

## An experimental study of ionic exchange on zirconium phosphate

*Distribution of microquantitative of cations was studied in the system water solution- amorphous and crystalline zirconium phosphate, by determination coefficient of cations with + 2 charge, depending on change of acidity of water solution, concentration of cations and temperature of the system the method of macroscopic thermodynamics was applied for the case when small quantities of ions are present in the system that exchange.*

*Experiments were carried out at temperature from 298.16 to 348.16 K. The following series of cations was obtained in the affinity of the changes to an amorphous zirconium phosphate: Mg < Ca < Sr < Ba < Zn < Cu. [1]*

*In all experiments samples were equilibrium for 24 hours in glass ampules, which were sealed before equilibration. Measurements were carried out granula  $r_o = 45\mu\text{m}$  (crystalline) in chosen systems. It is established, by investigation of the mechanism of kinetics of bivalent cations on ZrP, that kinetics in the investigated system is determined by diffusion through the inert contacting layer of the liquid around the particle.*

*Considering that the mass-action law is valid for the ion exchange processes studied with the possibility of the application of Gibbs-Duhem's equation, were able to determine activities and activity factors of the components in the solid phase as a function of the exchanger loading.*

**Key words:** ion exchange, zirconium phosphate, chemical equilibrium

### INTRODUCTION

Estimation of the theoretical and practical over-takes in this field was necessary in order to obtain the estimat of quality of ionic exchange for ion-exchange of zirconium phosphate, which is resistant to the radioactivity high temperatures and high pressures.

The ion exchange selectivity of different types of zirconiumphosphate is well- known and has been described in many papers [2-18]. Palmer at all [6] found that at pH = 2, the selectivity of zirconium phosphate for Cu<sup>2+</sup> was higher than for Fe<sup>3+</sup> and Al<sup>3+</sup>. The thermodynamics of ion exchange on different types of zirconium phosphate has been studied for various systems [15 - 21].

The expected accuracy of experimental values obtained did not agree [18 -24]. This is explained by fact that is by higher acidity of the solution increases the load of the zirconiumphosphate for Cu<sup>2+</sup>- ion on the principal of osmotic pressure, the preference by exchange has ion with less equivalent volume in the

solvent state. The line which possess through the points on graphis  $\ln K = f\left(\frac{1}{T}\right)$  conditions certain error in determining the slope, which shold be multiplied with universal constant R and according the theory errois would be accumulated.

### EXPERIMENTAL

Amorphous zirconium phosphate with P: Zr = 1.86 and exchange capacity of 1.8 mmol amonijevog jona (NH<sup>+</sup><sub>4</sub>) per gram of sorbent at pH = 3.4 was prepared by precipitating zirconium oxide dichloride with phosphoric acid in the appropriate ratio [8]. The crystallinity was checked by X - ray diffraction of powdered samples, and found to be the same as that of samples 3 and 4 described by Ilić [8,14] and Pekarek [4]. Samples equilibrated in air were kept either in a thermostatted room at 298. 16 K. An environment of 52% relative humidity was achieved in the vapor phase above as turated solution of Mg(NO<sub>3</sub>)<sub>2</sub> · 6 H<sub>2</sub> O at 298. 16 K.

All measurements on the system CuCl<sub>2</sub> - HCl were carried out at a constant ionic strength of 0.1. All solutions were prepared using water redistilled from a quartz apparatus. Copper was determined by complexation titration with disodium salt of ethylene-

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Paper received: 28.06.2011.

diaminediacetic acid in the presence of urotropine and glycinethymol blue.

RESULTS AND DISCUSSION

Zirconium phosphate as an ion - exchanging substance was synthesised in an amorphous as well as crystalline state. The structure of the material obtained was analysed by X- ray method.

The distribution coefficient,  $K_d$ , of  $Cu^{2+} / H^+$  ionic ratio was measured for the system of aqueous

solution amorphous and crystalline zirconium phosphate in dependence on:

- (i) temperature,
- (ii) acidity of aqueous solution,
- (iii) concentration of  $Cu^{2+}$  - ion.

For experimental conditions used the thermodynamics characteristics of the proces of ion - exchange were calculated, i. e., the exchange enthalpy  $\Delta H$ , entropy  $\Delta S$  and free enthalpy  $\Delta G$  (Table I).

