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Determination of ion-exchange kinetic parameters for the poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger

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ABSTRACT

The kinetics and mechanism for the ion-exchange processes like Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ at different temperatures using approximated Nernst–Plank equation under the particle diffusion controlled phenomenon were studied for the poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger. Some physical parameters, i.e. fractional attainment of equilibrium $U(\tau)$, self-diffusion coefficients (D_0), energy of activation (E_a) and entropy of activation (ΔS^*) have been estimated. These investigations revealed that the equilibrium is attained faster at higher temperature probably due to availability of thermally enlarged matrix of poly-*o*-methoxyaniline Zr(IV) molybdate composite cation exchange material. These results are useful for predicting the ion-exchange process occurring on the surface of this cation-exchanger.

1. Introduction

It is well recognized that the combination of insulating or conducting organic polymers as supporting materials and inorganic precipitates of polyvalent metal acid salt precursors by sol–gel method yielding composite materials is of great interest in our laboratory [1–8]. Composite materials were considered to be the best way to solve the limitations of poor thermal and radiation stabilities and less stability in high acidic and basic medium associated with the use of organic as well as inorganic ion exchange materials, respectively. Furthermore, insoluble acid salts of polyvalent metals produced by mixing rapidly the elements of groups of III, IV and V of periodic table possessing ion exchange properties are reported to be not very much reproducible and granular thereby limiting their suitability for column operation. Consequently, Zr(IV) molybdate one of the members of insoluble salts of polyvalent metals was particularly selected to overcome the limitations associated with inorganic ion exchanger by creating a composite cation exchanger. Hence, research has been motivated to the investigators to have various applications of organic–inorganic composite ion-exchangers in analytical chemistry owing to their better mechanical, chemical, thermal and radiation stabilities, reproducibility and possessing good selectivity for heavy toxic metals [9–20], indicating useful environmental applications [21–23]. New aapplications of composite materials have been explored in the fields of heterogeneous catalysis [24,25], protective coatings [26], solid polymer electrolyte membrane fuel cells [27,28], ion selective membrane electrodes [23,29], gas perm-selectivity [30,31], ion transport [32,33] and ion exchange [34]. In most of these fields, information related to the ion exchange kinetics and the mobility of counter ions in the lattice structure is needed. Kinetics studies envisage the three aspects of ion exchange process, viz. the mechanism of ion exchange, rate determining step and the rate laws obeyed by the ion exchange system. Moreover, the earlier approaches [35–38] of kinetic behavior are based on the old *Bt* criterion [39,40], which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities [41] of the exchanging ions involved. The Nernst–Planck [42,43] equations with some additional assumptions provide more appropriate values in obtaining the values of the various kinetic parameters precisely. Though many studies on the kinetics of ion exchange on organic and inorganic ion exchangers have been reported [44–47], relatively less information exists on the kinetics of exchange on composite ion

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Abbreviations: $U(\tau)$, fractional attainment of equilibrium; D_0, self-diffusion coefficients; E_a, energy of activation; ΔS^*, entropy of activation; $(NH_4)_2S_2O_8$, ammonium persulphate; $ZrOCl_2\cdot 8H_2O$, zirconium oxychloride; $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ammonium molybdate; i.d., internal diameter; DMW, demineralize water; EDTA, ethylene diamine terta acetic acid; $\bar{D}_{H^+}$, inter diffusion coefficients of counter ion H^+; $\bar{D}_{M^{2+}}$, inter diffusion coefficients of counter ion M^{2+}; r_o, particle radius; α, mobility ratio; $Z_{H^+}/Z_{M^{2+}}$, charge ratio; τ, a dimensionless time parameter; H^+, hydrogen ion; M^{2+}, metal ion; *S*, slope; *d*, the ionic jump distance; *k*, the Boltzmann constant; *R*, the gas constant; *h*, Plank's constant; *T*, temperature.

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Table 1
Conditions of preparation of poly-*o*-methoxyaniline, Zr(IV) molybdate and poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchange materials [8].

Samples	Mixing volume ratios (V/V)					Appearance of beads after drying	Na^+ ion-exchange capacity (mequiv. dry g^{-1})
	$ZrOCl_2 \cdot 8H_2O$ in 4 M HCl	0.1 M $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in DMW	pH of the inorganic precipitate	10% *o*-methoxyaniline in 1 M HCl	0.2 M $(NH_4)_2S_2O_8$ in 1 M HCl		
S-1	–	–	–	1	1	Greenish	0.35
S-2	1 (0.2 M)	2	1.0	–	–	White	1.75
S-3	1 (0.2 M)	2	1.0	1	1	Greenish-Blackish	2.56

exchange materials. Hence, in this study poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger was selected to evaluate the ion-exchange mechanism occurring over the surface of the cation-exchanger. However, the synthesis and physico-chemical characterization of this electrically conducting composite cation exchanger has also been studied and results are published [8]. The composite cation exchanger was found highly selective for cadmium a heavy toxic metal ion indicating the utility for the removal of Cd(II) from waste stream [8].

2. Experimental

2.1. Reagents and instruments

The main reagents such as ammonium persulphate, $(NH_4)_2S_2O_8$ (98%), *o*-methoxyaniline (99%), zirconium oxychloride, $ZrOCl_2 \cdot 8H_2O$ (98%) and ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (99%) used for the synthesis of the material were obtained from Central Drug House Pvt. Ltd. India and General Scientific Chemicals Ltd. India. Solutions for kinetic measurement were made using analytical reagent grade nitrate salts of Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn (99%) obtained from Central Drug House Pvt. Ltd. India. Nitric acid, HNO_3 (35%) and hydrochloric acid, HCl (35%) were obtained from E-Merck, India. All other reagents and chemicals were of analytical reagent grade. A digital pH meter (Elico LI-10, India) to adjust the pH and a water bath incubator shaker for all equilibrium studies having a temperature variation of ±0.5 °C (MSW-275, India) were used.

