HEATS OF IMMERSION AND HEAT OF H^+/Cu^{2+} EXCHANGE FOR AMORPHOUS ZIRCONIUM PHOSPHATE

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Heats of immersion of amorphous and crystalline zirconium phosphates in water were determined, and heat of H^+/Cu^{2+} exchange on amorphous zirconium phosphate at 298·15 K was obtained by direct calorimetric measurement.

The properties of amorphous and crystalline zirconium phosphates (ZrP) have been described by a number of authors[1-3]. The selectivity of zirconium phosphates for cation adsorption depends on the structure of these materials[1,2,4,5]. For amorphous ZrP at pH = 2 Palmer and Fuerstenau[6] found the sorption selectivity to be higher for Cu^{2+} than for cations with +3 charge (Fe, Al). Alberti and Conte[7] established the following affinity sequence for sorption of cations with +2 charge on amorphous ZrP: Mg < Ca < Sr < Ba < Zn < Cu. Structural changes of crystalline α-ZrP in ion exchange reactions with Cu^{2+} have been studied by Clearfield and Kalnins[8], who found the cations Mn^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+} to exchange irreversibly[9] on α-ZrP. For amorphous ZrP the exchange of Cu^{2+} is reversible, the adsorption isotherm being S-shaped[10], particularly at 298·15 K.

Enthalpy changes for ion exchange reactions on various types of ZrP have so far been obtained mostly in an indirect way, from equilibrium constants determined by sorption measurements at various temperatures under static conditions[2,11,12]. So obtained enthalpy changes are endothermic for exchange reactions involving alkali metals and alkali earth metals, and exothermic for UO_2^{2+}, Ce^{3+} and Eu^{3+} (ref.[2]).

In this work we have attempted to determine heats of ion exchange on amorphous ZrP by direct calorimetric method, and to compare the results with those derived from adsorption isotherms. We also studied the effect of the interaction between sorbent and the solution in which the exchange process was occurring.

The study was performed for H^+/Cu^{2+} exchange on amorphous ZrP. The choice of this system was motivated by literature data[10] indicating a surprisingly large endothermic effect of 24 – 35 kJ per mol of sorbed Cu^{2+} accompanying the exchange, as contrasted with heats of exchange for other cations of +2 charge which do not exceed 10 kJ/mol.

EXPERIMENTAL

Amorphous zirconium phosphate with P : Zr = 1·86 and an exchange capacity of 1·8 mmol NH_4^+ per gram of sorbent at pH = 3·4 was prepared by precipitating zirconium oxide dichloride with phosphoric acid in the appropriate mass ratio[13]. Crystalline α-ZrP was prepared as described by Clearfield and Smith[14]. The crystallinity was checked by X-ray diffraction of powdered samples, and was found to be the same as that of samples 3 and 4 described by Nancollas and Pekárek[15] or samples prepared by Clearfield and Stynes[16]. Samples equilibrated in air were kept either in a thermostatted room at 298·15 K in the case of measurements on Calvet calorimeter, or in non-thermostatted environment in the case of measurements on LKB calorimeter. An environment of 52% relative humidity was achieved in the vapour phase above a saturated solution of $Mg(NO_3)_2.6\,H_2O$ at 298·15 K. All measurements on the system $CuCl_2$–HCl were carried out at a constant ionic strength of 0·1. The heats were measured on an LKB 8700-1 calorimeter (Sweden) using 100 ml reaction cells with a high rate of stirring of the system, and on a Calvet heat-flow microcalorimeter (Setaram, France) using *c.* 10 ml reaction cells where only occasional and very limited stirring could be applied. Both calorimeters were calibrated by means of the heat of ionization of tris(hydroxy-methyl)-amino-methane (NBS 724a standard reference material) in 0·1M-HCl (ref.[17]). All solutions were prepared using water redistilled from a quartz apparatus[18]. Copper was determined by complexation titration with disodium salt of ethylenediaminediacetic acid in the presence of urotropine and glycinethymol blue[19].

