

## Temperature Effect on Ion Exchange Behaviour of Aluminium (III) Phosphate

A.NAEEM, S.MUSTAFA<sup>\*</sup>, S.MURTAZA, B.DIL ARA AND A. HAMID  
*National Centre of Excellence for Physical Chemistry,  
University of Peshawar, Pakistan*

(Received 13<sup>th</sup> June, 2000, revised 16<sup>th</sup> July, 2001)

**Summary:** The ion exchange behaviour of  $\text{AlPO}_4$  was determined potentiometrically for  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions under different experimental conditions of metal ions concentrations and temperatures. The potentiometric titration data were also employed to determine the deprotonation constants of  $\text{AlPO}_4$  in the temperature range 303-323K, which were found to be dependent upon the temperature, concentration and nature of the metal cations. The values of deprotonation ( $\text{pK}_a$ ) constants were used to estimate the apparent thermodynamic parameters. Both the positive values of  $\Delta H$  and  $\Delta S$  showed that the deprotonation process was endothermic and spontaneous in nature.

### Introduction

Materials, like metal (IV) phosphates have been studied in details potentiometrically during the last decade [1-3]. An extensive literature on the ion exchange properties of ZrP has been summarized in recent review articles [2]. On the other hand, very little is known about the ion exchange of metal ions on metal (III) phosphates like  $\text{FePO}_4$ ,  $\text{AlPO}_4$  and  $\text{CrPO}_4$  which are also highly insoluble solid materials and are assumed to be responsible for the adsorption processes in many soil and water systems [4-7]. Various applications of the metal (III) phosphates can be conceived in different fields such as heterogeneous catalysis, mineral processing, soil science and for the recovery of precious material from industrial waste waters and sea water etc. etc. The present work deals with the determination of the ion exchange properties of  $\text{AlPO}_4$  by using the method of potentiometric titrations and to evaluate the deprotonation constants of the solid as a function of concentration, temperature and nature of the metal cations. To our knowledge, no data regarding the deprotonation of  $\text{AlPO}_4$  prior to this study is available in the literature.

### Results and Discussion

#### *Characterization of Aluminium(III) Phosphate*

The X-ray diffraction pattern of aluminium(III) phosphate showed that the material is amorphous in nature. The point of zero charge was found to be 4.20. The value of PZC obtained here is in accordance with the observation of Cole and Jackson [8]. The surface area of the sample determined by the BET method was found to be 60

$\text{m}^2/\text{g}$ . The electron probe microanalysis gave the Al/P molar ratio to be 1.02, which suggests the formula of the solid to be  $\text{AlPO}_4 \cdot x\text{H}_2\text{O}$ , where x may vary from 2-3. These results are in close agreement with those reported elsewhere for the metal(III) phosphates [5].

#### *Potentiometric Titration Studies of Aluminium(III) Phosphate*

The potentiometric titration curves of aluminium(III) phosphate in the presence of  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  solution are presented in Fig.1, 2. The exchange capacity of  $\text{AlPO}_4$  is observed to be 4.20 meq/g which is comparable in magnitude with the exchange capacity of metal(IV) phosphates [2]. The exchange of the metal cations as can be seen from Fig.1 is accompanied by the release of protons from the solid into the aqueous solutions. As such, the shift in the curves towards the low pH values may be taken as the affinity of the exchanger towards the metal cations. It is obvious from these Figures that both the concentration of divalent metal cations (Fig. 1) and temperature (Fig.2) have a positive effect on the pH shift i.e., the shift increases with the increase in concentration and temperature of the system. The decrease of pH with the increase of metal ions concentration may result from the release of additional protons induced by the greater sorption of  $\text{M}^{2+}$  ions. Further, the present curves do not exhibit plateaus at constant pH, as were observed in case of TiP and ZrP [2], indicating the absence of any new phase formed during the titration process. As such, the nature of the present types of curves clearly

<sup>\*</sup>To whom all correspondence should be addressed.

establishes that  $\text{AlPO}_4$  behaves as a weak acid cation exchanger like the phosphates of zirconium [2] and iron [4].

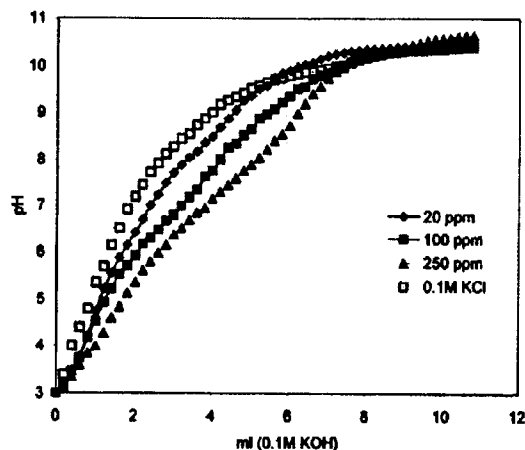


Fig. 1: Potentiometric titration curves of  $\text{AlPO}_4$  in the presence of  $\text{Ca}^{2+}$  at 303K.

