions at the surface because of the differences of surface forces.

However, thermodynamic data can forecast the final state of a system from an initial non-equilibrium mode. It is therefore important to determine how sorption rates depends on the concentrations of metal ions in a solution and how rates are affected by the sorption capacity or by the character of the exchanger in terms of thermodynamics. Herein, thermodynamic experiment was designed to give the information of a more fundamental nature relating to the mechanism and conveniently process ion-

exchange at the surface of PANI-TWP. The significance of the thermodynamic method is its ability to predict correlations among experimental results in the absence of detailed knowledge of the structure of the system. Also, thermodynamic studies of metal ions exchange on PANI-TWP are of considerable interest as the cation exchanger can be used at high temperature.

Polyaniline-Sn(IV)tungstophosphate, a crystalline cation exchanger with good ion-exchange properties was successfully synthesized and used for the removal of heavy metal ions as reported in our previous work [1]. However, the ion exchange mechanism and ion-exchange phenomenon (considered as diffusion of ion through particles of the exchanger and its adherent film) of the exchanger is being reported in the present paper. In these studies, ion exchange process is analysed based upon the measured equivalent fractions of the ingoing ion in the solution (X_M) and solid (\bar{X}_M) phases with that of selectivity co-efficient. The thermodynamic equilibrium constant (K), standard free energies (ΔG°), enthalpies (ΔH°) and entropies (ΔS°) of the exchange process are obtained from the plots of \bar{X}_M versus $\ln K_c$, where K_c is the selectivity co-efficient.

A novel organic-inorganic hybrid cation exchanger has been synthesized via sol-gel method. Ion exchange equilibria of rare earth metal ions have been evaluated at different temperatures. ΔG° values indicate spontaneous nature of tetravalent metal ions exchange. The exchange of rare earth metal ions by PANI-TWP is endothermic in nature. Thermodynamic parameters favour the exchange of rare earth metal ions by PANI-TWP.

Materials and methods

Reagents and Instruments

All chemicals and reagents were of analytical grade used without further purification. All metals were purchased from Merck. All solutions were prepared in triply distilled water. A water bath incubator shaker having a temperature variation of $\pm 0.5^\circ\text{C}$ was used for the equilibrium studies.

Synthesis of Hybrid Ion Exchanger

The 'organic-inorganic' hybrid cation-exchanger polyaniline-

Sn(IV)tungstophosphate (PANI-TWP) was synthesized by sol-gel method as described in our previous paper [1]. The polymer of aniline was obtained by mixing an equal volume ratio of ammonium persulfate and aniline with continuous stirring at $8\pm 2^\circ\text{C}$ temperature. The inorganic precipitate of Sn(IV)tungstophosphate was prepared at room temperature by adding different volume ratios of mixture of ortho-phosphoric acid and sodium tungstate to the solution of stannic chloride. A white colour precipitate was formed by adding ammonia solution with continuous stirring and the pH of the mixture was adjusted to 0.75.

The hybrid ion-exchanger PANI-TWP has been synthesized by equal mixing of polymer gel with the inorganic precipitate of Sn(IV)tungstophosphate by varying synthesis conditions as well as continuously stirring for 3 h at room temperature. The resultant slurries were kept for 24 h at room temperature, filtered and washed thoroughly with demineralised water. Material was then broken down by grinding and sieving into desired particle size (30–60 mesh). The dried material was then converted into H^+ form by treatment with 1 M HNO_3 solution. The finished product was then utilised for further studies.

Physico-chemical and Ion Exchange Characterization

Point zero charge, Physical characteristics, cation exchange capacity (CEC) and chemical stability of PANI-TWP were studied (Table 1).

PZC determination by salt addition method

To understand the Surface chemistry of the sorbent and hence to determine the point of zero charge (pH_{PZC}), the pH at the point of pH_{PZC} of the sorbent was measured by the pH method. 0.2 g of sorbent was taken in titration flasks of 100 mL capacity with 40 mL of 0.1 M KNO_3 solution. The pH of the suspension was adjusted between 2-11 by adding KOH or HCl solutions. After the pH stabilization mixture was kept in water shaker bath for 24 h at 303 K. The final pH value of suspension was recorded after 24 h of equilibration by using a pH meter. The PZC of the sample was calculated by plotting ΔpH (final pH–initial pH) versus pH_i . The resulting curve has an intersection point at a pH of around 3.2, where the surface charge is zero. Fig.1 represents the PZC of the sorbent which was

found to be at 3.2. The PZC value of sorbent is shown in Table 1. It can be seen that the final pH of the sorbent is acidic in range, hence indicate the surface of sorbent has a slightly acid PZC and the number of acidic sites indicate the number of functional groups [12].