2.2. Preparation of organic–inorganic composite cation-exchange material

Organic–inorganic composite cation exchanger poly-*o*-methoxyaniline Zr(IV) molybdate was prepared as reported by Inamuddin and Ismail [8]. The procedure for the preparation is given below:

2.2.1. Preparation of reagent solutions

The solutions of 0.2 M ammonium persulphate $[(NH_4)_2S_2O_8]$ and 10% *o*-methoxyaniline were prepared in 1 M HCl, while 0.2 M zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) and 0.1 M ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ solutions were prepared in 4 M HCl and demineralized water (DMW), respectively.

2.2.2. Preparation of poly-o-methoxyaniline

Poly-*o*-methoxyaniline gel was prepared by mixing similar volume ratio of the solution of 0.2 M ammonium persulphate $[(NH_4)_2S_2O_8]$ into 10% *o*-methoxyaniline solution with continuous stirring by a magnetic stirrer at 0 °C for 2 h. Green colored gel of poly-*o*-methoxyaniline was obtained. The gel was kept for 24 h in a refrigerator.

2.2.3. Preparation of Zr(IV) molybdate inorganic cation exchanger

Inorganic ion-exchanger Zr(IV) molybdate was prepared by adding 0.2 M zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) solution to an aqueous solution of 0.1 M ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in 1:2 mixing volume ratio at room temperature (25 ± 2 °C). The white precipitate of Zr(IV) molybdate was obtained, when the pH of the mixture was adjusted to 1 by adding aqueous ammonia or hydrochloric with constant stirring.

2.2.4. Preparation of poly-o-methoxyaniline Zr(IV) molybdate composite cation-exchange material

The gel of poly-*o*-methoxyaniline was added into the white inorganic precipitate of Zr(IV) molybdate and mixed thoroughly with constant stirring. The resultant green colored gel was kept for 24 h at room temperature (25 ± 2 °C) for digestion. At the final stage, the composite cation-exchanger gel was filtered off by suction; washed with demineralize water (DMW) to remove excess acid. The washed gel dried over P_4O_{10} at 40 °C in an oven. The dried product was washed again with acetone to remove oligomers present in the material, and dried at 40 °C in an oven. The composite cation exchanger caries fixed molybdate ionic groups which are converted into H^+/counter ion form by treating with 0.5 M HNO_3 for 24 h with occasional shaking intermittently replacing the supernatant liquid with fresh acid 2–3 times. The excess acid was removed after several washings with DMW and finally dried at 50 °C. The composite cation exchanger was cracked and the particle size of approximately 125 μm was obtained by sieving and stored in desiccator. The ion exchange capacity was determined by standard column process. For this purpose, one gram (1 g) of the dry cation-exchangers, sample S-1, S-2 and S-3 in the H^+-forms were taken into three different glass columns having an internal diameter (i.d.) ~1 cm and fitted with glass wool support at the bottom. The bed length was approximately 1.5 cm long. 1 M $NaNO_3$ as eluent was used to elute the H^+ ions completely from the cation-exchange columns, maintaining a very slow flow rate (~0.5 ml min^{-1}). The effluents were titrated against a standard 0.1 M NaOH solution for the total ions liberated in the solutions using phenolphthalein indicator and the ion-exchange capacities in mequiv. g^{-1} are determined. The conditions of preparation, the ion-exchange capacity, and physical appearances of the organic, inorganic and composite cation-exchangers are given in Table 1. The ion exchange capacity of composite cation exchanger poly-*o*-methoxyaniline Zr(IV) molybdate was found to be 2.56 mequiv. dry g^{-1}, which is higher than that of its inorganic counterpart Zr(IV) molybdate (1.75 mequiv. dry g^{-1}). Thus, sample S-3 was selected for detailed kinetic studies.

2.3. Kinetic measurements

Composite cation exchanger particles of mean radii ~125 μm (50–70 mesh) in H^+ form were used to evaluate various kinetic parameters. The rate of exchange was determined by limited batch technique as follows.

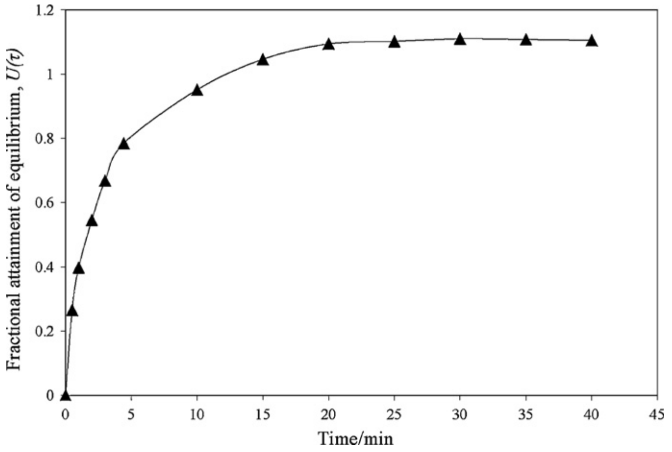

Fig. 1. A plot of $U(\tau)$ versus t (time) for M^{2+}–H^+ exchanges at 33 °C on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger for the determination of infinite time.

A total of 20 ml fractions of the 0.02 M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) were shaken with 200 mg of the cation-exchanger in H^+-form in several stoppered conical flasks at desired temperatures [25,33, 50 and 65 (±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 as usual by ethylene diamine terta acetic acid (EDTA) titrations [48]. Each set was repeated four times and the mean values were taken for calculation.

