



Evaluation of thermodynamic and kinetic parameters for conducting nanocomposite polypyrrole zirconium titanium phosphate



Asif Ali Khan*, Leena Paquiza

Analytical and Polymer Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002, India

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ABSTRACT

The kinetics and mechanism for the ion-exchange processes like Mg(II)–H(I), Ca(II)–H(I), Sr(II)–H(I), Ba(II)–H(I), Ni(II)–H(I), Cu(II)–H(I), Mn(II)–H(I) and Zn(II)–H(I) at different temperatures using approximated Nernst–Planck equation under the particle diffusion controlled phenomenon were studied for the polypyrrole zirconium titanium phosphate nanocomposite cation exchanger. TEM proves the formation of the nanocomposite 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^\ddagger) have been estimated. These results are useful for predicting the ion exchange process occurring on the surface of this cation-exchanger.

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1. Introduction

Nano-ordered composite materials consisting of organic polymers and inorganic materials have creation of high-performance or high-functional polymeric materials because of their unique property to combine the significant features of organic polymers with those of inorganic materials [1–4]. The sol–gel reaction makes possible to incorporate the organic polymer segments in the network matrix of inorganic materials. Applications of these materials have been explored in the fields of catalyst [5,6], coatings [7,8], gas permselectivity [9], fuel cell [10,11], chemical sensors [12], and ion exchange [13–15]. Among them composite materials possessing ion-exchange properties have recently drawn particular interest because ion-exchange is important for a variety of applications such as water treatment, chemical separation, and electrochemical sensing [16]. Hybrid framework composite, including both metal–organic coordination polymers and systems that contain extended inorganic connectivity (extended inorganic hybrids), have recently developed into an important new class of ion-exchanger and has been of explored in our laboratory [17–22].

'Organic–inorganic' composite materials are used for the fabrication of various electrometric sensors for analytical purposes. The ion-selective membrane electrode assembly will be

portable; therefore it can be used in laboratory analysis as well as in industry, process control, physiological measurements, and environmental monitoring. Successful ion-selective membrane electrodes can be commercially feasible in place of high cost instruments.

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 [23–25] of kinetic behavior are based on the old Bt criterion [26,27] which is not very useful for a true ion-exchange (non-isotopic exchange) process because of the different effective diffusion coefficients and different mobilities [28] of the exchanging ions involved. The Nernst–Planck [29,30] 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 [31,32], relatively less information exists on the kinetics of exchange on composite ion.

The present research evaluates the ion-exchange process occurring over the surface of nanocomposite cation exchanger polypyrrole zirconium titanium phosphate (PPy-ZTP). The synthesis and physico-chemical characterization of this electrically conducting nanocomposite has also been studied and results are published [19,20]. The nanocomposite was found highly selective for toxic metal ion mercury and successfully used as indicator electrode indicating its utility for the removal of Th(IV) from waste stream [20].

* Corresponding author. Tel.: +91 571 2720323.

E-mail address: paquiza001@gmail.com (A.A. Khan).

2. Experimental

2.1. Reagents and Instruments

The main reagents used were obtained from CDH, Loba Chemie, E-Merck and Qualigens (India Ltd., used as received). All other reagents and chemicals were of analytical grade.

Following instruments were used during present research work: digital pH-meter (Elico Li-10, India); a digital potentiometer (Equiptronics EQ 609, India); an electronic balance (digital, Sartorius-210S, Japan), Transmission electron microscope – TEM Philips EM 400 and an automatic temperature controlled water bath incubator shaker – Elcon (India) were used.

2.2. Preparation of nanocomposite polypyrrole zirconium titanium phosphate (PPy-ZTP)

The nanocomposite cation exchanger was prepared by sol–gel mixing of polypyrrole (an organic polymer) into the inorganic precipitate of zirconium titanium phosphate (ZTP) with varying mixing ratio. The preparation method for inorganic precipitate of zirconium titanium phosphate (ZTP) was very similar to that of Alberti and Constantino [33], with slight modification [34]. In white inorganic gel of ZTP, FeCl₃ solution was first added which turned the gel color into light yellow, then the solution of pyrrole (in toluene) was added dropwise with constant stirring for 1 h. The resultant mixture turned first to green and then slowly into black slurries, which was kept for 24 h at room temperature (25 ± 2 °C). The dried products were immersed in 1 M HNO₃ solution for 24 h to convert it in H⁺ form. The excess acid was removed after several washing with DMW. The materials were finally dried at 40 °C and sieved to obtain shiny black granules of polypyrrole zirconium titanium phosphate (PPy-ZTP). The conditions of preparation, the ion-exchange capacity, and physical appearances of the organic, inorganic and nanocomposite cation exchangers are given in Table 1. The ion exchange capacity was determined by standard column process as described in our previous work [20]. On the basis of Na⁺ exchange capacity (I.E.C) and yield percentage, sample **PP-9** was selected for further studies.

