

## Effect of Precipitation on the Sorption of Metal Cations by $\text{AlPO}_4$

A.NAEEM, S.MUSTAFA, B.DILARA, N.REHANA AND S.MURTAZA  
*National Centre of Excellence for Physical Chemistry,  
University of Peshawar, Peshwar, Pakistan*

(Received 28<sup>th</sup> January, 2002, revised 2<sup>nd</sup> May 2003)

**Summary:** The precipitation of divalent metal cations  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  with and without  $\text{AlPO}_4$  is measured potentiometrically as a function of temperature and concentration of the divalent metal cations. The shift of the titration curves at a given temperature in the presence of exchanger is related to the metal ions adsorption at the pH values below the plateau formation in the titration curves. The order of precipitation of the divalent metal cations is observed to be  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$  which is parallel to the values of their solubility products. Law of mass action is applied to distinguish between the ion exchange sorption and precipitation of the metal cations. It is found that the process of the uptake of metal cations changes from adsorption to precipitation with the increase in concentration, pH and temperature of the system.

### Introduction

Adsorption is by definition a general term describing the attachment of species from a solution to its co-existing solid surfaces. Three types of processes are identical for the sorption phenomena: (i) surface adsorption, which is limited to accumulation of sorbate onto external surface, (ii) absorption, ion exchange, or diffusion into the solid, and (iii) precipitation or co-precipitation. These processes often act together, and the dominance of one specific process is often hard to be distinguished without careful chemical measurements and advanced analytical techniques. The ion exchange sorption of metal cations on both the organic and inorganic ion exchangers have been undertaken in great detail in the literature [1-4]. However, the role of precipitation in the overall process of the uptake is still not clear as both the adsorption of the metal cations and then hydrolysis and precipitation involve the release of  $\text{H}^+$  ions. The mechanism responsible for the uptake of metal cations by the exchanger is, thus, still a point of conjecture.

Different authors [5, 6] predicted that the sorption process may be accompanied by the precipitation of the metal cations under the given experimental conditions but no detailed study regarding the effect of the precipitation on the adsorption process of metal ions on the various adsorbents have been reported. During the present investigation an attempt has been made to evaluate potentiometrically the effect of precipitation on the ion exchange sorption of metal cations by  $\text{AlPO}_4$  particles.

### Results and Discussion

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

The X-ray diffraction (XRD) showed that the sample  $\text{AlPO}_4$  is amorphous and its surface area determined by the  $\text{N}_2$  adsorption method is found to be  $60 \pm 1 \text{ m}^2/\text{g}$ . The Al/P molar ratio determined by the electron probe microanalysis (EPM) is nearly equal to 1 which is close to the values reported elsewhere [7]. Fourier transform infra-red (FTIR) spectrum showed that the sample is hydrated  $\text{AlPO}_4$  and its spectrum is found to be similar as reported in our earlier papers [8,9].

#### *Potentiometric Titration Studies of $\text{AlPO}_4$*

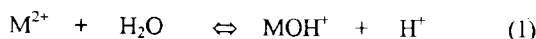
In the present study, a simple procedure based on the alkalimetric titrations of the solid suspension is described which shows the change in the process of the uptake of the metal cations from adsorption to precipitation. This method briefly consists of determining the difference between the amount of base used in potentiometric titrations of the metal cations alone and in the presence of the  $\text{AlPO}_4$  under similar experimental conditions.

The potentiometric titration curves of aluminium(III) phosphate in the presence of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  with  $0.1 \text{ mol.dm}^{-3}$  KCl solution are presented in Fig.1 - 4. As is evident from these figures, the divalent transition metal ions shift the titration curves of the sample towards the low pH region, indicating a specific interaction, which results in the release of protons from the exchanger. The shift in the titration curves tends to increase with the

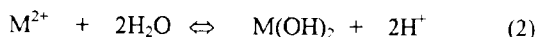
increase in both the concentration and temperature, indicating the enhanced dissociation of protons from the solid into the aqueous phase.