RESULTS AND DISCUSSION

Based on sorption isotherms measured over a temperature range from 298·15 to 348·15 K, the H^+/Cu^{2+} exchange on amorphous zirconium phosphate was concluded[10] to be an endothermic process. However, trial calorimetric measurements on the same system have clearly demonstrated that the net heat effect is exothermic. This contradiction may be a consequence of the ion exchange reaction proper being accompanied by a markedly exothermic reaction occurring when the sorbent comes into contact with the sorption medium. To verify this supposition, we measured heats of immersion of zirconium phosphates in the media in which the exchange process was studied. In doing this, we used samples with differently developed crystalline structures and with various degrees of dehydration. Results of measurements of heats of immersion in water using a Calvet microcalorimeter are presented in Table I.

It can be seen from the table that immersion heats for amorphous zirconium phosphates are substantially more sensitive to moisture content than those for crystalline ZrP. This is apparently due to the difference in structure: while crystalline α-ZrP is a well-defined compound[14] of the composition $Zr(HPO_4)_2.H_2O$, amorphous sorbents, particularly those with P : Zr < 2, whose structure has not yet been definitely identified[1], contain various kinds of hydroxide functional groups which may markedly affect the strength of the bond of water to the sorbent. The uncertainty in immersion heats of amorphous ZrP, reaching values of about 2 J/g, is probably due to fluctuations in moisture content and/or to inhomogeneous distribution of moisture in the samples. For amorphous zirconium phosphates equilibrated in air it may be concluded that the same mechanism applies to the bonding of water molecules removed upon standing over silica gel and P_4O_{10}: the heats of dehydration agree surprisingly well, being, respectively, 8·51 and 8·45 J/mmol of sorbed water. Water adsorbed on samples equilibrated at 52% relative humidity is bound to the sorbent much more weakly, the heat of dehydration making only *c.* 1·9 J/mmol of sorbed

TABLE I

Heats of immersion of amorphous and crystalline zirconium phosphates (ZrP) containing various amounts of bound water, measured on Calvet microcalorimeter

ZrP	Storage environment	Time of storage h	Mass change relative to sample kept in air, mg/g	Heat of immersion J/g	Average value with maximum and minimum deviation J/g	
Amorph.	air	>260	—	−19·73	−17·27	+2·46 −1·82
				−16·26		
				−15·84		
				−15·45		
				−19·05		
	52% relat. humidity	93	+127·4	− 3·73	—	
	silica gel	145	− 14·1	−23·91	—	
	P_4O_{10}	100	−103·1	−65·66	—	
Cryst.	air	>260	—	− 3·14	− 3·06	+0·29 −0·26
				− 2·80		
				− 2·96		
				− 3·35		
	52% relat. humidity	95	+ 41·5	− 2·67	—	
	P_4O_{10}	125	− 11·9	− 6·61		

water. Crystalline zirconium phosphates show markedly lower immersion heats than do amorphous samples. Also, the scatter of heat of immersion values for samples equilibrated in air is distinctly lower. Immersion heats for these samples are about 5·4 J/mmol of sorbed water. It might seem that crystalline samples are more suitable for the study of heats of ion exchange, as the uncertainties involved are smaller. However, there are other factors which rule out the use of crystalline sorbents for this purpose. Firstly, sorption capacities of these sorbents for M^{2+} cations are too low under the conditions considered[8], making the measurement of the accompanying heat effects very difficult. Secondly, the H^+/Cu^{2+} exchange on crystalline preparations is an irreversible process[9].

The measurements were carried out at various concentrations of Cu^{2+} and at a constant ionic strength of 0·1 maintained by 0·1M-HCl. In addition, we examined the effect of acidity of the solution on the values of immersion heats using a Calvet microcalorimeter. The results, summarized in Table II, show that this effect is unimportant: the values are within experimental uncertainty of parallel determinations, and the average values compare very well with those given in Table I. Owing to all these facts, and particularly to unsatisfactory consistency of heat of immersion values for samples equilibrated in air, samples for measurements of heat changes accompanying the ion exchange process on ZrP and for determinations of heats