2.3. Characterization of hybrid composite material

The particle size and morphology of the prepared composite material has been characterized by using TEM techniques.

2.4. Ion-exchange kinetics

2.4.1. Concentration variation study

Nanocomposite cation-exchanger was grounded and then sieved to obtain particles of definite mesh size (25–50, 50–70,

70–100 and 100–125). Out of them the particles of mean radii ~125 μm (50–70 mesh) in H⁺ were selected to evaluate various kinetic parameters. The concentration effect on the mechanism of exchange was studied at 25 °C by taking different metal ion concentrations from 0.01 M to 0.04 M at intervals of 0.01 M for the forward process.

2.4.2. Temperature variation study

20 ml fractions of the 0.01 M metal ion solutions (Mg, Ca, Sr, Ba, Ni, Cu, Mn and Zn) prepared in DMW were shaken with 200 mg of the cation-exchanger in H⁺-form in several conical flasks at the desired temperatures [25, 40, 55 and 70 °C] for different time intervals (0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 min). The supernatant liquid was removed immediately after every prescribed time interval and determinations were made, usually by EDTA titration [35]. Each set was repeated four times and the mean values were taken for calculations.

3. Results and discussion

The present study showed nanocomposite polypyrrole zirconium titanium phosphate (PPy-ZTP) has high Na⁺ exchange capacity (3.68 meq g⁻¹) as compared to its inorganic counterpart ZTP (3.36 meq dry g⁻¹) (Table 1). Improvement in ion exchange and granulometric properties are considered due to the presence of binding polymer, polypyrrole.

In order to check the reproducibility of prepared composite, it was synthesized five times under identical condition of concentration of reagents, mixing ratio and drying temperature. The composition and ion exchange capacity and yield of each product were examined. The averages and standard deviation of the ion exchange capacity and yield were found to be 3.66 ± 0.02% for PPy-ZTP.

The TEM micrograph of polymer polypyrrole and PPy-ZTP proves that proposed 'polymeric-inorganic' cation exchanger is a nanocomposite (Fig. 1).

3.1. Kinetic studies on nanocomposite PPy-ZTP

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 rate-controlling mechanism can be film diffusion, if the slow step is diffusion across the hydrodynamic film that surrounds the exchanger particles or particle diffusion, if the slow step is diffusion inside the exchanger beads themselves.

In the first case, a concentration gradient is set up within the liquid film, whereas inside the exchanger a uniform concentration

Table 1
Conditions of preparation and the ion-exchange capacity of polypyrrole zirconium titanium phosphate.

Sample no.	Mixing volume ratio (v/v) of inorganic			Mixing volume ratio (v/v) of organic		Appearance of the sample	I.E.C. (meq/gm)
	0.1 M TiCl ₄ in H ₂ SO ₄	0.1 M ZrOCl ₂ in H ₂ SO ₄	Na ₂ HPO ₄ in DMW	% Pyrrole in Toluene	0.1 M FeCl ₃ in DMW		
PP-1	1(1 M)	1(1 M)	1(2 M)	0.5	1	Gray	1.02
PP-2	1(0.2 M)	1(0.1 M)	2(0.2 M)	–	–	White	3.36
PP-3	1(0.1 M)	2(2 M)	1(0.2 M)	20	1	Black	2.15
PP-4	–	–	–	33	2	Black	0.72
PP-5	1(1 M)	1(1 M)	1(0.2 M)	33	1	Black	1.28
PP-6	1(1 M)	1(2 M)	2(0.2 M)	33	1	Black	2.5
PP-7	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	2	Shiny black	3.1
PP-8	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	2	Shiny black	3.34
PP-9	1(0.2 M)	1(0.1 M)	2(0.2 M)	33	2	Blackish purple	3.68

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