

SPECIATION OF Mo(VI) OXYANIONS IN NATURAL WATERS

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Molybdenum is an essential trace element, whose mobility is highly dependent on the hydrological cycle. In most conditions prevailing in natural waters, Mo(VI) anions are the only thermodynamically stable soluble species. So, the speciation and concentration of the main anionic components are important in determining its bioavailability and environmental impact. Its chemical speciation in natural aquatic scenarios has been poorly studied mostly because molybdenum biological relevance has been only recently acknowledged. In this work we report the potentiometric study of oxyanions of Mo(VI) and their interaction with some other metal ions: Na⁺, K⁺, Ca²⁺, Mg²⁺, Sr²⁺, Ba²⁺, Cu²⁺, Zn²⁺ and Cd²⁺. Experimental conditions were chosen to simulate the natural waters media (20.0 °C, low ionic strength, 0.15 M). The results show that, in the absence of metal ions, MoO₄²⁻ is the predominant species for pH values above 4.4. The formation of the protonated forms of MoO₄²⁻ and of the polynuclear species only occurs for acidic conditions. For samples containing low molybdenum concentrations, such as those normally encountered in natural waters, HMoO₄⁻ predominates from pH 3.6 to pH 4.4 and H₂MoO₄ is the most abundant species below pH 3.6. Polymeric species [Mo₈O₂₆]⁴⁻ and [Mo₇O₂₄]⁶⁻ appear only when the total molybdenum concentration is greater than 1 mM, being of no relevance in natural waters. The stoichiometry and the stability constants of the formed species in the presence of metal ions were also measured. Cation charge has a major influence on the thermodynamic equilibria: while interaction with the monovalent ions is negligible, the M²⁺ cations are bound to anionic molybdenum species to a considerable extent. For total molybdenum concentration below 1 mM, the predominant form of molybdenum (VI) is still MoO₄²⁻ above pH 4.4, with a variable percentage of [M(MoO₄)], depending on the metal ion concentration. As the pH value becomes lower than 4.4, the most abundant species become [M(HMoO₄)]. For example, 10⁻⁷ M Mo(VI) in the presence of mean natural waters concentrations of Ca²⁺ (16.5 mM) shows the predominance of [Ca(MoO₄)] for pH values above 4.4, and [Ca(HMoO₄)]⁺ for more acidic media. So, results show that in conditions simulating natural waters, availability of soluble anionic molybdate species is strongly influenced by pH media and the presence of +2 metal ions.

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