Ion-exchange properties and mobility of Cu^{2+} ions in zirconium hydrophosphate ion exchangers

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Abstract

Three types of inorganic ion exchangers based on zirconium hydrophosphate were synthesised using the following methods: (I) phosphatising of dried zirconium hydroxide gel; (II) phosphatising of makeup zirconium hydroxide gel; (III) mixing together of $ZrOCl_2$ and H_3PO_4 solutions. The influence of synthesis conditions on exchange and kinetic properties of ion exchangers were analysed. It was found that the maximal molar P:Zr ratio in ion exchanger can be reached using method (II). Copper ion mobility in ion exchangers increases with increasing P:Zr ratio. The effective diffusion coefficients of Cu^{2+}, which were obtained by kinetic methods at pH 2.5 reaches 1.8×10^{-13} to 7.7×10^{-13} $m^2\,s^{-1}$.
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1. Introduction

Inorganic ion exchangers based on amorphous zirconium hydrophosphate (ZHP) as and its derivatives are notably promising materials for the removal of heavy metal ions, for instance Cs^+ [1–3], Co^{2+}[2,4–6], Ni^{2+} [2,7], Cu^{2+}[2,4–6,8], Pb^{2+} [6,9], Hg^{2+} [9], Zr^{4+} [10], Cd^{2+}, Fe^{3+}, Cr^{3+} [6], from very dilute solutions. These ion exchangers are characterised by appreciable exchange capacity and considerable selectivity towards the above metal ions. However a substantial imperfection of such ion exchangers is the relatively slow exchange kinetics due to sluggish particle diffusion [7,11] in comparison to transport processes in flexible ion-exchange resins [12–14]. Nevertheless it is known that particle diffusion in ZHP ion exchangers depends on their composition and their structure formed during the synthesis process [15]. This allows us to suppose that it is possible to produce inorganic ion exchangers with improved diffusion rates of metal ions.

In this context, the present investigation was aimed at studying the influence of synthesis conditions on the exchange and kinetic properties of ZHP. The investigation involved assessment of Cu^{2+} ion mobility in ion exchangers obtained by different methods.

2. Experimental

2.1. Synthesis of ZHP ion exchangers

ZHP ion exchangers containing different amounts of functional groups were synthesised for the investigation. The synthesis of ZHP-1, ZHP-2 and ZHP-5 included preparation of zirconium hydroxide (ZH) gel and subsequent treatment of dried gel with H_3PO_4 (method I). This procedure included the following steps:

1. ZH precipitation from a fresh 1 M $ZrOCl_2$.solution at room temperature. The precipitant (a mixed solution containing glycerol, urotropine and urea) was gradually added to the $ZrOCl_2$ solution during 10 min under vigorous stirring. A volume of each solution was 1 dm^3.
2. Washing of fresh gel with 1 dm^3 of deionised water during 30 min using decantation method. This step was repeated 12 times. Finally the washings pH reached 7.5–8.

Nomenclature

$\bar{A}_{Cu}$	exchange capacity of ion exchanger towards Cu^{2+} after exchange process completion (mol kg^{-1})
$\bar{A}_{Cu}(t)$	exchange capacity of ion exchanger towards Cu^{2+} at predetermined time (mol kg^{-1})
$\bar{A}_{Na}$	total exchange capacity of ion exchanger towards Na^+ (mol kg^{-1})
d_p	effective particle diameter (m)
$\bar{D}_{Cu}$	Cu^{2+} diffusion coefficient in ion exchanger (m^2 s^{-1})
$\bar{m}$	molar P:Zr ratio in ion exchanger
t	time (s)
$t_{0.5}$	time of 50% exchange (s)

3. Storage of the ZH gel in deionised water for 12 h.
4. Filtering of the gel.
5. Drying of the gel at 333 K during 5 h.
6. Treatment of the ZH gel with a 5 M H_3PO_4 solution at ≈373 K.
7. Washing of the ion exchanger with 1 dm^3 of deionised water with a decantation method. This step was repeated 10 times. Finally the effluent pH reached 5.5–6.
8. Drying of the sample in a dessicator at room temperature during 48 h. It was found that this time is sufficient for reaching a constant weight of the ion exchanger.