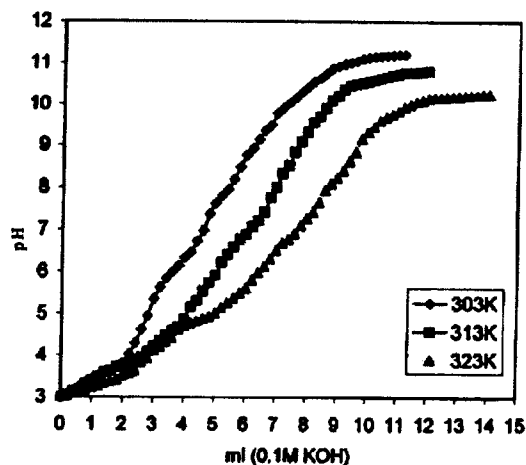
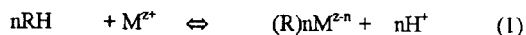


Fig. 2: Potentiometric titration curves of the  $\text{AlPO}_4$  in the presence of 100 ppm  $\text{Cu}^{2+}$  at different temperatures.

The cation exchange reaction between the metal ions and the exchanger, may be represented as



where R represents the exchanger phase and n is the number of RH groups involved in the formation of complexes. It is also important to note that the affinity of the exchanger towards the  $\text{Cu}^{2+}$  is

relatively greater than  $\text{Ca}^{2+}$  ions which is parallel to the hydrolysis constant for these metal cations, showing the importance of hydrolysis in governing the metal ion exchange on aluminium(III) phosphate.

#### Determination of the Deprotonation Constants ( $pK_a$ )

The  $pK_a$  values of cation exchanger  $\text{AlPO}_4$  were computed from the potentiometric titration data by using the equation (2).

$$\text{pH} = \text{pK}_a + n \log (\alpha/1-\alpha) \quad (2)$$

where  $\alpha$  refers to the degree of the dissociation,  $pK_a$  represents the dissociation constants and n is a constant characteristics of a given system. Equation (2) was applied to the data with the assumption that the pHs in the exchanger and in the aqueous phase are the same. As was suggested by Gregor and Bregman [9], the presence of large excess of salt displaces all of the hydrogen ions into the solution and yields results comparable to those, which would be obtained as if the exchanger was soluble.

As can be seen from Fig. 3, the data fit very well to the straight lines according to equation (2). The values of the deprotonation constants ( $pK_a$ ) calculated from intercepts of the straight lines are given Table 1. One can observe that the  $pK_a$  values are sufficiently high which indicate that the affinity of the exchanger towards hydrogen ions is greater than the incoming divalent metal cations. It can also be observed that the  $pK_a$  values decrease with the increase in the concentration of the metal ions, indicating an increase in the deprotonation of the exchanger as a result the exchanger takes up more of the metal ions from the aqueous solution. The dependence of  $pK_a$  upon the nature of divalent metal cations suggests that the deprotonation process is also influenced by its selectivity. The lower values of  $pK_a$  in the presence of  $\text{Cu}^{2+}$  indicate its greater affinity towards the solid as compared to the  $\text{Ca}^{2+}$ , which is in accordance with selectivity sequence shown by the exchanger. The present values of  $pK_a$  are also in agreement with the values reported in the literature for other metal phosphates [5,10].

Table 1: Dissociation constants ( $pK_a$ ) of  $\text{AlPO}_4$  in the presence of metal ions at different temperatures

Temp. (K)	$\text{Cu}^{2+}$	$\text{Ca}^{2+}$
303	7.76	7.83
313	7.06	7.41
323	6.45	6.96

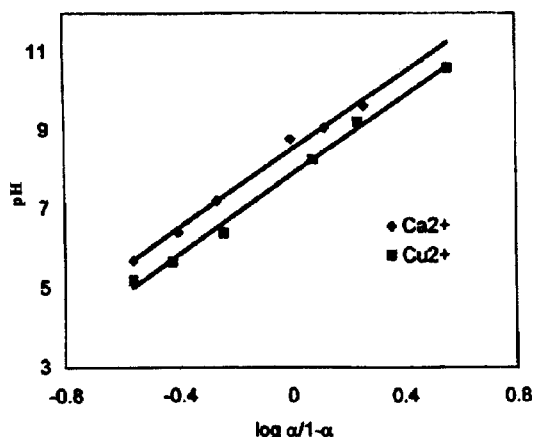


Fig. 3: Plots of pH vs- $\log \alpha/1-\alpha$  for  $\text{AlPO}_4$  in the presence of 100 ppm  $\text{M}^{2+}$  at 303K.

#### Dependence of $pK_a$ on the Temperature

The data in Table 1 represent that the values of the deprotonation constants of  $\text{AlPO}_4$  in the presence of both  $\text{Cu}^{2+}$  and  $\text{Ca}^{2+}$  ions decrease linearly with the increase in temperature, corresponding to the greater deprotonation of the exchanger. It shows that more of the hydrogen ions are released from the solid into the aqueous phase with the rise in temperature as a result more of the metal cations get a chance to be adsorbed on the exchanger.