Table 1. Physico-chemical and ion exchange characteristics of PANI-TWP cation exchanger

Properties	Observation
Appearance	Dark green opaque granular
point of zero charge	3.2
Moisture content, %	9.64
Apparent density, g l ⁻¹	0.30
True density, g l ⁻¹	1.34
Void volume fraction	0.78
Pore volume	0.14
Concentration of the fixed ionogenic group mmole g ⁻¹	1.70
Volume capacity of the sorbent, meq. g ⁻¹	0.37
Cation exchange capacity meq g ⁻¹	1.43
Chemical stability Acids	HCl, HNO ₃ , H ₂ SO ₄ , CH ₃ COOH, HCOOH
Bases	NaOH, KOH, NH ₃
Organic solvent	DMSO, (CH ₃) ₂ CO, n- butanol

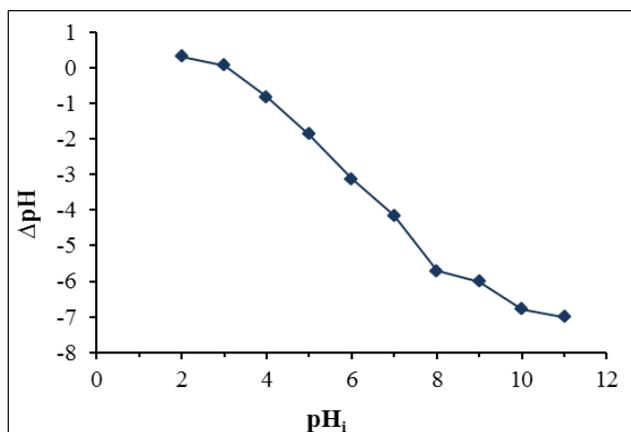


Figure 1. PZC of PANI-TWP at 303 K in 0.1 mol /dm³ KNO₃.

Moisture Content Determination

Percentage moisture content is the quantity of water contained in the exchanger. For

determination of percentage moisture content, 2 g of sample was kept in DMW for 24 h. The material was then filtered and dried at room temperature to remove surface moisture and weighed. This dried material was kept into an oven at 100⁰C for 24 h and reweighed after cooling in a desiccator. The percentage moisture (ability of the exchanger to hold moisture) was calculated using the formula:

$$\% \text{ Moisture content} = 100 - (\% \text{ solid})$$

$$\% \text{ Solid} = \frac{\text{Weight of dried material}}{\text{Weight of material before drying}} \times 100$$

Apparent Density (D_{col})

The apparent density is an important physical and quality ensuring indication that determination should be reproducible. The apparent mass per unit volume of wet material of individual particles is also known as apparent density. The density is the measure of the number of molecules and is definite for each material and is dependent on the type of exchanger and ionic group. For D_{col} calculation, the exact weight of the exchanger was taken in a calibrated glass column. After backwashing, water was drained and the exchanger was allowed to settle. Apparent density was determined using the equation:

$$\text{Apparent density} = \frac{\text{Weight of ion exchanger}}{\text{Volume of ion exchanger bed}}$$

True Density (D_{ie})

The true density was calculated by taking a specific amount of exchanger in previously weighed specific gravity bottle (W). The bottle was again weighed along with the ion exchanger (W_i). The bottle was now filled with water along with ion exchange material and weighed (W_{iw}). The weight of the specific gravity bottle containing water was also noted (W_w). The true density was calculated by using the equation:

$$D_{ie} = \frac{(W_i - W)}{(W_w - W_{iw}) + (W_i - W)}$$

Void Volume Fraction

The void volume fraction was calculated by using the formula:

$$\text{Void volume fraction} = 1 - \frac{D_{col}}{D_{ie}}$$

Pore Volume Determination

The Pore volume was calculated by taking an exchanger into a beaker. The weight of sample plus beaker was noted as W_0 . 2 g of dry exchanger was taken into beaker with 50 mL of

distilled water and the mixture was boiled for 20 minutes. After the air in the pores had been displaced, the sample was drained and the dried superficially and weight was recorded as W_F . The pore volume of the exchanger was calculated by using the formula below:

$$\text{Pore Volume} = \frac{W_F - W_o}{w_o} \times \text{density of water}$$

Volume Capacity of the sorbent (Q)

Volume capacity of exchanger was evaluated using the formula:

$$Q = (1 - \text{Void volume fraction}) \times C_r$$

Cation exchange capacity (CEC)

Na^+ ion exchange capacity in meq g^{-1} of PANI-TWP was calculated by standard column method at room temperature. For this a solution of 0.1 M NaNO_3 was passed through a glass column containing 1 g of exchanger by maintaining the flow rate of 0.5 mL min^{-1} and the effluent was titrated against 0.1 M NaOH solution. The CEC of the exchanger is calculated using the formula:

$$\text{Cation Exchange Capacity (CEC)} = \frac{\text{volume of titrant} \times \text{concentration of titrant}}{\text{weight of ion exchanger}}$$

Concentration of the Fixed Ionogenic Group (C_r)

Concentration of the fixed ionogenic group of PANI-TWP was calculated using the formula:

$$C_r = \frac{D_{ig} \times (100 - \% \text{ moisture}) \times \text{CEC}}{100}$$

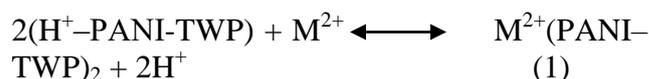
Equilibrium Experiments

For equilibrium experiments the exchanger (0.2 g) together with 20 mL fraction of metal ion solutions having a constant ionic strength (0.03 M) was taken in a stoppered conical flask and shaken at desired temperatures (30 and 60 °C) in a shaker bath for 6 h. After the attainment of equilibrium the supernatant liquid was removed and the metal ions concentration was estimated by EDTA titration.