3. Results and discussions

In this study, poly-*o*-methoxyaniline Zr(IV) molybdate organic–inorganic composite cation exchanger was prepared by sol–gel mixing of electrically conducting polymer poly-*o*-methoxyaniline green colored gel into the white precipitate of inorganic ion-exchanger Zr(IV) molybdate [8]. The composite cation-exchanger, sample S-3 possessed ion-exchange capacity 2.56 mequiv. g^{-1} which is higher than its inorganic counter part Zr(IV) molybdate, sample S-2 ion exchange capacity 1.75 mequiv. g^{-1} and good granulometric property (Table 1). Improvement in ion exchange and granulometric properties are considered due to the presence of binding polymer, i.e. poly-*o*-methoxyaniline. Obviously, the rate determining step in ion exchange process is inter-diffusion of the exchanging counter ions either within the ion exchanger itself (particle diffusion) or in an adherent liquid 'film' (film diffusion) which is not affected by agitation of the solution. A simple kinetic criterion is used to predict whether particle or film diffusion will be rate controlling step under a given set of conditions. The infinite time of exchange is the time necessary to obtain equilibrium in an ion exchange process. Thus, the ion-exchange rate becomes independent of time after this time interval. Fig. 1 shows that 20 min was required for the establishment of equilibrium at 33 °C for Mg^{2+}–H^+ exchange. Similar behavior was also 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 all exchange systems. 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 and τ versus time (t) (t in min) plots are also straight lines passing through the origin at and above 0.02 M of metal ion concentration (Fig. 2), which confirms the particle diffusion controlled phenomenon. Below the metal ion concentration of 0.02 M, film diffusion control phenomenon was more prominent. Thus, kinetic measurements were made under conditions favoring a particle diffusion-controlled ion-exchange phenomenon for the exchanges of Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+, Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+. 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 kinetic results are expressed in terms of the fractional attainment of equilibrium, $U(\tau)$ with time according to the equation:

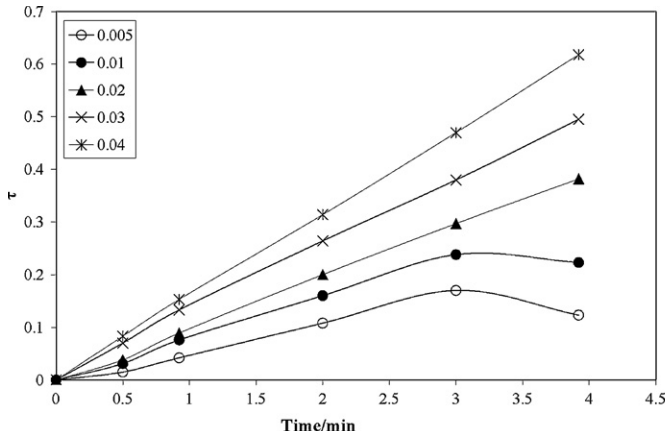

Fig. 2. Plots of τ versus t (time) for M^{2+}–H^+ exchanges using different metal solution concentrations at 33 °C on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

$$U(\tau) = \frac{\text{the amount of exchange at time `}t\text{'}}{\text{the amount of exchange at infinite time}} \quad (1)$$

Plots of $U(\tau)$ versus time (t) (t in min), for Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+ and Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+, Zn^{2+}–H^+ exchanges (Figs. 3 and 4), respectively, 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 τ, a dimensionless time parameter. On the basis of the Nernst–Planck equation, the numerical results can be expressed by explicit approximation [49–51]:

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

where τ is the half time of exchange $= \overline{D}_{H^+} t / r_0^2$, α is the mobility ratio $= \overline{D}_{H^+} / \overline{D}_{M^{2+}}$, r_0 is the particle radius, $\overline{D}_{H^+}$ and $\overline{D}_{M^{2+}}$ are the inter diffusion coefficients of counter ions H^+ and M^{2+}, respectively, in the exchanger phase. The three functions $f_1(\alpha)$, $f_2(\alpha)$ and $f_3(\alpha)$ depend upon the mobility ratio (α) 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 $1 \le \alpha \le 20$, 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 τ was obtained on solving Eq. (2) using a computer. The plots of τ versus time (t) at the four temperatures for Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+, Ba^{2+}–H^+ and Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+, Zn^{2+}–H^+ exchanges as shown in Figs. 5 and 6, respectively, are straight lines passing through the origin, confirming the particle diffusion control phenomenon for M^{2+}–H^+ exchanges at a metal ion concentration of 0.02 M. It is obvious that the particle diffusion controlled exchange is more rapid when the counter ion