Table I - Thermodynamic characteristic  $\Delta H, \Delta G, \Delta S$  of the ion exchange  $Cu^{2+}/H^+$  on zirconium phosphate

T (K)	lnK (—)	$\Delta G$ ( $\frac{kJ}{mol}$ )	$\Delta H$ ( $\frac{kJ}{mol}$ )	$\Delta S$ ( $\frac{J}{molK}$ )
298.16	-1.971	+1.167	+24.081	0.076
323.16	-0.933	+0.599	+24.081	0.072
348.16	-0.370	+0.370	+24.081	0.068

Table II - Measured values of conceentration and fractions  $\beta_{Cu^{2+}}, X_{Cu^{2+}}$  in dependence on temperature and constant HCl (for 200 cm<sup>3</sup> of aqueous solution and 1 g of solid phase)

concentration of cooper ion		concentration of HCl at equilibrium ( $\frac{mol}{dm^3}$ )	equivalent fraction	
input solution ( $\frac{mol}{dm^3}$ )	equilibrium solution ( $\frac{mol}{dm^3}$ )		$Cu^{2+}$ -ion in solid phase ( $\beta_{Cu^{2+}}$ )	$Cu^{2+}$ -ion in liquid phase ( $X_{Cu^{2+}}$ )

T = 298. 16 K

0.03332	0.03059	$2.22529 \cdot 10^{-3}$	0.6074	0.9694
0.03299	0.03104	$6.83744 \cdot 10^{-3}$	0.4324	0.9008
0.02998	0.02857	0.01429	0.3138	0.7999
0.02498	0.02398	0.02931	0.2673	0.6207
0.02000	0.01901	0.04292	0.2225	0.4697
0.01501	0.01442	0.05816	0.1750	0.3315
0.01021	0.00962	0.07117	0.1311	0.2128
0.00502	0.00472	0.08777	0.0669	0.1028

Table III - Measured values of concentrations and fractions  $\beta_{Cu^{2+}}$ ,  $X_{Cu^{2+}}$  in dependence on temperature and constant HCl (for 200 cm<sup>3</sup> of aqueous solution and 1g of solid phase).

concentration of cooper ion		concentration of HCl at equilibrium ( $\frac{mol}{dm^3}$ )	equivalent fraction	
input solution ( $\frac{mol}{dm^3}$ )	equilibrium solution ( $\frac{mol}{dm^3}$ )		Cu <sup>2+</sup> -ion in solid phase ( $\beta_{Cu^{2+}}$ )	Cu <sup>2+</sup> -ion in liquid phase ( $X_{Cu^{2+}}$ )

T = 323. 16K

0.03332	0.02989	0, 01024	0,7624	0,8538
0.03299	0.02956	0,01142	0,7429	0,8381
0.02998	0.02701	0,01897	0,6601	0,7401
0.02498	0.02257	0,03230	0,5352	0, 5829
0.02000	0.01800	0,03152	0,4460	0,4401
0.01501	0.01340	0,05983	0,3570	0,3094
0.01021	0.00908	0,07404	0,2505	0,1970
0.00502	0.00446	0,08777	0,1251	0,0922

Tabele IV - Measured values of concentrations and fractions  $\beta_{Cu^{2+}}$ ,  $X_{Cu^{2+}}$  in dependence on temperature and constant HCl ( 200 cm<sup>3</sup> of aqueous solution amd 1 g of solid phase)

concentration of cooper ion		concentration of HCl at equilibrium ( $\frac{mol}{dm^3}$ )	equivalent fraction	
input solution ( $\frac{mol}{dm^3}$ )	equilibrium solution ( $\frac{mol}{dm^3}$ )		Cu <sup>2+</sup> -ion in solid phase ( $\beta_{Cu^{2+}}$ )	Cu <sup>2+</sup> -ion in liquid phase ( $X_{Cu^{2+}}$ )

348.16K

0.03332	0.02958	0,01126	0,8302	0,8401
0.03299	0,02942	0,01463	0,7935	0,8009
0.02998	0,02670	0,02055	0,7281	0,7221
0.02498	0,02222	0,03430	0,6126	0,5644
0.02000	0,01775	0,04750	0,5009	0,4274
0.01501	0,01324	0,06081	0,3941	0,3033
0.01021	0,00888	0,07427	0,3940	0,1929
0.00502	0,00429	0,08501	0,1631	0,0916

The calculation was based on the best-fitt approximation of experimental values of the distribution coefficients. The resulting positive values of the enthalpies indicate the endoter,ic effect of Cu<sup>2+</sup>/H<sup>+</sup> ions exchange on the zirconium phosphate was measured on the following three levels (of Kelvin scale ): 298.16 and 348.16 degrees. The distribution coeffi-

cient for Cu<sup>2+</sup>/H<sup>+</sup> exchange increases with increasing temperature (Table II and Fig.1).

Thermodynamic constants of equilibrium, K<sub>21</sub>, were evaluated from the experimental data by Högfeltdt [1, 11-13]. as well as by Ruvarac - Vesely [5]. method, resulting K<sub>21</sub> values following the both method well agree with each ather.

The kinetics of ion exchange process of  $\text{Cu}^{2+}/\text{H}^{+}$  was measured for an amorphous as well as a crystalline state at various levels of copper ion ( $\text{Cu}^{2+}$ ) concentration and acidity of aqueous solution. The exchange proceeds more rapidly on an amorphous zirconiumphosphate than on it's crystalline form. The kinetics on crystalline form was more sensitive to concentrations of the relevant ions in the region of experimental condition used.

