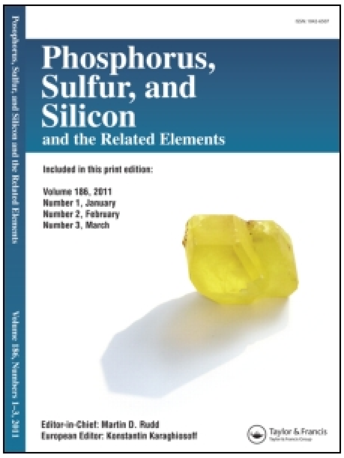

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PROTONATION AND COMPLEXATION CONSTANTS OF PHOSPHONIC ACIDS WITH CATIONS OF ENVIRONMENTAL INTEREST

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Abstract Protonation and complexation constants of two phosphonic acids : nitrilotris(methylenephosphonic acid) (AMP) and 1-hydroxyethane-1,1'-diphosphonic acid (HEDP) were determined with different cations of environmental interest (Ca) and heavy metals (Cu(II), Zn, Ni, Cd, Pb). These equilibrium constants were calculated with the PKAS and BEST computer programs, with special attention to the uncertainty on the calculated values. Conditional complexation constants of AMP and HEDP with Cu(II) and Ca(II) were determined by ionometry. The insoluble HEDP complexes with Pb(II) and Cd(II) were identified and the corresponding solubility products determined.

Key Words : AMP, HEDP, heavy metals, calcium, complexation, protometry, ionometry.

INTRODUCTION

In this study, we determined protonation and complexation constants for two phosphonic acids : nitrilotris(methylenephosphonic acid) (AMP) and 1-hydroxyethane-1,1'-diphosphonic acid (HEDP) with different cations. These two phosphonic acids are used in detergents as builders, because of their complexing properties, especially the complexation with calcium and heavy metal cations.

The aim of this work is to study the potential mobilization of cations in river sediments. To calculate the cation speciation, the protonation and complexation constants of compounds present in water, such as AMP or HEDP, must be available. The cations studied here are those usually encountered in natural waters (Ca, Zn) and anthropogenic heavy metals (Cu(II), Ni, Cd, Pb).

The complexing properties of HEDP and AMP with many of these cations have already been studied, but there are quite large differences between these results. We determined these equilibrium constants with special attention to the uncertainty on the calculated values.

MATERIALS AND METHODS

AMP and HEDP were Fluka products, pure grade. Metal salts (nitrate) were pure grade compounds, the cation salt solutions were standardized with EDTA.

The equilibrium constants were calculated from the data obtained by potentiometric titrations performed at 25° C in 0.1 $mol.L^{-1}$ KNO_3 solution under a purified nitrogen stream.

pH titrations were carried out with a Metrohm automatic titrator model 716-DMS. The combined glass electrode was calibrated by titration with hydrochloric acid and sodium hydroxide solutions. The Martell and Motekaitis [1] computer programs were used to analyze the pH-metric data.

An Orion ionometer model 940SE was used with calcium and copper selective electrodes in the ionometric experiences. The ionometric titration data was exploited using the Buffle, Ruzic, and Scatchard methods [2].

DETERMINATION OF EQUILIBRIUM CONSTANTS

Protometry

The determination of the equilibrium constants needs to take into consideration different data :

* experimental data as concentrations, volumes, pH,

* theoretical data as water ionic product, activity coefficients.

The uncertainty of each one of these parameters leads to the uncertainty of the equilibrium constants.

Protonation constants These constants have been determined by using the PKAS computer program [1]. Differences between our results and those found in the literature [3] are small.

Complexation constants These constants have been determined by using the BEST program [1]. To determine these constants, one needs to take into account the parameters quoted above, but also the complexed cation species which may interfere. Speciation diagrams were used (SPE program [1]) to determine which hydroxide species could be neglected and at which pH value we can stop the exploitation, still considering all the phosphonic complex species. It appears that hydroxide species do not interfere with AMP, while the hydroxide/cation complexes cannot be neglected with HEDP.

The AMP complexation constants are close to those found in the literature [3] but there is a quite large difference in the case of HEDP complexation constants. Moreover, a better concordance between calculated and experimental pH values was obtained with AMP in comparison to HEDP.

Hydroxide/cation complexes interference complicates the determination of the complexation constants, particularly for HEDP, and surely is the cause of the difficulties to obtain a good concordance. The existence of other complexes, such as hydroxide/phosphonate/cation ternary complexes which could also interfere, might be an other possible reason for the difficulties to refine calculated pH to experimental pH.

Affinity with the different cations The equilibrium constants values and the titration curves point out the following order :

AMP :	Cu (II) > Zn > Pb > > Cd > Ni >> Ca
HEDP :	Cu (II) > Zn > > Cd > Ni > Ca

The affinity order for all the cations is the same for AMP and HEDP. The AMP complexing properties for each cation are higher than those of HEDP, particularly with copper and zinc (difference of six log units).

Uncertainty Each experiment was performed in triplicates and was reproduced three times. The standard deviation $\sigma(n-1)$ was calculated on all the results : the uncertainty is lower for the AMP equilibrium constants than for HEDP.

The complexation constants values for species present at higher pH are difficult to estimate accurately because of the interferences from hydroxide/cation complexes. In general it is difficult to assess data for the species representing less than 18 % on the speciation diagrams.

Ionometry

These experiments allowed to determine conditional complexation constants at a given pH. Calcium and copper ion selective electrodes were used at pH 3 and 5. Hydroxide precipitation problems did not allow to work at higher pH values.

These data were analyzed using the Buffle, Ruzic, and Scatchard methods [2]. There is quite good concordance between the results obtained with the three methods, and a good reproducibility of the results. These values confirm those obtained by protometry. AMP is more complexing than HEDP for both cations. Copper is better complexed than calcium for each phosphonate.

Carbonates

All the potentiometric experiments for Ca with HEDP or AMP were carried out under normal atmosphere. No difference was observed in comparison with those performed under nitrogen atmosphere. Under a normal atmospheric CO_2 partial pressure, carbonates do not interfere and the phosphonic acids behavior was not modified.

SPECIATION DIAGRAMS

We are interested in determining which are the dominating species in the pH range of natural waters (5 to 9), considering phosphonic acid and cation concentrations in our experimental conditions (2.10^{-3} mol.L^{-1}), and phosphonate concentrations closer to those found in natural waters (2.10^{-7} mol.L^{-1}), always keeping a phosphonate/cation ratio L/M = 1/1. Speciation diagrams for cations which have a comparable affinity with a phosphonate (Cu, Zn and Pb ; Ni and Cd) have the same type of dominating species.

At the experimental concentration, ML *is the dominating species in any case and* MHL is also significant in the case of AMP. At lower concentration, the dominating species are the same for AMP whereas free metal and ML are the dominating species for HEDP.

INSOLUBLE COMPLEXES

Precipitates of HEDP with Cd and Pb were characterized [4]. Polarography experiments confirmed by electronic microscopy examinations showed that the insoluble complex stoichiometries are : CH_3-$C(OH)(PO_3)_2Pb_2$ and CH_3-$C(OH)[PO_2(OH)]_2Cd$.

A kinetic study shows that the HEDP-Pb complex solubility is 5.10^{-7} mol.L^{-1} (after 8 days) whereas the HEDP-Cd complex solubility is $4.8.10^{-4}$ mol.L^{-1} (after 15 days).

CONCLUSION

This study points out that AMP, brought by domestic detergents, will contribute to the mobilization of cations in river sediments more than HEDP.

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