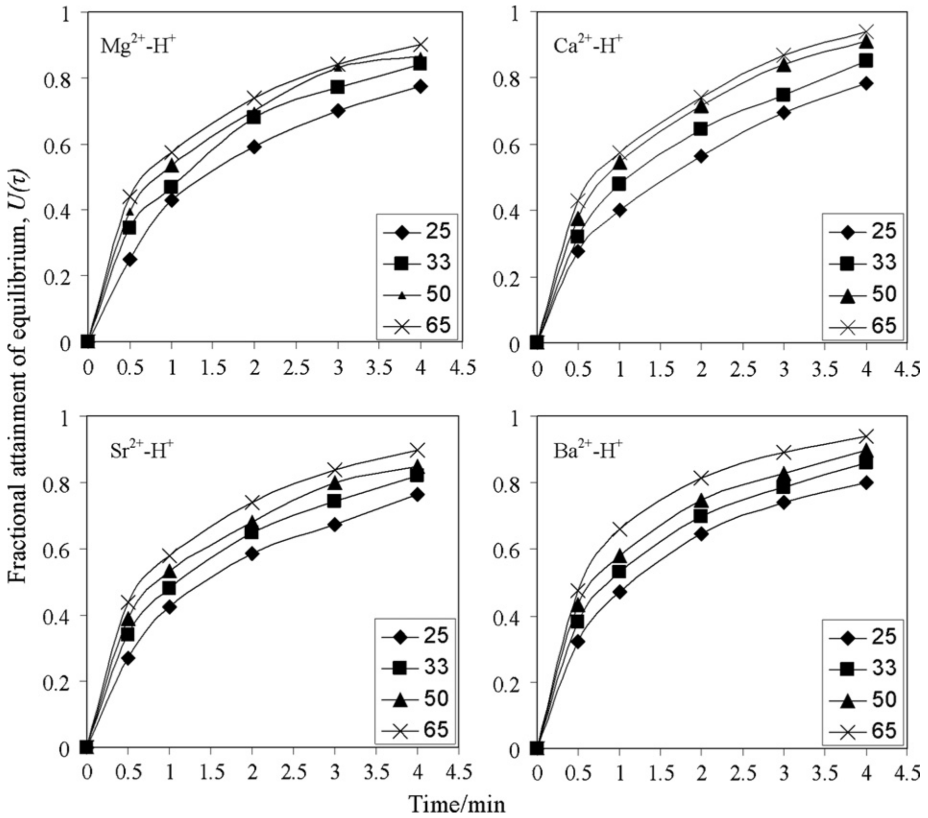

Fig. 3. Plots of $U(\tau)$ versus t (time) for Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+ and Ba^{2+}–H^+ exchanges at different temperatures on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

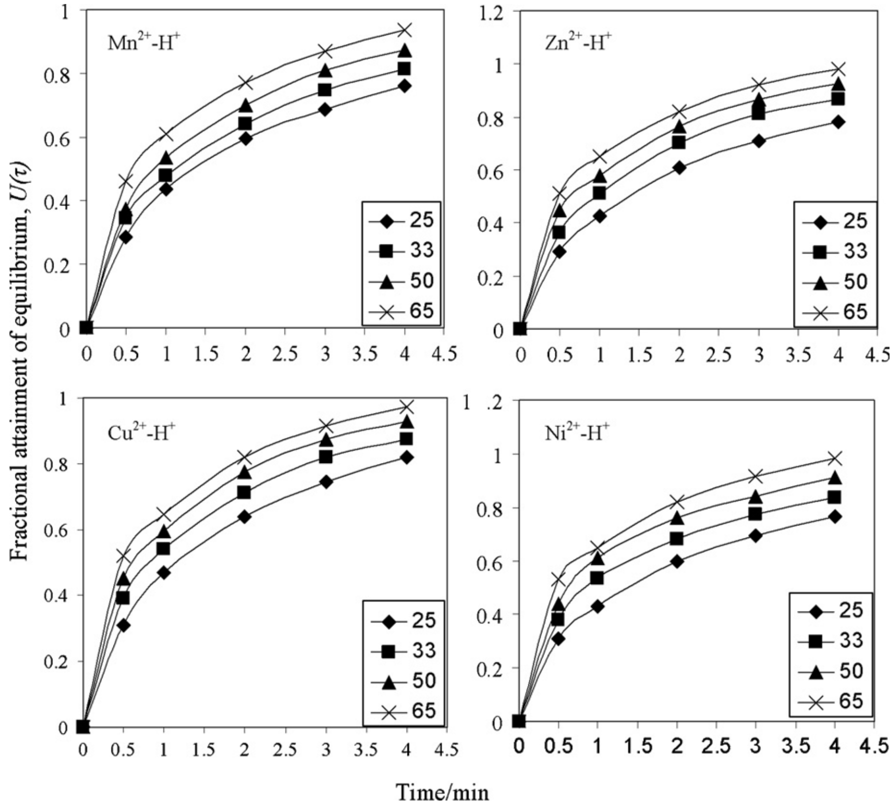

Fig. 4. Plots of $U(\tau)$ versus t (time) for Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ exchanges at different temperatures on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