The cation exchange reaction is accompanied by the addition of base which is required not only to neutralize the surface protons but also to hydrolyze the metal cations present in the aqueous phase. The shift in the titration curves towards the lower pH values with the addition of the metal cations is, thus, indicative of the replacement of surface protons by the sorbed metal cations [7-12] as well as the hydrolysis and precipitation of the metal cations as both the hydrolysis and precipitation involve the release of  $H^+$  ions. The decrease in the pH of the aqueous suspension in the system may be described by the following tentative mechanisms:

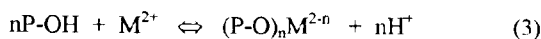
a. Hydrolysis of metal cations



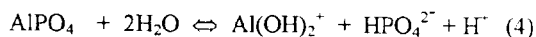
b. Precipitation of the metal cation



c. Cation exchange reaction



d. Hydrolysis of the exchanger



One can distinguish between the adsorption and precipitation of the metal cations with the assumption that the sample  $AlPO_4$  is hydrolytically stable as its dissolution under the given experimental conditions was observed [9, 10, 12] to be almost negligible. This simplification rules out the possibility of reaction (4) and, thus, the release of protons can be attributed either to the hydrolysis/precipitation (reactions 1 and 2) or to the cation exchange process (reaction 3).

To distinguish between the ion exchange sorption and precipitation of the metal ions, the blank titration curves i.e. without  $AlPO_4$ , of metal ions  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ni^{2+}$ , and  $Mg^{2+}$  along with  $0.1 \text{ mol.dm}^{-3}$  KCl are also presented in Fig. 1 - 4. As is obvious from the curves there is a marked shift in the

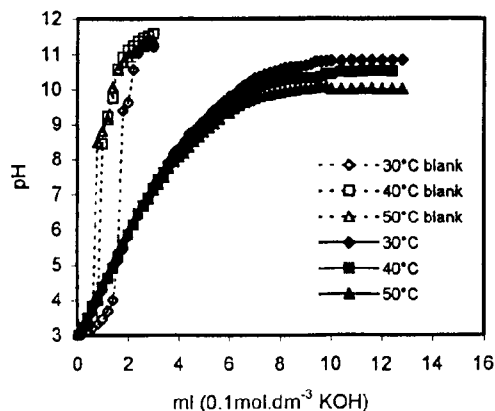


Fig. 1: Potentiometric titrations of  $AlPO_4$  in the presence of 20 ppm  $Ni^{2+}$  at different temperatures. (Blank indicates the potentiometric titration curves of metal ion in the absence of  $AlPO_4$ ).

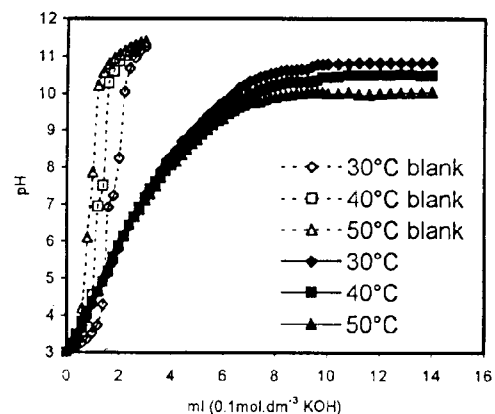


Fig. 2: Potentiometric titration curves of  $AlPO_4$  in the presence of 20 ppm  $Cu^{2+}$  at different temperatures.

presence of  $AlPO_4$  towards the lower pH values in comparison to the blank titration curves of the divalent metal cations. The amount of replaceable protons responsible for the ion exchange reaction can be estimated from the difference between the blank run and each curve of metal cations in the presence of the  $AlPO_4$ . The ratio of the excess amount of base consumed in the presence of the  $AlPO_4$  thus gives the extent of surface protons responsible for the sorption of metal cations [6, 10]. The shape of the curves (Fig. 1 and 2) demonstrates that the precipitation effect is negligible in case of the lower concentrations of all

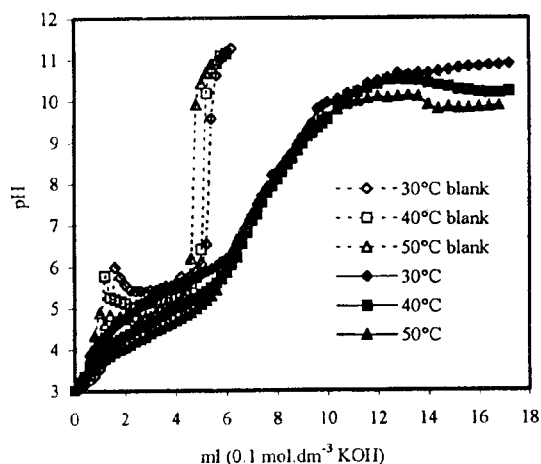


Fig. 3: Potentiometric titration curves of  $\text{AlPO}_4$  in the presence of 250 ppm  $\text{Cu}^{2+}$  at different temperatures.