The composition of the mixed precipitant, which was used for the preparation of ZHP-1 and ZHP-2 (step 1), was as follows: 1.4 mol dm^{-3} glycerol, 2 mol dm^{-3} urotropine and 2 mol dm^{-3} urea. ZH gel was formed approximately 10 min after the end of precipitant addition. In order to obtain ZHP-5 sample the 1.4 mol dm^{-3} glycerol, 2 mol dm^{-3} urotropine and 6 mol dm^{-3} urea was used as a precipitant. In this case gel was formed 1 min after the end of precipitant solution addition.

ZH gel was treated with phosphoric acid (step 6) during 0.5 h (ZHP-1) or 1 h (ZHP-2 and ZHP-5). Increasing of the phosphatising time was found to cause deterioration of mechanical properties of ion exchangers.

The procedure for the synthesis of ZHP-4 (method II) was similar to that described for ZHP-1, ZHP-2 and ZHP-5, however step 4 (drying of ZH gel) was excluded. The urea concentration in the precipitant was 2 mol dm^{-3}, the time of ZH gel phosphatising was 1 h.

ZHP-3 ion exchanger was obtained by mixing together 2 M $ZrOCl_2$ and 2 M H_3PO_4 solutions (method III) and dispersing the gel obtained in octane at room temperature as described in [2]. The volume of each solution was 1 dm^3. The gel was washed with 10 dm^3-deionised water and dried at room temperature in a dessicator for 48 h.

The ion exchangers were sieved, and fractions of 0.16–0.25 mm (ZHP-1–ZHP-3) or 0.125–0.225 mm (ZHP-4, ZHP-5) were selected.

2.2. Characterisation of ZHP ion exchangers

The molar P:Zr ratio, $\bar{m}$, was determined by dissolving samples in concentrated H_2SO_4 and measuring the concentration of P and Zr by colourimetric methods [16]. Zirconium and phosphorus were assayed as metal complexes with pyrocatechin violet (at 600 nm) and molybdate (at 400 nm), respectively. The analysis was performed with a Pye Unicam 8800 UV/VIS spectrophotometer. The specific surface area and average pore diameter were determined from the nitrogen adsorption isotherm obtained using Tristar 3000 adsorption measurement instrumentation. The water content was determined as a weight loss after thermal treatment of the samples at 423 K during 4 h. Under these conditions water, which is associated with functional groups by means of hydrogen bonds, is removed [15].

The dependence of the maximum exchange capacity of samples for Na^+ ions on pH was determined as follows. A 1 M NaCl solution, which had a predetermined pH adjusted by addition of HCl, was passed through an ion-exchange column 6 mm in diameter until the solution conductivity at the column outlet became equal to that at the column inlet. Solution conductivity was measured with HI 9932 (Hanna Instruments) apparatus. The superficial velocity of the solution was fixed at 0.08 cm s^{-1}. After loading, the samples were washed with water, dried at room temperature and treated with a 2 M H_2SO_4 solution. The Na^+ content of the washings was determined using a PFM-U4.2 (Analitpribor) flame photometer. The maximum exchange capacity $\bar{A}_{Na}$ was calculated from the data obtained.

After desorption, the samples were also dissolved in concentrated H_2SO_4. The acid solution was analysed using a flame photometric method. It was found that the Na^+ content of the solution was lower than the sensitivity of the analysis technique. Thus it may be suggested that treatment of ion exchangers with 2 M H_2SO_4 results in a complete desorption of Na^+ ions.

2.3. Investigation of ion-exchange kinetics

To investigate the exchange kinetics a weighted amount of ion exchanger was placed as a thin bed between two polyethylene grids fixed on the end of a rigid tube (Fig. 1). The diameter and length of the tube were 1.5 and 10 cm, respectively. A 0.1 M $CuSO_4$ solution was previously acidified with H_2SO_4 up to pH 2.5. The solution was pumped from a reservoir at the inlet through the tube and into a waste reservoir using a CHM vacuum pump (Temp). In fact the solution circulated through the thin ion exchanger bed since the fluid system was closed. The volume of the solution was 1 dm^3.

The solution circulated through the ion exchanger bed for a predetermined time. After this time lapsed, the contact be-