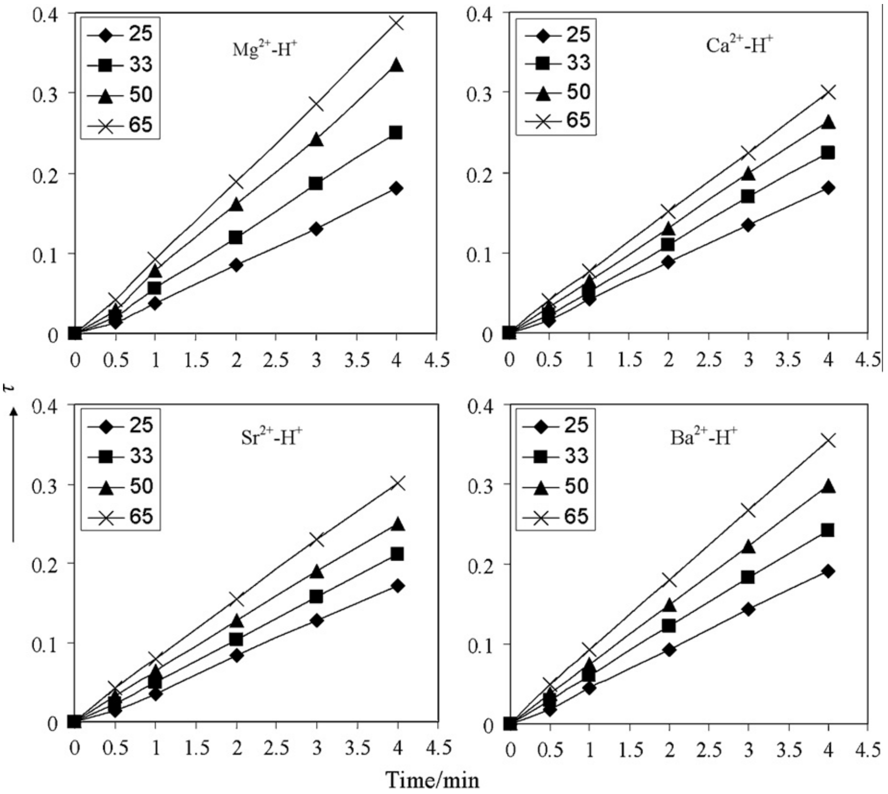

Fig. 5. Plots of τ versus t (time) for Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+ and Ba^{2+}–H^+ exchanges at different temperatures on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

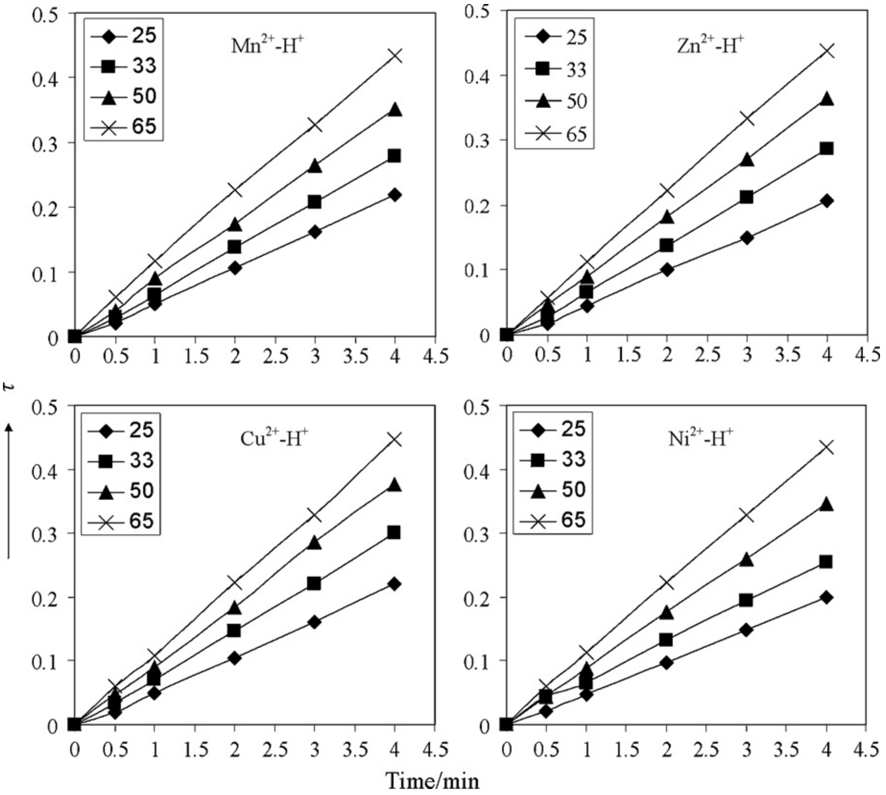

Fig. 6. Plots of τ versus t (time) for Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ exchanges at different temperatures on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

Table 2
Slopes of various τ versus time (t) plots on poly-*o*-methoxyaniline Zr(IV) molybdate cation-exchanger at different temperatures.

Migrating ions	S (s^{-1}) × 10^2			
	25 °C	33 °C	50 °C	65 °C
Mg(II)	4.59	6.37	8.45	9.72
Ca(II)	4.6	5.71	6.64	7.46
Sr(II)	4.41	5.33	6.26	7.5
Ba(II)	4.85	6.07	7.44	8.81
Cu(II)	5.56	7.53	9.45	11.09
Ni(II)	5.01	6.28	8.64	10.83
Zn(II)	5.56	7.02	8.83	10.73
Mn(II)	5.23	7.25	9.07	10.96

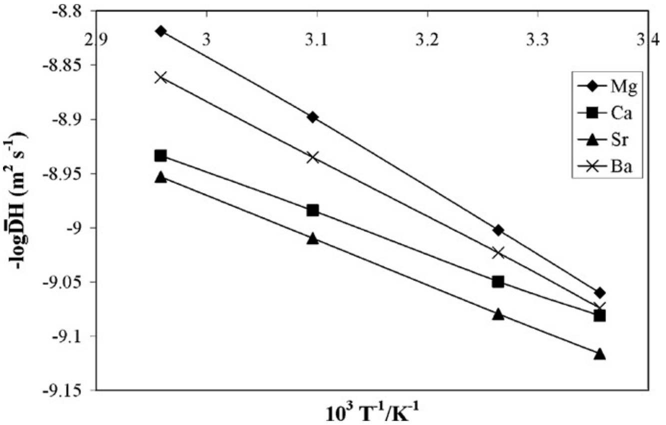

Fig. 7. Plots of $-\log D_H$ versus $10^3\,T^{-1}$/K^{-1} for Mg^{2+}–H^+, Ca^{2+}–H^+, Sr^{2+}–H^+ and Ba^{2+}–H^+ exchanges on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

which is initially in the ion exchanger is the faster one, while for the film diffusion controlled exchange, the counter ion which is preferred by the ion exchanger is taken up at the higher rate and released at the lower rate.