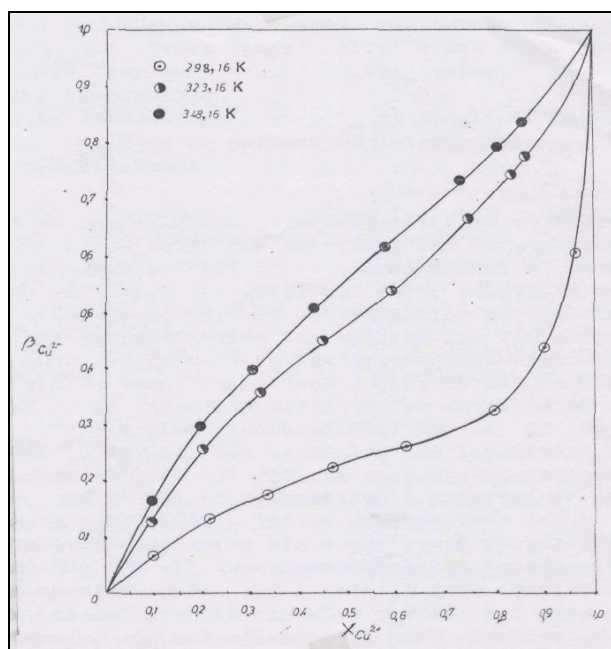


Figure 1 - Equilibrium function  $\beta_{\text{Cu}^{2+}} = f(X_{\text{Cu}^{2+}})$  for ion exchange  $\text{Cu}^{2+}/\text{H}^{+}$  on an amorphous zirconiumphosphate at temperatures 298.16 K, 323.16 K and 348.16 K

Heats of wetting of amorphous zirconiumphosphate ( 15 to 66 J/g ) was 3 to 20 times higher than those on crystalline zirconiumphosphate ( which was 2.6 to 6.6 J/g)

### CONCLUSION

In order to examine the mechanism and legalities of the process of the ionic exchange of bivalent cations on zirconiumphosphate, in static circumstances, and to use it in medicine (material for dialysis in nephrology, stomatology, etc.), a little scorbed  $\text{Cu}^{2+}$ -ion was chosen in this study.

Thermodynamics equilibrium constant could be determined based upon the investigation of that composition of ionehchanger in which the ratio chemical activity ions are exchanged in the solid phase equally. In that case modified equation for the thermodynamic equilibrium constant has the following log form.

By the given expression we could determine the equilibrium constant proces  $\text{Cu}^{2+}/\text{H}^{+}$  exchange of ions on zirconiumphosphate, without preliminary determination of factors of activity ions,  $g_{\text{H}^{+}}$  and  $g_{\text{Cu}^{2+}}$ , in solid phase. We have reduced calculation on the graphic form of given function which influences the equivalent of ion  $\text{Cu}^{2+}$  on the value of function  $\log \frac{a_{\text{H}^{+}}^2}{a_{\text{Cu}^{2+}}}$ , on the ordinate of the graphic denoted by  $\log K$ .

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## IZVOD

### EKSPERIMENTALNO ISPITIVANJE JONSKE IZMENE NA CIRKONIJUMFOSFATU

*Ispitivana je raspodela mikrokoličine katjona u sistemu vodeni rastvor - amorfni i kristalni cirkonijumfosfat i koeficijent aktivnosti katjona sa oksidacionim brojem +2, u zavisnosti od kiselosti vodenog rastvora, koncentracije jona i temperature metodom makroskopske termodinamike za slučaj kada su u sistemu prisutne male količine jona koje se izmenjuju.*

*Eksperimenti su rađeni na temperaturi od 298,16 do 348,16 K. Dobijen je sledeći niz katjona u afinitetu izmene na amorfnom cirkonijumfosfatu:  $\text{Mg} < \text{Ca} < \text{Sr} < \text{Ba} < \text{Zn} < \text{Cu}$  [1].*

*U svim eksperimentima uzorci su uravnotežavani 24 časa u staklenim ampulama, koje su pre uravnotežavanja zatopljene. Merenja su vršena sa granulama kristalnog ZrP, prečnika,  $r_0 = 45 \mu\text{m}$ .*

*Utvrđen je, ispitivanjem, mehanizam kinetike katjona sa oksidacionim brojem +2, na ZrP, tj. da kinetiku u ispitivanom sistemu određuje difuzija kroz nepokretni dodirni sloj tečnosti oko čestice.*

*Uzimajući da zakon hemijske ravnoteže važi i za posmatrani proces jonske izmene, na koji se može primeniti Gibbs- Duhemova jednačina, mi smo bili u mogućnosti da odredimo aktivnost jona u čvrstoj fazi u funkciji obima izmene.*

**Ključne reči:** jonska izmena, cirkonijumfosfat, hemijska ravnoteža

Rad primljen: 28.06.2011.