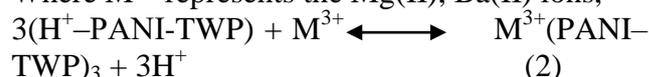
Results and discussions

Structural characterization

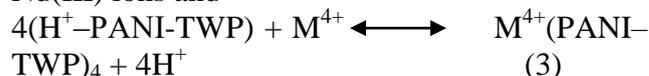
Ion exchange is a sorption phenomenon where the mechanism of adsorption occurs on the surface of exchanger. The sorbed ion replaces the ion on the exchanger surface on the charge basis can be represented by the equations:



Where M^{2+} represents the Mg(II), Ba(II) ions,

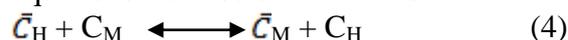


Where M^{3+} represents the Y(III), Gd(III) and Nd(III) ions and



Where M^{4+} represents the Th(IV) and Zr(IV) ions.

The generalized form of these three equations can also be written as:



Where, barred and unbarred quantities represent the equivalent concentrations in exchanger and solution phases, respectively.

Equivalent ionic fractions of counter-ions in exchanger and solution phases \bar{X}_M , \bar{X}_H , X_M and X_H were calculated from the expressions:

$$\bar{C}_M = \frac{C_M}{C}; X_M = \frac{C_M}{C}; \bar{C}_H = \frac{C_H}{C}; X_H = \frac{C_H}{C} \quad (5)$$

Where \bar{C} and C are the total electrolyte concentrations in the solid ($\bar{C} = \bar{C}_M + \bar{C}_H$) and solution phases ($C = C_M + C_H$).

The separation factors were calculated using the following relation [13]:

$$\alpha_H^M = \frac{\bar{X}_M \bar{X}_H}{\bar{X}_H \bar{X}_M} \quad (6)$$

For ion exchange equilibrium involving ion exchanger and metal ion solution, the selectivity co-efficients can be calculated from the expression:

$$K_c = \frac{\bar{X}_M (X_H)^n}{(X_H)^n \bar{X}_M} \quad (7)$$

Where \bar{X}_M and \bar{X}_H are equivalent ionic fractions in ion exchanger phase, X_M and X_H are equivalent ionic fractions in solution phase of metal ions and H^+ respectively.

The selectivity co-efficient is very important, as it is well known, especially in the thermodynamic analysis of electrolyte solutions and interfacial electrochemistry. Though, selectivity co-efficient has no unit, its magnitude depend on the concentration units. The selectivity co-efficient value is taken unity [14].

The separation factor values for Mg(II), Ba(II), Y(III), Gd(III), Nd(III), Th(IV) and Zr(IV) ions exchanges on $\text{H}^+ - (\text{PANI-TWP})$ were calculated at 30, 40, 50 and 60°C by Equation (6) and are summarized in Tables 2.

Ion exchange for one or two counter ions is often expressed by the separation factor. Separation factor is usually not constant it depends upon the concentration of solution, temperature and

equivalent ionic fractions. It is a thermodynamic factor that is a measure of relative retention of two substances, formally called selectivity or selectivity factor.

Table 2. Values of the separation factor for the bi, tri and tetravalent metal ions using PANI-TWP at 30,40,50 and 60°C.