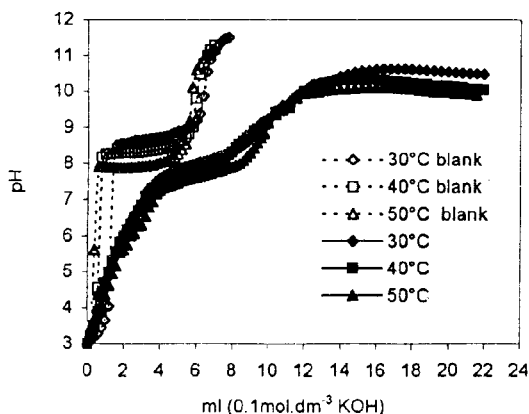


Fig. 4: Potentiometric titration curves of  $\text{AlPO}_4$  in the presence of 250 ppm  $\text{Ni}^{2+}$  at different temperatures.

the metal cations at both the high pH and temperature of the system indicating that the  $\text{H}^+$  ions are liberated from the solid to the aqueous phase according to reaction (3). However, the effect of precipitation becomes pronounced when the concentration of the divalent metal cations in solution is increased beyond a certain limit, which depends upon the nature of the metal cations (Fig. 3, 4 and 5). The above facts suggest that in case of high concentration of metal ions the process of sorption is replaced by the precipitation. Fig. 1- 4 show that the temperature also plays a significant role in the precipitation of divalent

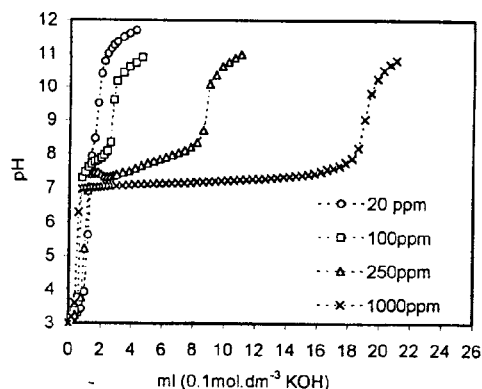


Fig. 5: Blank titration curves of the various concentrations of  $\text{Zn}^{2+}$  at 303K.

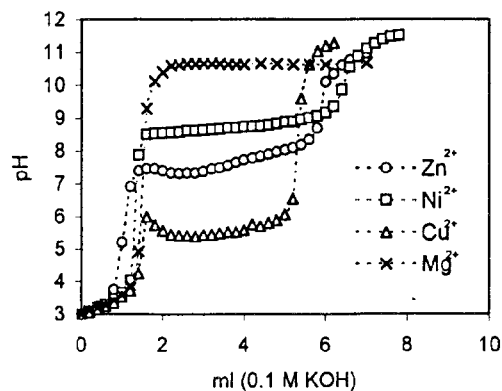


Fig. 6: Blank titration curves of 250 ppm of various divalent metal ions at 303K.

metal cation. The plateau formation takes place at lower pH values at higher temperatures, suggesting that the precipitation of metal cations is favored at higher temperatures.

The blank titration (without  $\text{AlPO}_4$ ) curves of the divalent metal cations are also presented in Fig. 6 which show the extent of precipitation follows the trend  $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Mg}^{2+}$ , which is in agreement with the values of their solubility products given in the literature [13, 14]. Further, the plateaus in the titration curves begin to start nearly at pH 5.4, 7.4, 8.5 and 10.5 for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Mg}^{2+}$  respectively, which are the corresponding pH values at which their hydrolysis begins to take place in the aqueous solution. The dip in the plateau in lower pH region especially in case of  $\text{Cu}^{2+}$  ion suggests that the rate of precipitation, which is  $\text{OH}^-$  consuming process

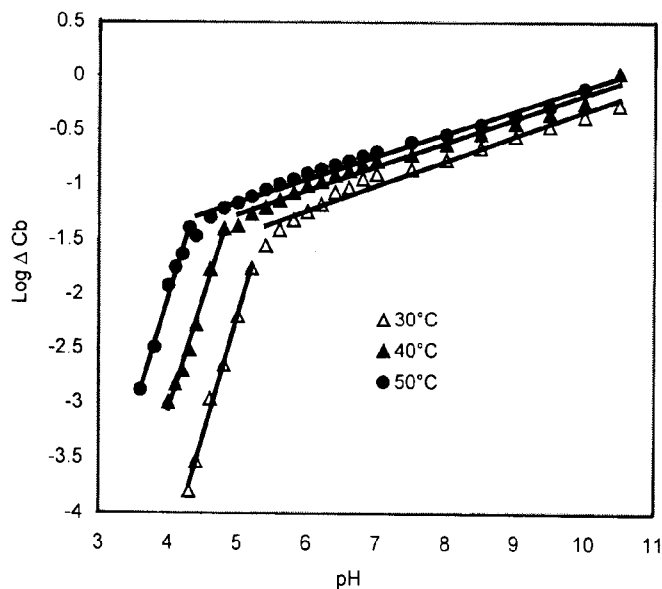


Fig. 7: Plots of Log  $\Delta C_b$  vs. pH for 20 ppm  $\text{Cu}^{2+}$  at different temperatures.

is faster than the rate of addition of base. Similar results were observed elsewhere [15].