The slopes (S values) of various τ versus time (t) plots are given in Table 2. The S values are related to $\overline{D}_{H^+}$ as follows:

$$S = \frac{\bar{D}_{H^+}}{r_0^2} \tag{3}$$

The values of $-\log \overline{D}_{H^+}$ obtained by using Eq. (3) plotted against $1/T$ are straight lines as shown in Figs. 7 and 8, thus verifying the validity of the Arrhenius relation:

$$\bar{D}_{H^+} = D_0 \exp\left(\frac{-E_a}{RT}\right) \tag{4}$$

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 Eq. (4), putting the value of $\overline{D}_{H^+}$ at 273 K. The entropy of activation (ΔS^*) was then calculated by substituting D_0 in Eq. (5).

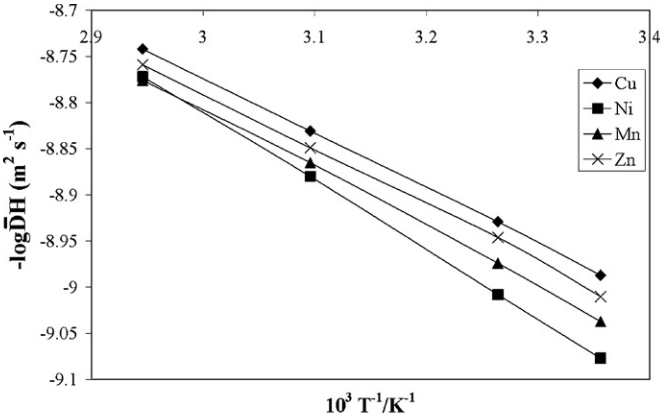

Fig. 8. Plots of $-\log D_H$ versus $10^3\,T^{-1}$/K^{-1} for Ni^{2+}–H^+, Cu^{2+}–H^+, Mn^{2+}–H^+ and Zn^{2+}–H^+ on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchanger.

$$D_0 = 2.72d^2\left(\frac{kT}{h}\right)\exp\left(\frac{\Delta S^*}{R}\right) \tag{5}$$

where d is the ionic jump distance taken as 5×10^{-10} m, k is the Boltzmann constant, R is the gas constant, h is Plank'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 (ΔS^*), thus obtained are summarized in Table 3.

The kinetic study reveals that equilibrium is attained faster at a higher temperature (Figs. 3 and 4), 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 τ versus time (t) plots, as shown in Figs. 5 and 6. The positive values of activation energy indicated that the minimum energy is required to facilitate the forward (M^{2+}–H^+) ion-exchange process. Negative values of the entropy of activation (ΔS^*) suggest a greater degree of order achieved during the forward ion-exchange (M^{2+}–H^+) process. However, results showed that there is no definite relation between the ionic radii and mobility of metal ions with activation energy and entropy of activation.

4. Conclusion

The ion exchange kinetic mechanism of composite cation exchanger is being governed by the particle diffusion controlled phenomenon which is faster than the film diffusion controlled phenomenon during the forward exchange process (M^{2+}–H^+). Activation energy is calculated by using verified and validated Arrhenius equation. The negative values of (ΔS^*) indicate that the ion exchange process is more feasible on this composite cation exchange material when the exchanger phase is in H^+-form and exchanged by a metal ion.

Table 3
Values of D_0, E_a and ΔS^* for the exchange of H^+ ions with some metal ions on poly-*o*-methoxyaniline Zr(IV) molybdate composite cation-exchange material.

Metal ion exchange with H(I)	10^9 Ionic mobility/ m^2 V^{-1} s^{-1}	10^2 Ionic radii/nm	10^8 D_0/m^2 s^{-1}	10^2 E_a/kJ mol^{-1}	(S^*/J K^{-1} mol^{-1}
Mg(II)	55	7.8	9.63	60.85	−0.68
Ca(II)	62	10.6	1.49	37.44	−1.49
Sr(II)	62	12.7	1.85	41.10	−1.40
Ba(II)	66	14.3	5.21	53.34	−0.95
Cu(II)	57	7.0	0.10	59.52	−2.67
Ni(II)	52	7.8	0.27	65.73	−2.24
Zn(II)	56	8.3	0.11	60. 58	−2.63
Mn(II)	55	9.1	0.13	63.67	−2.55

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References

[1] A.A. Khan, Inamuddin, M.M. Alam, Preparation, characterization and analytical applications of a new and novel electrically conducting fibrous type polymeric-inorganic composite material: polypyrrole Th(IV) phosphate used as a cation-exchanger and Pb(II) ion-selective membrane electrode, Mater. Res. Bull. 40 (2005) 289–305.

[2] A.A. Khan, Inamuddin, Preparation, physico-chemical characterization, analytical applications and electrical conductivity measurement studies of an 'organic–inorganic' composite cation-exchanger: polyaniline Sn(IV) phosphate, React. Funct. Polym. 66 (2006) 1649–1663.

[3] Inamuddin, S.A. Khan, W.A. Siddiqui, A.A. Khan, Synthesis, characterization and ion-exchange properties of a new and novel 'organic–inorganic' hybrid cation-exchanger: nylon-6,6, Zr(IV) phosphate, Talanta 71 (2007) 841–847.

[4] S.A. Nabi, Mu. Naushad, Inamuddin, Synthesis, characterization and analytical applications of a new highly thermally and chemically stable semi-crystalline inorganic ion-exchanger: Zr(IV) tungstomolybdate, J. Hazard. Mater. 142 (2007) 404–411.

[5] A. Siddiqui, S.A. Khan, Inamuddin, Synthesis, characterization and ion-exchange properties of a new and novel 'organic–inorganic' hybrid cation-exchanger: poly(methyl methacrylate) Zr(IV) phosphate, Colloids Surf. A: Physicochem. Eng. Aspects 295 (2007) 193–197.