$\alpha_{\text{H}}^{\text{Ba}}$	$\alpha_{\text{H}}^{\text{Mg}}$	$\alpha_{\text{H}}^{\text{Gd}}$	$\alpha_{\text{H}}^{\text{Nd}}$	$\alpha_{\text{H}}^{\text{Y}}$	$\alpha_{\text{H}}^{\text{Th}}$	$\alpha_{\text{H}}^{\text{Zr}}$
At 30°C						
0.249	0.252	0.581	0.590	0.591	0.252	0.252
0.224	0.229	0.572	0.589	0.582	0.229	0.248
0.188	0.206	0.570	0.556	0.553	0.206	0.236
0.166	0.189	0.511	0.526	0.513	0.189	0.202
0.149	0.157	0.490	0.474	0.514	0.157	0.169
0.134	0.131	0.482	0.453	0.484	0.131	0.152
0.117	0.103	0.441	0.392	0.455	0.103	0.140
0.109	0.075	0.343	0.321	0.425	0.075	0.119
0.099	0.048	0.294	0.293	0.346	0.048	0.102
0.061	0.004	0.264	0.232	0.326	0.004	0.078
At 40°C						
0.221	0.249	0.581	0.593	0.590	0.259	0.249
0.203	0.241	0.572	0.581	0.619	0.229	0.243
0.163	0.205	0.561	0.552	0.589	0.221	0.221
0.140	0.185	0.554	0.520	0.528	0.198	0.198
0.140	0.155	0.497	0.498	0.517	0.154	0.154
0.131	0.126	0.466	0.467	0.476	0.126	0.126
0.105	0.099	0.453	0.405	0.436	0.108	0.108
0.099	0.084	0.394	0.307	0.395	0.079	0.079
0.089	0.034	0.306	0.385	0.365	0.060	0.060
0.063	0.009	0.227	0.134	0.324	0.005	0.005
At 50°C						
0.252	0.224	0.553	0.588	0.559	0.260	0.241
0.246	0.207	0.542	0.567	0.528	0.235	0.247
0.237	0.179	0.504	0.556	0.467	0.214	0.234
0.229	0.172	0.495	0.515	0.376	0.193	0.207
0.215	0.151	0.466	0.494	0.355	0.168	0.172
0.207	0.134	0.367	0.423	0.254	0.143	0.123
0.198	0.111	0.338	0.472	0.230	0.116	0.105
0.193	0.069	0.321	0.391	0.079	0.096	0.072
0.161	0.039	0.241	0.192	0.058	0.076	0.063
0.070	0.021	0.180	0.181	0.027	0.054	0.045
At 60°C						
0.235	0.236	0.591	0.362	0.888	0.260	0.255
0.235	0.191	0.511	0.613	0.837	0.236	0.235
0.218	0.162	0.502	0.644	0.826	0.207	0.229
0.193	0.099	0.441	0.595	0.666	0.188	0.204
0.167	0.075	0.343	0.501	0.595	0.167	0.180
0.157	0.054	0.361	0.493	0.494	0.140	0.143
0.119	0.029	0.282	0.301	0.343	0.116	0.084
0.108	0.025	0.201	0.162	0.312	0.089	0.063
0.072	0.015	0.184	0.125	0.144	0.067	0.036
0.066	0.005	0.042	0.061	0.091	0.039	0.027

The selectivity co-efficient (K_c) has been in Table 3. calculated using equation (7) and is summarized

Table 3. Values of the selectivity co-efficient for the bi, tri and tetravalent metal ions using PANI-TWP at 30, 40, 50 and 60°C

Ba ²⁺	Mg ²⁺	Gd ³⁺	Nd ³⁺	Y ³⁺	Th ⁴⁺	Zr ⁴⁺
At 30°C						
0.233	0.231	0.57	0.57	0.57	0.221	0.824
0.189	0.180	0.53	0.54	0.55	0.151	0.206
0.135	0.135	0.50	0.46	0.49	0.099	0.166
0.105	0.078	0.37	0.39	0.39	0.069	0.095
0.084	0.054	0.34	0.28	0.37	0.029	0.045
0.068	0.045	0.30	0.25	0.31	0.016	0.029
0.052	0.029	0.24	0.17	0.26	0.006	0.022
0.045	0.014	0.11	0.09	0.20	0.002	0.011
0.038	0.006	0.07	0.07	0.12	0.00	0.006
0.014	0.001	0.05	0.03	0.09	0.00	0.002
At 40°C						
0.185	0.236	0.56	0.58	0.57	0.221	0.211
0.158	0.220	0.53	0.54	0.57	0.152	0.192
0.101	0.159	0.50	0.46	0.49	0.134	0.130
0.075	0.129	0.47	0.39	0.39	0.069	0.084
0.075	0.091	0.32	0.34	0.36	0.033	0.031
0.065	0.059	0.28	0.26	0.12	0.021	0.014
0.042	0.037	0.25	0.18	0.23	0.010	0.008
0.037	0.027	0.17	0.07	0.16	0.002	0.002
0.031	0.004	0.08	0.09	0.13	0.001	0.001
0.015	0.00	0.03	0.01	0.09	0.00	0.00
At 50°C						
0.241	0.190	0.45	0.55	0.58	0.242	0.184
0.231	0.162	0.44	0.51	0.57	0.173	0.203
0.213	0.121	0.35	0.47	0.55	0.116	0.167
0.199	0.113	0.32	0.36	0.51	0.076	0.100
0.176	0.087	0.27	0.33	0.50	0.044	0.049
0.162	0.068	0.13	0.21	0.45	0.023	0.012
0.148	0.047	0.10	0.29	0.44	0.009	0.007
0.139	0.019	0.08	0.16	0.29	0.001	0.002
0.098	0.006	0.04	0.02	0.26	0.002	0.001
0.023	0.002	0.02	0.02	0.20	0.001	0.00
At 60°C						
0.227	0.249	0.56	0.32	0.86	0.243	0.231
0.209	0.224	0.39	0.54	0.79	0.172	0.167
0.180	0.206	0.35	0.49	0.77	0.100	0.152
0.141	0.161	0.27	0.45	0.53	0.069	0.094
0.106	0.140	0.17	0.52	0.40	0.042	0.058
0.090	0.119	0.16	0.27	0.27	0.021	0.023
0.054	0.087	0.07	0.08	0.11	0.009	0.028
0.045	0.084	0.03	0.02	0.07	0.004	0.001
0.019	0.063	0.01	0.01	0.01	0.001	0.00
0.016	0.036	0.001	0.001	0.002	0.00	0.00

The plots of $\log K_c$ versus \bar{X}_M shows that the variation of K_c values corresponding to different \bar{X}_M values of bivalent, trivalent and tetravalent metal ions (Fig. 2, 3, 4) has been observed that selectivity co-efficient values at 60°C for bivalent and trivalent metal ions are generally higher than tetravalent metal ions. Whereas, reverse is the trend at 30°C. But the overall thermodynamic exchange is complex and plots are different for different metal ions. This may be due to the considerations of different entropy fixations by different metal ions, their different hydrated radii, and the different sorption affinities of the material for different metal ions at different temperatures.