TABLE II

Heats of immersion of air-equilibrated amorphous zirconium phosphate in water and weakly acidic solutions of hydrochloric acid, measured on Calvet microcalorimeter

Environment	Heat of immersion J/g	Average value J/g	
H_2O	−16·05	−16·83	+0·45 −0·78
	−17·28		
	−17·18		
0·01 mol/l HCl	−17·28	—	
0·05 mol/l HCl	−17·94	−17·15	+0·79 −1·65
	−15·50		
	−17·63		
	−17·52		
0·09 mol/l HCl	−19·07	−17·87	+1·20 −0·81
	−17·06		
	−18·15		
	−17·21		

of immersion in the solutions studied were weighed and sealed simultaneously. We believe that this measure can partly reduce the uncertainty interval of heat of exchange determinations.

Experimental results obtained on Calvet microcalorimeter for H^+/Cu^{2+} exchange on amorphous ZrP in 0·01M-HCl are listed in the upper part of Table III. Because of insufficient stirring of the system, the exchange reaction proceeded for about 4 h; even then, however, it remained uncertain whether it reached equilibrium, since heat effects of this slow reaction may be so small as to become indistinguishable from noise level.

For this reason, further systems were investigated on LKB calorimeter which permits a high rate of stirring in the reaction cell, accelerating markedly the overall ion exchange process. The samples were kept in a non-thermostatted room and under other atmospheric conditions, and so the heats of immersion are not comparable with results presented in Tables I and II. Only systems with low acidities were suitable for determination of heats of H^+/Cu^{2+} exchange. Where the HCl concentration exceeded 0·01 mol/l, the extent of ion exchange was too small, leading to large errors in analytically determined Cu^{2+} concentrations and in small endothermic heats of ion exchange determined against the background of high exothermic heats of sorbent immersion. The small exchange capacity of the sorbent in HCl solutions of concentrations above 0·01 mol/l is consistent with the pattern of the adsorption isotherm, which is S-shaped[10], the Cu^{2+} sorption rising sharply only in the region of weakly acidic solutions. The average value of the heat of H^+/Cu^{2+} exchange calculated from the data measured on LKB calorimeter, $+5{\cdot}12^{+2{\cdot}9}_{-2{\cdot}3}$ kJ/mol Cu^{2+}, agrees, within the uncertainty limits, with the value obtained with Calvet microcalorimeter. It is clear that the scatter in the values of these heats arises largely from uncertainty associated with the determination of heats of immersion, since the relatively small endothermic heats of ion exchange are obtained as differences between several times higher exothermic heats of reaction and immersion. Our calorimetric values of heats of H^+/Cu^{2+} exchange disagree greatly with results obtained indirectly from studies of Cu^{2+} adsorption isotherms at various temperatures[10]. For systems with Cu^{2+} concentrations between $2 \cdot 10^{-4}$ and $3{\cdot}3 \cdot 10^{-3}$, this was found to be +24·1 kJ/mol when calculated from the temperature dependence of the equilibrium constant[10], and +34·9 kJ/mol Cu^{2+} when the method of Ekedahl and coworkers[20] was applied. Not only are these values highly discrepant, they are also surprisingly high compared with literature data[21,22] for heats of exchange of $M^+ - M^{3+}$ cations. According to the sources, the heats of exchange decrease from about +40 to about +10 kJ/mol on going from Cs^+ to Na^+, and show values of +3·6 and +7·2 kJ/mol for Ca^{2+} and Sr^{2+} cations, respectively, while assuming a negative value of −4·4 kJ/mol (exothermic reaction) for Ce^{3+}. Even though the uncertainty in the heats of H^+/Cu^{2+} exchange obtained by direct calorimetric measurement is large, the differences between the present results and va-

TABLE III

Heat changes in H^+/Cu^{2+} exchange on amorphous zirconium phosphate, measured on Calvet and LKB calorimeters at 298·15 K