The standard enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) changes were calculated from the linear plots of  $pK_a$  vs.  $1/T$  (Fig. 4) according to the equation given in the literature [2, 5].

$$pK_a = -\Delta S/2.303R + \Delta H/2.303RT \quad (3)$$

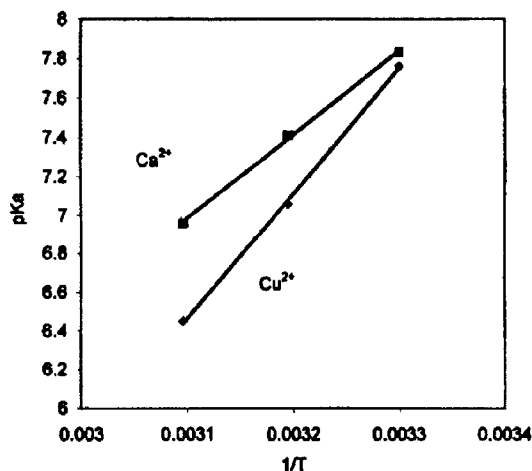


Fig. 4: Plots of  $pK_a$  vs.  $1/T$  for  $\text{AlPO}_4$ .

The values of  $\Delta H$  are found to be in the range of 81.46 – 122.80 kJ/mol which show the endothermic behaviour of the deprotonation process, as energy is needed to dissociate the protons from the surface of the solid. The positive values of  $\Delta H$  were also reported for the proton desorption enthalpies of alumina by Machesky and Jacobs [11]. The values of  $\Delta S$  are found to be between 118.74 and 256.83 J/mol.K for  $\text{Ca}^{2+}$  and  $\text{Cu}^{2+}$  ions respectively. These changes in the  $\Delta S$  values may be correlated with the changes in the hydration status of the metal cations and protons in the exchanger phase and aqueous solution.

#### Experimental

##### Reagent

The analytical grade reagents were used without further purification.

##### Characterization of Aluminium(III) phosphate

The  $\text{AlPO}_4$  was characterized by using X-ray diffractometry, Surface area, Point of zero charge (PZC), and Electron probe microanalyses (EPM). The method of characterization of  $\text{AlPO}_4$  is almost the same as was reported in our earlier papers [4,5].

##### Potentiometric Titration of Aluminium(III) phosphate

60 ml of  $\text{M}^{2+}$  ions with 0.1M KCl solutions containing 0.2 gm of sample were taken in a double walled pyrex glass cell. The initial pH of the solutions was adjusted to the pH 3 with 0.1M KOH or 0.1M HCl. After equilibration for one hour at the desired temperature the suspensions were readjusted to the pH 3, with a pH meter model Orion SA 520. The standardized solution of 0.1M KOH was added by means of micro-burette with increments of 0.2 ml. The suspension pH was recorded every 2 min. as a function of volume of titrant added till the final pH reached 11.

#### Conclusions

From the above discussion, it is inferred that the  $\text{AlPO}_4$  behaves as a weak acid and its exchange capacity is found to be 4.20 meq/g, which is comparable in magnitude with the other metal phosphates. The affinity of  $\text{AlPO}_4$  towards  $\text{Cu}^{2+}$  is found to be relatively greater than  $\text{Ca}^{2+}$  ions. The deprotonation constants of  $\text{AlPO}_4$  were found to decrease with the increase in both the temperature and concentration of the metal cations. The positive

values of  $\Delta H$  and  $\Delta S$  showed that the deprotonation process of the exchanger is endothermic and spontaneous in nature.

**Acknowledgement:**

We greatly appreciate the financial support of Pakistan Science Foundation (PSF) for funding this project.

**References**

1. K. Dorfner, "Ion Exchangers", Walter de Gruyter Berlin, New York, 1991.
2. A. Clearfield, "Inorganic Ion Exchange Materials", CRC Press, Boca Raton Fl, 1982.
3. A.I. Bortun and J.R. Garcia, T.A. Budovitskaya, V.V. Strelko and J. Rodriguez, *Mater. Res. Bull.*, **31**, 487 (1996).
4. S. Mustafa, A. Naeem and N. Rehana, *J. Chem. Soc. Faraday Trans.*, **89**, 3843 (1993).
5. S. Mustafa, A. Naeem and S. Murtaza, *J. Colloid Interface Sci.*, **204**, 284 (1998).
6. S. Mustafa, A. Naeem and S.T. Hussain, *Adsorption Sci. Technol.*, **17**, 715 (1999).
7. T. Mishra, K.M. Parida and S.B. Rao, *Sep. Sci. Technol.*, **33**, 1057 (1998).
8. C.V. Cole and M.L. Jackson, *J. Phys. Chem.*, **54**, 128 (1950).
9. H.P. Gregor and J.I. Bregman, *J. Am. Chem. Soc.*, **70**, 2370 (1948).
10. S.C. Lahiri, *J. Ind. Chem. Soc.*, **42**, 715 (1965).
11. M.L. Machesky and P.F. Jacobs, *Colloids Surf.*, **53**, 297 (1961).