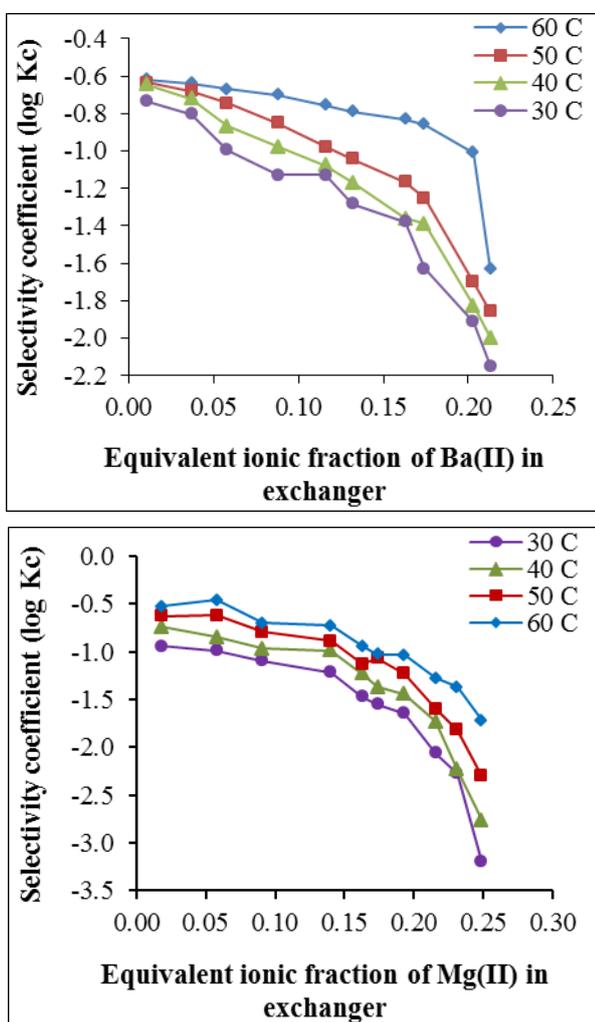


Figure 2: Plots of $\log K_c$ vs. \bar{X}_M for Mg(II)–H(I) and Ba(II)–H(I) sorption on on PANI–TWP at 30, 40, 50 and 60 °C.

Various thermodynamic parameters such as equilibrium constant (K), standard Gibbs free energy change (ΔG°), standard entropy change (ΔS°) and standard enthalpy change (ΔH°) have been evaluated by standard equation.