[6] A.A. Khan, A. Khan, Inamuddin, Synthesis and characterization of a new nanocomposite cation-exchanger poly-o-toluidine Th(IV) phosphate and its application in the fabrication of ion-selective membrane electrode, Talanta 72 (2007) 699–710.

[7] Z. Alam, Inamuddin, S.A. Nabi, Synthesis and characterization of a thermally stable strong acidic Cd(II) selective composite cation-exchanger: polyaniline Ce(IV) molybdate, Desalination 250 (2010) 515–522.

[8] Inamuddin, Y.A. Ismail, Synthesis and characterization of poly-o-methoxyaniline Zr(IV) molybdate Cd(II) selective composite cation-exchanger, Desalination 250 (2010) 523–529.

[9] A. Nilchi, A. Khanchi, H. Atashi, A. Bagheri, L. Nematollahi, The application and properties of composite sorbents of inorganic ion exchangers and polyacrylonitrile binding matrix, J. Hazard. Mater. 137 (2006) 1271–1276.

[10] S.A. Shady, Selectivity of cesium from fission radionuclides using resorcinol formaldehyde and zirconyl-molybdopyrophosphate as ion-exchangers, J. Hazard. Mater. 167 (2009) 947–952.

[11] H. Zhang, J.H. Pang, D. Wang, A. Li, X. Li, Z. Jiang, Sulfonated poly(arylene ether nitrile ketone) and its composite with phosphotungstic acid as materials for proton exchange membranes, J. Membr. Sci. 264 (2005) 56–64.

[12] B. Pandit, U. Chudasma, Synthesis, characterization and application of an inorgano organic material: p-chlorophenol anchored onto zirconium tungstate, Bull. Mater. Sci. 24 (2001) 265–271.

[13] S.A. Nabi, A.H. Shalla, EDTA–stannic(IV)iodate: preparation, characterization and its analytical applications for metal content determination in real and synthetic samples, J. Porous Mater. 16 (2009) 587–597.

[14] K.G. Varshney, M.Z.A. Rafiquee, A. Somya, M. Drabik, Synthesis and characterization of a Hg(II) selective n-butyl acetate cerium(IV) phosphate as a new intercalated fibrous ion exchanger: effect of surfactants on the adsorption behaviour, Indian J. Chem. A: Inorg. Phys. Theor. Anal. Chem. 45 (2006) 1856–1860.

[15] K.G. Varshney, N. Tayal, Polystyrene thorium(IV) phosphate as a new crystalline and cadmium selective fibrous ion exchanger. Synthesis characterization and analytical applications, Langmuir (2001) 2589–2593.

[16] J.-K. Moon, K.-W. Kim, C.-H. Jung, Y.-G. Shul, E.-H. Lee, Preparation of organic–inorganic composite adsorbent beads for removal of radionuclides and heavy metal ions, J. Radioanal. Nucl. Chem. 246 (2000) 299–307.

[17] K.G. Varshney, A. Agrawal, S.C. Mojumdar, Pectin based cerium (IV) and thorium (IV) phosphates as novel hybrid fibrous ion exchangers synthesis, characterization and thermal behaviour, J. Therm. Anal. Calorim. 81 (2005) 183–189.

[18] K.G. Varshney, P. Gupta, Synthesis, characterization and applications of a new phase of crystalline and mercury selective acrylamide cerium(IV) phosphate: a novel fibrous ion exchanger, Indian J. Chem. 42A (2003) 89–93.

[19] A.P. Gupta, H. Agarwal, S. Ikram, Studies on new composite material polyaniline zirconium (IV) tungstophosphate; Th (IV) selective cation exchanger, J. Indian Chem. Soc. 80 (2003) 57–59.

[20] M.J. Shaw, P.N. Nesterenko, G.W. Dicinoski, P.R. Haddad, Selectivity behaviour of a bonded phosphonate–carboxylate polymeric ion exchanger for metal cations with varying eluent compositions, J. Chromatogr. A 997 (2003) 3–11.

[21] T.S. Koseoglu, E. Kir, S.P. Ozkorucuklu, E. Karamızrak, Preparation and characterization of P2FAn/PVDF composite cation-exchange membranes for the removal of Cr(III) and Cu(II) by Donnan dialysis, React. Funct. Polym. 70 (2010) 900–907.

[22] C.S. Sundaram, S. Meenakshi, Fluoride sorption using organic–inorganic hybrid type ion exchangers, J. Coll. Interf. Sci. 333 (2009) 58–62.

[23] A.A. Khan, Inamuddin, Applications of Hg(II) sensitive polyaniline Sn(IV) phosphate composite cation-exchange material in determination of Hg^{2+} from aqueous solutions and in making ion-selective membrane electrode, Sens. Actuators B: Chem. 120 (2006) 10–18.

[24] H. Li, Z. Zheng, M. Cao, R. Cao, Stable gold nanoparticle encapsulated in silica-dendrimers organic–inorganic hybrid composite as recyclable catalyst for oxidation of alcohol, Micropor. Mesopor. Mater. 136 (2010) 42–49.

[25] K. Dallmann, R. Buffon, Sol–gel derived hybrid materials as heterogeneous catalysts for the epoxidation of olefins, Catal. Commun. 1 (2000) 9–13.

[26] S. Chaudhari, S.R. Sainkar, P.P. Patil, Corrosion protective poly(o-ethoxyaniline) coatings on copper, Electrochim. Acta 53 (2007) 927–933.

