

Ionization Constants of Phosphoric Acid in H₂O and D₂O from 25 °C to 300 °C at 20 MPa: Deuterium Isotope Effects under Hydrothermal Conditions

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Values of the ionization constant of phosphoric acid in H₂O and D₂O ($K_{\text{H}_3\text{PO}_4}$ and $K_{\text{D}_3\text{PO}_4}$), and their deuterium isotope effect, $\Delta pK = pK_{\text{D}_3\text{PO}_4} - pK_{\text{H}_3\text{PO}_4}$, have been determined from 100 to 300 °C at $p = 20$ MPa, using a flow-through AC conductance cell built at the University of Delaware. Measurements were made on dilute (ionic strength $\sim 10^{-4}$ mol·kg⁻¹) solutions of phosphoric acid, potassium phosphate, hydrochloric acid and potassium hydroxide in H₂O and D₂O, injected in sequence at each temperature and pressure, so that systematic errors in the measured conductance of each solution would cancel. Experimental values for the molar conductivity, L , of the strong electrolytes were used to calculate the molar conductivity at infinite dilution, L° , using the Fuoss-Hsia-Fernández-Prini ("FHFP") equation. These were used to calculate the molar conductivity at infinite dilution for phosphoric acid which was in turn used to calculate the degree of dissociation and finally the ionization constants of phosphoric acid. This same procedure was done for the pertinent deuterated solutes in D₂O. Measured values of $\log K_{\text{H}_3\text{PO}_4}$, $\log K_{\text{D}_3\text{PO}_4}$ and ΔpK , were obtained to a precision of ± 0.003 . The values for ΔpK lie within the range 0.34 ± 0.03 on the aquamolal scale, with a shallow minimum and maximum at 150 and 250 °C, respectively. The temperature dependence of ΔpK from the present study differs from that of D₂PO₄⁻ and acetic acid, the two other accurate studies in the literature at these high temperatures (Mesmer and Herting, *J. Solution Chem.* **1978**, *7*, 901-909; Erickson et al., *J. Phys. Chem B.* **2011**, *115*, 3038-3151). These dropped from the values of $\Delta pK = 0.58 \pm 0.01$ and $\Delta pK = 0.49 \pm 0.01$ at 25 °C, respectively, to values at 125 °C that were approximately 0.1 unit lower and were then independent of temperature up to 275 °C.