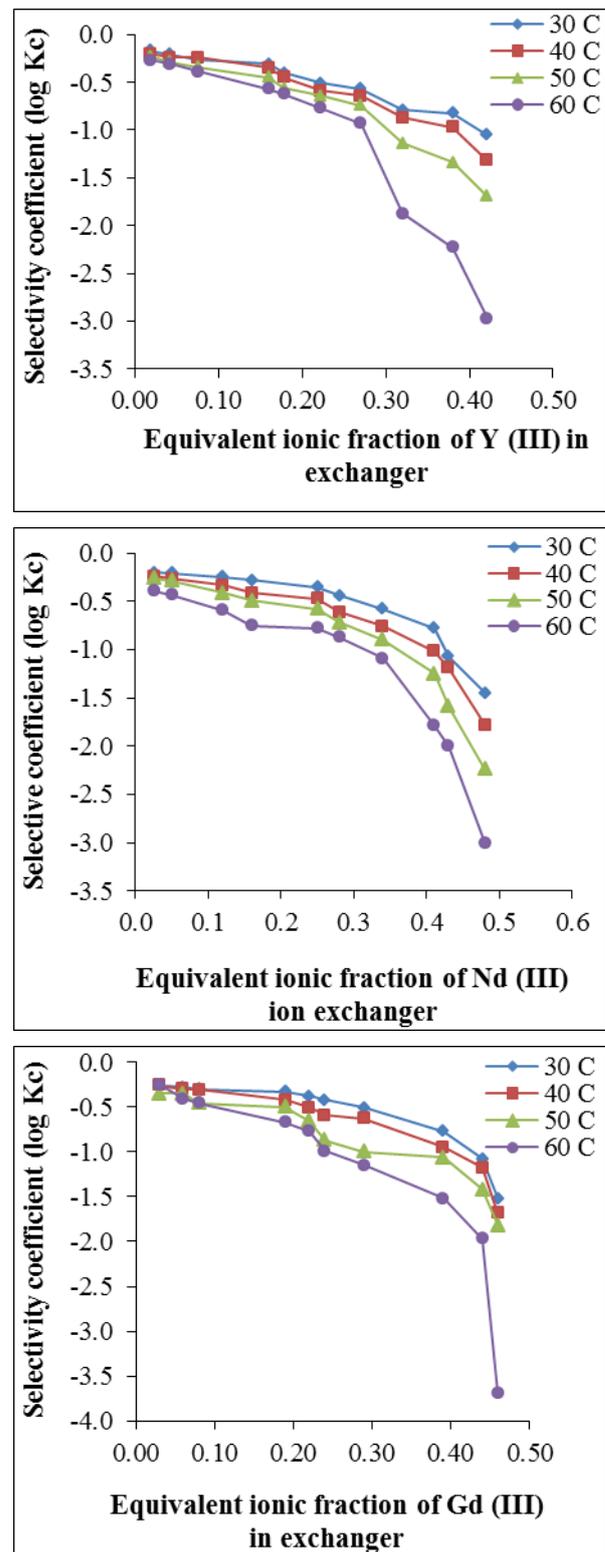


Figure 3. Plots of $\log K_c$ vs. \bar{X}_M for Y(III)–H(I), Nd(III)–H(I) and Gd(III)–H(I) sorption on PANI–TWP at 30, 40, 50 and 60°C.

The thermodynamic equilibrium constants (K) were calculated at different temperatures using the relation [15].

$$\ln K = (Z_A - Z_B) - \int_0^1 \ln K_c d \bar{X}_M \quad (8)$$

Where, Z_A and Z_B are the charges of competing ions. The integrals were estimated from the areas

under the curve of $\ln K_C$ versus \bar{X}_M (Fig. 2–4) using computer software and also, the K values are summarized in Table 4.

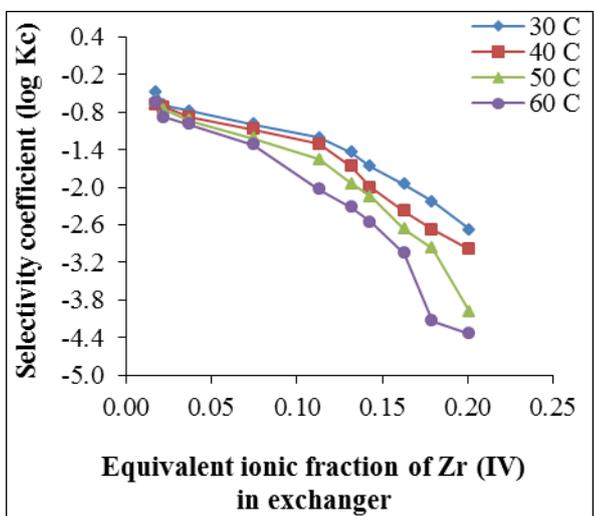
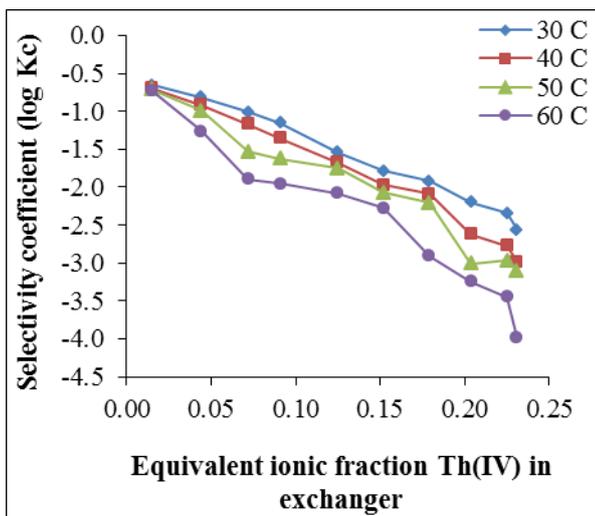


Figure 4. Plots of $\log K_c$ vs. \bar{X}_M for Th(IV)–H(I) and Zr(IV)–H(I) sorption on PANI–TWP at 30, 40, 50 and 60°C.

Standard free energy was calculated from K as:

$$\Delta G^\circ = \left(\frac{-RT \ln K}{z_M z_H} \right) \quad (9)$$

Standard enthalpy was calculated from van't Hoff isochore as:

$$\Delta H^\circ = \left[\ln K_2 - \ln K_1 \right] \left(\frac{T_1 T_2}{T_2 - T_1} \right) R \quad (10)$$

and the ΔS° has been calculated from Gibbs–Helmhotz equation:

$$\Delta S^\circ = \left(\frac{\Delta H^\circ - \Delta G^\circ}{T} \right) \quad (11)$$

Ion exchangers owe their characteristic properties to a peculiar feature of their structure. For an ion-exchange process the most important factor is the size and hence, charges of cation. The smaller is the size of cation, the more hydrated it will be and vice-versa. Consequently,

the tetravalent metal ions Th^{4+} and Zr^{4+} that are highly charged are least hydrated and bivalent metal ions Mg^{2+} and Ba^{2+} are highly hydrated. The value of thermodynamic parameter occurs as a function of charge of interchanging metal ions and estimated parameters for interchange are K, ΔG° , ΔH° and ΔS° (Table 4).