[27] Y. Zhang, H.M. Zhang, C. Bi, X.B. Zhu, An inorganic/organic self-humidifying composite membranes for proton exchange membrane fuel cell application, Electrochim. Acta 53 (2008) 4096–4103.

[28] J.L. Malers, M.A. Sweikart, J.L. Horan, J.A. Turner, A.M. Herring, Studies of heteropoly acid/polyvinylidenedifluoride–hexafluoroproylene composite membranes and implication for the use of heteropoly acids as the proton conducting component in a fuel cell membrane, J. Power Sources 172 (2007) 83–88.

[29] S.A. Nabi, Z. Alam, Inamuddin, A cadmium ion-selective membrane electrode based on strong acidic organic inorganic composite cation-exchanger: polyaniline Ce(IV) molybdate, Sens. Transd. J. (S & T e-Digest) 92 (2008) 87–89.

[30] C. Guizard, A. Bac, M. Barboiu, N. Hovnanian, Hybrid organic–inorganic membranes with specific transport properties: applications in separation and sensors technologies, Sep. Purif. Technol. 25 (2001) 167–180.

[31] M. Iwata, T. Adachi, M. Tonidokoro, Hybrid sol–gel membranes of polyacrylonitrile–tetraethoxysilane composites for gas permselectivity, J. Appl. Polym. Sci. 88 (2003) 1752–1759.

[32] P. Lacan, C. Guizard, P.L. Gall, Facilitated transport of ions through fixed-site carrier membranes derived from hybrid organic–inorganic materials, J. Membr. Sci. 100 (1995) 99–109.

[33] M. Kumar, B.P. Tripathi, V.K. Shahi, Ionic transport phenomenon across sol–gel derived organic–inorganic composite mono-valent cation selective membranes, J. Membr. Sci. 340 (2009) 52–61.

[34] A. Nilchi, A. Khanchi, H. Atashi, A. Bagheri, L. Nematollahi, The application and properties of composite sorbents of inorganic ion exchangers and polyacrylonitrile binding matrix, J. Hazard. Mater. A137 (2006) 1271–1276.

[35] A. Clearfield, A.S. Medina, On the mechanism of ion exchange in crystalline zirconium phosphates. III. The dehydration behavior of sodium ion exchanged phases of α-zirconium phosphate, J. Inorg. Nucl. Chem. 32 (1970) 2775–2780.

[36] G. Alberti, R. Bertrami, M. Caseola, U. Costantino, J.P. Gupta, Crystalline insoluble acid salts of tetravalent metals—XXI ion exchange mechanism of alkaline earth metal: ions on crystalline $ZrHNa(PO_4)_2\cdot 5H_2O$, J. Inorg. Nucl. Chem. 38 (1976) 843–848.

[37] I.P. Saraswat, S.K. Srivastava, A.K. Sharma, Kinetics of ion exchange of some complex cations on chromium ferrocyanide gel, Can. J. Chem. 57 (1979) 1214–1217.

[38] N.J. Singh, J. Mathew, S.N. Tandon, Kinetics of ion exchange. A radiochemical study of rubidium(1+)–hydrogen(1+) and silver(1+)–hydrogen(1+) exchange on zirconium arsenophosphate, J. Phys. Chem. 84 (1980) 21.

[39] G.E. Boyd, A.W. Adamson, L.S. Myers, The exchange adsorption of ions from aqueous solutions by organic zeolites. II. Kinetics, J. Am. Chem. Soc. 69 (1947) 2836–2848.

[40] D. Reichenberg, Properties of ion-exchange resins in relation to their structure. III. Kinetics of exchange, J. Am. Chem. Soc. 75 (1953) 589–597.

[41] F. Helfferich, Ion Exchange, McGraw-Hill, New York, 1962 (Chapter 6).

[42] W. Nernst, Z. Physik. Chem. 4 (1889) 129.

[43] M. Planck, Ann. Phys. Chem. 39 (1890) 161.

[44] A. Sari, D. Çitak, M. Tuzen, Equilibrium, thermodynamic and kinetic studies on adsorption of Sb(III) from aqueous solution using low-cost natural diatomite, Chem. Eng. J. 162 (2010) 521–527.

[45] K.G. Varshney, A.A. Khan, S. Rani, Forward and reversible ion exchange kinetics for Na^+–H^+ and K^+–H^+ exchanges on crystalline antimony (V) silicate cation exchanger, Colloids Surf. A: Physicochem. Eng. Aspects 25 (1987) 131–137.

[46] K.G. Varshney, A. Gupta, K.C. Singhal, Synthetic, analytical and kinetic studies on a crystalline and thermally stable phase of antimony(V) arsenosilicate cation exchanger, Colloids Surf. A: Physicochem. Eng. Aspects 82 (1994) 37–48.

[47] A.P. Gupta, P.K. Varshney, Investigation of some kinetic parameters for M^{2+}–H^+ exchanges on zirconium(IV) tungstophosphate—a cation exchanger, React. Polym. 32 (1997) 67.

[48] C.N. Reilley, R.W. Schmidt, F.S. Sadek, Chelon approach (I) survey of theory and application, J. Chem. Educ. 36 (1959) 555–565.

[49] S. Kodama, K. Fukui, A. Mazume, Relation of space velocity and space time yield, Ind. Eng. Chem. 45 (1953) 1644–1648.

[50] F. Helfferich, M.S. Plesset, Ion exchange kinetics: a nonlinear diffusion problem, J. Chem. Phys. 28 (1958) 418–424.

[51] M.S. Plesset, F. Helfferich, J.N. Franklin, Ion exchange kinetics: a nonlinear diffusion problem. II. Particle diffusion controlled exchange of univalent and bivalent ions, J. Chem. Phys. 29 (1958) 1064–1069.