Dissociation Constants of Phosphoric Acid at 25°C and the Ion Pairing of Sodium with Orthophosphate Ligands at 25°C

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The first and second acidity constants of phosphoric acid were determined in a 0.70 ionic strength solution of both a sodium and a potassium ion background salt at 25°C. These experimentally determined constants were compared to literature values as well as values calculated from a theoretical model. Assuming negligible ion pairing of the phosphate ligand with the potassium ions, the stability constants of the NaHPO₄ and NaH₂PO₄ complexes were determined to be 1.3±0.3 and 0.49±0.07 (mol·L⁻¹), respectively. These constants were used to model the speciation of orthophosphate in a background of a sodium salt from pH 3 to 10.

KEY WORDS: Sodium phosphate; phosphoric acid; dissociation constants; marine systems.

1. INTRODUCTION

Precise studies of speciation modelling of complex aqueous systems require knowledge not only of metal-ligand interactions, but also of dissociation constants of weak acids whose conjugate bases are often ligands of significant concentration and complexing strength. Experimentally, acidity constants will be affected by the specific interaction of the background salt with the ligands as well as by the non-specific effects of ionic strength. The variation of reported acidity constants of weak acids is often the result of differences in ion pairing with the ions of the background salt used to maintain ionic strength or variations in activity coefficients caused by different concentrations of background salt.

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If specific interactions are not taken into account, the concentration of the free ligand is overestimated and the resulting equilibrium stability constants are underestimated. Although calculation of single ion activity coefficients at various ionic strengths can be made based on a number of conventions, these calculations at ionic strength above 0.10 are imprecise and it becomes preferable to determine the stability constants at the ionic strength of interest.

The magnitude of the deviations due to both factors will increase at higher concentrations of background salt. To ascertain correctly the total speciation in such systems, the extent of ion pairing must be examined by utilizing the concentrations and the stability constants of all species of possible significance. In stability studies involving orthophosphate ligands with trace metal ions in which a sodium salt is used to control ionic strength, the determination of ion association constants for the sodium ions with the phosphate ligands is of prime chemical importance, as is the determination of the proper $pK_a$ values of phosphoric acid at the temperature and ionic strength of interest. The system can be properly represented by accurately determining these acidity constants and conjugate base associations with the cations of the background salt and by incorporating these values into the chemical model.

2. THEORY

The determination of both the dissociation constants for phosphoric acid and the ion pairing constants for the cation of the background salt with HPO$_4^{2-}$ and H$_2$PO$_4^-$ can be made by titration of phosphoric acid. The first titration is conducted in the presence of the complexing ion and a second titration in the presence of a cation with ideally negligible complexing capacity. The variation in these acidity constants contains enough information to determine the stability constants of the complexing cation with the phosphate ligands. The derivation of equations necessary to determine the metal association constants follows.$^{(1)}$

The total phosphate in a dilute solution without metal ion pairing is

$$TPO_4 = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$$

where the terms in brackets represent molar concentrations and TPO$_4$ represents the analytical concentration of phosphate. If cation M ion pairs with phosphate ligands, and if the concentrations are low enough and the association weak enough so that no ternary complexes form, the following can be assumed

$$[H_2PH_4] = [H_2PO_4^-] + [MH_2PO_4^0]$$

$^{(1)}$