Uv-Vis Spectroscopy of aqueous solutions at high temperature: deprotonation of molybdic acid and tungstic acids.

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Molybdenum and tungsten occur in hydrothermal deposits throughout the Earth's crust but the transport and deposition chemistry for both elements is not well known at high temperatures and pressures. As a first step towards unravelling the aqueous chemistry of Mo and W under extreme conditions, we are studying the protonation equilibria of both molybdate (MoO_4^{2-}) and tungstate (WO_4^{2-}) as well as the formation of their polyanions up to 300^0C and at saturated vapour pressures.

The ionisation constants for molybdic and tungstic acids were determined spectrophotometrically. UV-Vis spectra at 25^0C were collected in 1 and 10cm quartz cuvettes. At high temperatures flow-through and stop-flow experiments were conducted in the high temperature Ti-alloy optical cell with quartz windows. Mathematical treatment of collected spectra involved factor analysis for determining number of absorbing species and orthogonalisation of absorbance matrix.

Aqueous solutions of sodium molybdate and sodium tungstate were prepared. pH was adjusted with perchloric acid and sodium hydroxide. Total molybdenum concentrations in sodium molybdate solutions were kept below 1×10^{-4} M in order to avoid polynuclear species. There is quite a big scatter in the literature for pK for molybdic acid at low temperatures [1,2,3,4], while at high temperatures there are no available data for comparison. In case of tungstic acid polynuclear species occur already at 1×10^{-5}M concentrations [6] which makes it impossible to work below mononuclear wall because of the low absorption (A=0.02-0.05 at to 5×10^{-6} M solutions in a 10cm quartz cuvette). Several models with different possible polynuclear species [5] were analysed and compared. Experiments with the higher total molybdenum concentrations are also under way.

References

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