When interchange reaction between solid ion exchanger and electrolyte solution occurs, generally two type of reactions may take place, either ion-exchange or sorption. Sorption is a physico-chemical process which predominantly depends upon the interchange of metal ions between the two phases which increases with the increase in temperature. In present study, the chemical process was found to be responsible for both the sorption and ion exchange. K values increase with the increase in temperature of metal ions under study which shows that the metal ions have higher affinity for the exchanger at higher temperatures. In case of physical sorption, values of K may decrease with increase in temperature of metal ion solution [16,17]. The exchange is stoichiometric in nature, and essentially involves a diffusion process.

The free energy change ΔG° is a thermodynamic state function which indicates whether or not a process in a system will occur spontaneously. In the present system negative ΔG° value for all metal ions over entire temperature indicate that the exchanger has greater preference for metal ions than H^+ ions. The free energy (ΔG°) values increase with increasing temperature, indicating that exchange is favoured with increasing temperature. As dehydration is necessary for the occurrence of ion exchange [18], less negative ΔG° value detected in case of bivalent metal ions could be attributed for highly hydrated condition of ions. Being least hydrated, the exchange of ions take place more readily in case of tetravalent metal ions (more negative ΔG° values).

Enthalpy is a thermodynamic measure of the total energy change in a reaction. Enthalpy change for an ion exchange reaction may be due to five reasons: (1) the H^+ ions released from the exchanger while heat consumed for bond breaking (endothermic reaction); (2) formation of bond with incoming cation which releases heat (exothermic reaction); (3) heat requirement for intersection barrier (distance between exchanger phase and solution phase); (4)

enthalpy change when hydration and dehydration of exchanging ions in solution; (5) ion-exchange process a high degree of disorder is obtained into exchanger. An endothermic reaction is one with a positive enthalpy change and exothermic reaction is one with a negative enthalpy change. As dehydration is essential for ion exchange, to leave the hydration sphere and undergo ion exchange, some energy must be supplied to

cation [19]. More energy was required for dehydration to occur on the exchanger surface and higher values of enthalpy indicate the endothermicity of the process. The present study indicates that the process is endothermic in nature as enthalpy change is positive. The positive values of enthalpy indicate that probably dehydration occurred in case of tetravalent metal ions.

Table 4. Thermodynamic values for Mg(II)-H(I), Ba(II)-H(I), Y(III)-H(I), Nd(III)-H(I), Gd(III)-H(I), Th(IV)-H(I) and Zr(IV)-H(I) exchanges on PANI-TWP at 30, 40, 50 and 60 °C.

Metal ions	Temperature (°C)	Thermodynamic parameters			
		K	ΔG° (KJ mol ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (KJ mol ⁻¹ °C)
Mg(II)-H(I)	30	3.256	-1.487		0.077
	40	3.284	-1.547	0.829	0.059
	50	3.353	-1.624		0.049
	60	3.356	-1.676		0.041
Ba(II)-H(I)	30	3.491	-1.575		0.089
	40	3.495	-1.689	1.102	0.077
	50	3.518	-1.783		0.056
	60	3.625	-1.979		0.048
Y(III)-H(I)	30	9.214	-1.865		0.175
	40	9.216	-1.927	3.379	0.133
	50	10.288	-2.087		0.109
	60	10.389	-2.160		0.092
Nd(III)-H(I)	30	9.627	-1.902		0.189
	40	10.061	-2.003	3.768	0.144
	50	10.426	-2.098		0.117
	60	11.005	-2.213		0.099
Gd(III)-H(I)	30	9.913	-1.926		0.249
	40	10.932	-2.075	5.553	0.191
	50	11.042	-2.149		0.154
	60	12.089	-2.300		0.131
Th(IV)-H(I)	30	24.409	-2.012		0.267
	40	25.642	-2.111	5.999	0.203
	50	28.052	-2.238		0.165
	60	30.187	-2.358		0.139
Zr(IV)-H(I)	30	26.067	-2.054		0.298
	40	27.984	-2.167	6.892	0.226
	50	29.819	-2.279		0.183
	60	33.255	-2.425		0.155

A thermodynamic quantity representing the unavailability of a system's thermal energy for conversion into mechanical work is often interpreted as the degree of disorder or randomness in the system. Normally, entropy change occurs due to hydration of exchanging ions that may occur when they pass through the

channel of exchange as well as any change in solution structure around ions. Higher values of entropy indicate greater dehydration as well as greater disorder produced during interchange of ions. In the present study, the higher value of tetravalent metal ions is attributed to greater

dehydration, indicating the greater disorder fabricated during interchange of metal ions.

Conclusions

PANI-TWP cation exchanger prepared via sol-gel method exhibits good cation exchange capacity as well as thermodynamic properties suitable for ion exchange process. Ion exchange depends on the charge of metal ions, highly charged ions are least hydrated as compared to less charged ions and exchange easily. Free energy change (ΔG°) indicates that the tetravalent metal ions are least hydrated as compared to bivalent metal ions and exchange is spontaneous. Positive values of enthalpy designate the endothermic nature of the present system. Higher values of entropy designate the greater degree of disorderliness owing to higher dehydration which occurred throughout the interchange of metal ions.