To determine the mechanism of metal ions sorption an equation developed by us elsewhere [7], which gives information about the  $\text{H}^+/\text{M}^{2+}$  stoichiometry, was applied to the experimental data in the form:

$$\text{Log } \Delta C_b = \text{log } K + n\text{pH} \quad (5)$$

where  $\Delta C_b = C_{bs} - C_{bm}$ ,  $C_{bs}$  represents the molar concentration of base used in the presence of surface and metal ions,  $C_{bm}$  refers to the molar concentration of base used in the presence of metal ions only,  $\Delta C_b$  is the molar concentration of base used for the dissociation of the surface protons,  $K$  is the binding constant and  $n$  refers to the  $\text{H}^+/\text{M}^{2+}$  stoichiometry. Plots of  $\text{Log } \Delta C_b$  as a function of pH for the potentiometric titration studies of the divalent metal ions are shown in Fig. 7 and 8. As can be seen from these Figures, at least two distinct straight lines are observed for the metal ions sorption by the  $\text{AlPO}_4$ .

The values of  $n$  obtained from slopes for the lower portion of the curves are found to be almost equal to  $2 \pm 0.25$  for  $\text{Cu}^{2+}$  and  $1 \pm 0.20$  for  $\text{Ni}^{2+}$  and

$\text{Mg}^{2+}$  ions, which show the simplified equation (5) is best applicable in the region of low adsorption of metal cations for which the equation was primarily derived [7]. The stoichiometry of the metal ions sorption on  $\text{AlPO}_4$  thus determined proposes that the most probable mechanism for the metal ions uptake is the cation exchange, is given by the reaction (3). Similar mechanism for the metal ions uptake on the various exchangers has been reported elsewhere [16,17]. However, the lower values of  $n$  for the upper portion of the curves of Fig. 7 and 8 are found to be in the range of 0.16 – 0.30 which point towards the fact that the role of ion exchange (reaction 3) has diminished in the over all process of the uptake of metal cations and is replaced by the metal cations precipitation on the surface of the  $\text{AlPO}_4$ . We found similar results recently [15] in case of metal ion adsorption by  $\text{ZnO}$ .

### Experimental

#### Reagent

All the reagents used were of analytical grade and all the solutions were prepared in doubly distilled water using pyrex glass vessels. Chlorides of nickel, copper, zinc and magnesium were used for the preparation of their solutions. Similarly, potassium hydroxide and hydrochloric acid solutions were used

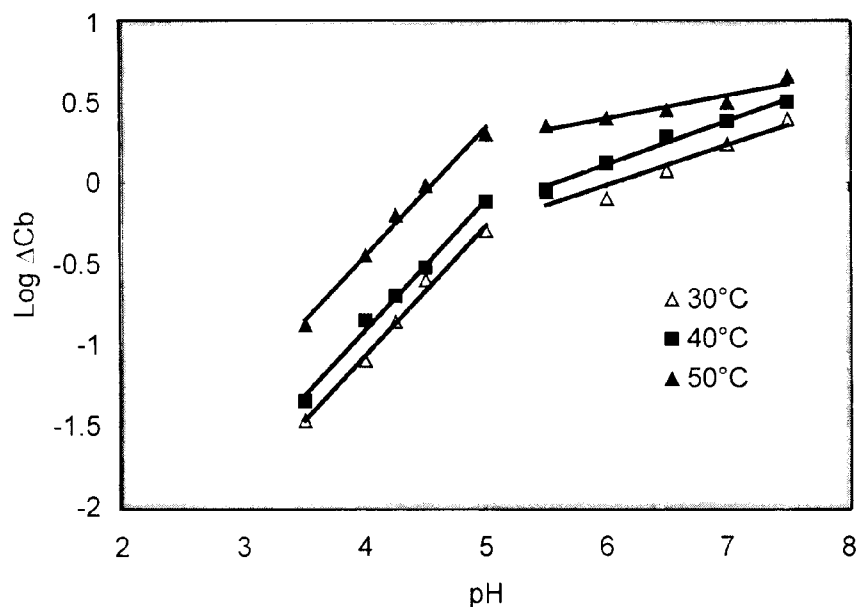


Fig. 8: Plots of Log  $\Delta C_b$  vs. pH for 250 ppm  $Ni^{2+}$  at different temperatures.

for adjusting pH of the suspension. The method of preparation and characterization for the exchanger  $AlPO_4$  is exactly the same as was reported in our previous papers [8 -10].