Calorimeter (cell volume, cm^3)	Sorbent	mg	System	Cu^{2+} concentration		Copper uptake mmol/g ZrP	Measured heat effect J	Heat of immersion	Heat of ion exchange kJ/mol Cu^{2+}
				initial mol/l	final mol/l			heat of reaction J/g ZrP	
Calvet (10)	amorphous ZrP kept in air at 298·15 K	67·90	H_2O (9 cm^3) + 0·1 mol/l HCl (1 cm^3)	—	—	—	−1·105	−16·272	+3·56
		67·86	0·033 mol/l $CuCl_2$ (9 cm^3) + 0·1 mol/l HCl (1 cm^3)	0·02941	0·02564	0·5556	−0·970	−14·295	
LKB (101)	amorphous ZrP kept in air in non-thermostatted environment	358·33	H_2O	—	—	—	−7·591	−21·184	+4·53
		428·68	0·33 mol/l $CuCl_2$	0·03292	0·03038	0·5984	−7·918	−18·471	
		407·26	H_2O	—	—	—	−8·676	−21·302	+8·02
		438·30	0·033 mol/l $CuCl_2$	0·03292	0·03078	0·5042	−7·564	−17·258	
		119·45	0·01 mol/l HCl	—	—	—	$-2·483_4$	−20·791	+2·82
		143·70	0·033 mol/l $CuCl_2$ (9 cm^3) + 0·1 mol/l HCl (1 cm^3)	0·02953	0·02874	0·0555	$-2·763_0$	−19·227	

lues derived from adsorption isotherms[10] by far exceed the limits of uncertainty of the direct measurement, making the latter values highly improbable.

REFERENCES

1. Amphlett C. B.: *Inorganic Ion Exchangers*, p. 92. Elsevier, Amsterdam 1964.
2. Veselý V., Pekárek V.: Talanta *19*, 219 (1972).
3. Clearfield A., in the book: *Inorganic Ion Exchange Materials* (A. Clearfield, Ed.), p. 3. CRC Press Inc., Boca Raton, Florida 1982.
4. Gal I., Ruvarac A.: Bull. Inst. Nucl. Sci. Boris Kidrich, Belgrade *13*, 1 (1962).
5. Gal I., Ruvarac A.: J. Chromatogr. *13*, 549 (1964).
6. Palmer B. R., Fuerstenau M. C.: Proc. 10th Int. Mineral Processing IMPC Congress, Paper 30, London 1973.
7. Alberti G., Conte A.: J. Chromatogr. *5*, 244 (1961).
8. Clearfield A., Kalnins J. M.: J. Inorg. Nucl. Chem. *38*, 849 (1976).
9. Clearfield A., Djurić Z.: J. Inorg. Nucl. Chem. *41*, 885 (1979).
10. Ilić P. V.: *Thesis*. University of Novi Sad, Yugoslavia 1980.
11. Ruvarac A., Veselý V.: J. Inorg. Nucl. Chem. *32*, 3939 (1970).
12. Nancollas G. H., Tilak B. V.: J. Inorg. Nucl. Chem. *31*, 3643 (1969).
13. Veselý V., Pekárek V : J. Inorg. Nucl. Chem. *25*, 697 (1963).
14. Clearfield A., Smith G. D.: Inorg. Chem. *8*, 431 (1969).
15. Nancollas G. H., Pekárek V.: J. Inorg. Nucl. Chem. *27*, 1409 (1965).
16. Clearfield A., Stynes J. A.: J. Inorg. Nucl. Chem. *26*, 117 (1964).
17. Rychlý R., Pekárek V.: J. Chem. Thermodyn. *9*, 391 (1977).
18. Stopka P., Vepřek-Šiška J.: Chem. Listy *67*, 424 (1973).
19. Körbl J., Kraus E., Přibil R.: Chem. Listy *51*, 1809 (1957).
20. Ekedahl E., Högfeldt E., Sillén L. G.: Acta Chem. Scand. *4*, 556 (1950).
21. Baetslé L.: J. Inorg. Nucl. Chem. *25*, 271 (1963).
22. Amphlett C. B., Eaton P., McDonald L. A., Miller A. J.: J. Inorg. Nucl. Chem. *26*, 297 (1964).

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