Acknowledgments

We are thankful to the Chairman, Department of Chemistry, Mohammad Ali Jauhar University, Rampur for providing research facilities, University Grants Commission (India) for financial assistance.

Conflict of interest

Authors declare there are no conflicts of interest.

References

- [1] Nabi SA, Akhtar A, Khan MdDA, Khan MA. Synthesis, Characterization and Electrical Conductivity of Polyaniline-Sn(IV) tungstophosphate Hybrid Cation Exchanger; Analytical Application for Removal of Heavy Metal Ions from Wastewater. *Desalination*. 2014;340:73-83.
- [2] Nabi SA, Shalla AH. Synthesis, characterization and analytical application of hybrid; acrylamide zirconium (IV) arsenate a cation exchanger, effect of dielectric constant on distribution coefficient of metal ion. *Hazard Mater*. 2009;163:657-664.
- [3] Akhtar A, Khan MdDA, Nabi SA. Synthesis, characterization and photolytic degradation activity of poly-o-toluidine-thorium(IV) molybdophosphate cation exchanger: Analytical application in metal ion treatment. *Desalination*. 2015;361:1-12.
- [4] Pandith AH, Varshney KG. Synthesis and ion exchange behavior of acrylonitrile-based zirconium phosphate-A new hybrid cation exchanger. *Colloids Surf A*. 2002;201:1-7.
- [5] Al-Othman ZA, Inamuddin, Naushad Mu. Organic-inorganic type composite cation exchanger poly-o-toluidine Zr(IV)tungstate: Preparation, physicochemical characterization and its analytical application in separation of heavy metals. *Chem Eng J*. 2011;172:369-375.
- [6] Li H, Zheng Z, Cao M, Cao R. Stable gold nanoparticle encapsulated in silica-dendrimers organic-inorganic hybrid composite as recyclable catalyst for oxidation of alcohol. *Microporous Mesoporous Mater*. 2010;136:42-49.
- [7] Dallmann K, Buffon R. Sol-gel derived hybrid materials as heterogeneous catalysts for the epoxidation of olefins. *Catal Commun*. 2000;1:9-13.
- [8] Zhang Y, Zhanga H, Bi C, Zhua Xi. Inorganic/organic self-humidifying composite membranes for proton exchange membrane fuel cell application. *Electrochimica Acta*. 2008;53:4096-4103.
- [9] Nabi SA, Alam Z, Inamuddin. A cadmium ion-selective membrane electrode based on strong acidic organic inorganic composite cation-exchanger: polyaniline Ce(IV) molybdate. *Sens Transd J*. 2008;92:87-89.
- [10] Iwata M, Adachi T, Tonidokoro M, Ohta M, Kobayashi T. Hybrid sol-gel membranes of polyacrylonitrile-tetraethoxysilane composites for gas permselectivity. *J Appl Polym Sci*. 2003;88:1752-1759.
- [11] Kumar M, Tripathi BP, Shahi VK. Ionic transport phenomenon across sol-gel derived organic-inorganic composite mono-valent cation selective membranes. *J Membr Sci*. 2009;340:52-61.
- [12] Chen Li, Ramadan A, Lu Li, Shao W, Luo F, Chen Ji. Biosorption of Methylene Blue from Aqueous Solution Using Lawny Grass Modified with Citric Acid. *J Chem Eng Data*. 2011;56:3392-3399.
- [13] Robinson RA, Stokes RH. Table of osmotic coefficient of electrolytes in aqueous solution at 25°C. *Trans Faraday Soc* 1949;45:612-624.

- [14] Singhal JP, Singh RP, Singh CP, Gupta GK. Thermodynamics of the exchange of nicotine on aluminium- montmorillonite. *J Soil Sci.*1976;27:42-47.
- [15] Gains GL, Thomas HC. Adsorption studies on clay mineral, II. A formulation of the thermodynamic of exchange adsorption. *J Chem Phys.* 1953;21:714-718.
- [16] Pehlivan E, Ersoz M, Pehlivan M, Yildiz S, Duncan HJ. The effect of pH and temperature on the sorption of Zinc(II), cadmium(II), and Aluminium(III) onto new metal-ligand complexes of sporopollenin. *J Colloid Interface Sci.* 1995;170:320-325.
- [17] Ho YS. Removal of copper ions from aqueous solution by tree fern. *Water Res.* 2003;37:2323-2330.
- [18] Kurtoğlu AE, Atun G. Determination of kinetics and equilibrium of Pb/Na exchange on clinoptilolite. *Sep Purif Technol.* 2006;50:62-70.
- [19] Akhtar A, Khan MdDA, Nabi SA. Ion exchange kinetics and equilibrium studies of metal ions onto a hybrid cation exchanger: Polyaniline-Sn(IV)tungstophosphate. *International Journal of Engineering Sciences and Research Technology.* 2015;4(1):89-98.