#### Potentiometric Titration of $AlPO_4$

Sixty ml of  $M^{2+}$  ions with  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  KCl solutions containing 0.2 g of  $AlPO_4$  were taken in a reaction vessel. The initial pHs of the each solution were adjusted to the pH 3 with  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  KOH or  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  HCl. The suspensions were then equilibrated for 1 hour with a constant stirring by means of magnetic stirrer at constant temperature. After equilibration the suspensions were readjusted to the pH 3, with a pH meter model Orion SA 520, using a combination of electrode of Orion research grade.

The standardized solution of  $0.1 \text{ mol} \cdot \text{dm}^{-3}$  KOH was added by means of micro-burette with increments of 0.2 ml. The suspension pH was recorded as a function of volume of titrant added till the final pH reached.

The blank titrations were performed under similar conditions of pH, temperature and concentration of the metal cations in the aqueous

solutions. The only difference in the experimental procedure was that in case of blank titration studies no exchanger ( $AlPO_4$ ) was present in the solutions of divalent metal cations.

#### Conclusions

It can be concluded from potentiometric titration data that the ion exchange sorption of the metal cation is the more favorable process of the uptake by the  $AlPO_4$  at low concentration and pH, which gradually changes into precipitation with the increase in concentration, temperature and pH of the aqueous solution. The role of precipitation in the overall process of sorption was observed to follow the trend  $Cu^{2+} > Zn^{2+} > Ni^{2+} > Mg^{2+}$ , which is in agreement with the values of their solubility products given in the literature [13].

#### Acknowledgment

This research was supported by the Pakistan Science Foundation under F-Pu/Chem (315).

#### References

1. Xu. Yuping and F.W. Schwartz, *Environ. Sci. Technol.*, **28**, 1472(1994).
2. B.B. Sahu, H.K. Mishra and K. Parida, *J. Colloid*

- Interface Sci.*, **225**, 511(2000).
3. W.Stumm and J.J.Morgan, "Aquatic Chemistry", An Introduction Emphasizing Chemical Equilibria in Natural Waters", Ed. 2<sup>nd</sup>, John Wiley and Sons, New York, p.283 (1981).
  4. J. Perrone, B. Fourest and E. Giffaut, *J.Colloid Interface Sci.*, **239**, 303(2001).
  5. S. Sugiyama, H. Matsumoto, H. Hiromu and J.B. Moffat, *Colloids Surf. A. Physiochem. Engg. Aspects*, **169**, 17(2000).
  6. M.A. Anderson and A.J. Rubin, Adsorption of inorganic at solid liquid interfaces, Ann Arbor Science Publication, Ann Arbor, MI, pp: 103, 210 (1981).
  7. S. Mustafa, A. Naeem and N. Rehana, *J.Chem.Soc.Faraday Trans.*, **89**, 3843 (1993).
  8. S. Mustafa, A. Naeem, N. Rehana and H.Y. Samad, *Adsorption Sci. Technol.*, **13**, 261 (1996).
  9. S. Mustafa, A. Naeem and S. Murtaza, *J. Colloid Interface Sci.*, **220**, 63 (1999).
  10. A. Naeem, S. Mustafa, N. Rehana, B.Dilara and S. Murtaza, *J.Colloid Interface Sci.*, **252**, 6 (2002).
  11. A. Naeem, S. Mustafa and B. Dilara, *J.Chem.Soc.Pak.*, **23**, 133(2001).
  12. A. Naeem, S. Mustafa, N. Rehana, B. Dilara and S. Murtaza, *Environ.Technol.*, **24**, 779 (2003).
  13. J.A. Dean, Lange's Handbook of Chemistry, 12<sup>th</sup> ed, McGraw Hill Book Company, New York, 5 (1979).
  14. A.Naeem, Sorption properties of metal(III) phosphates, Ph.D Thesis, Peshawar University, Pak., p.70(1996).
  15. S. Mustafa, P. Shahida, A. Naeem, B. Dilara, and N.Rehana, *Langmuir*, **18**, 2254(2002).
  16. H. Kaneko, M. Tsuji and M. Abe, *J.Nucl.Sci.Technol.*, **29**, 988(1992).
  17. S. Ahrland, N. Bjork, R. Blessing and R. Hermans, *J. Inorg. Nucl. Chem.*, **36**, 2377(1874).