

UV-Visible spectrophotometric measurements of metal complex formation at high temperatures: the stability of Mn (II) chloride species

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We are studying the stoichiometry and stability of metal complexes under hydrothermal conditions using uv-vis spectrophotometry. Absorbance measurements are performed in a flow-through Ti-Pd alloy cell which operates routinely up to 400°C and 750 bar with windows of uv-quality fused silica or synthetic sapphire. Pressure is controlled by means of a Dynamax SD-300 HPLC pump and back pressure regulator. Spectra are collected using a Cary 5E double beam spectrophotometer.

Manganese is one of the most abundant elements in the earth's crust and is easily mobilised and transported by hydrothermal solutions. Very few studies have been carried out on the high temperature aqueous chemistry of manganese (II). Manganese (II) forms a number of chloro-aquacomplexes which will play an important role in the hydrothermal transport and deposition of manganese in hydrothermal environments. We are therefore studying Mn (II) chloride complex formation spectrophotometrically up to 300 °C and at pressures close to the saturated vapour pressure (i.e. s.v.p. + 10 bar). Absorbance measurements were performed separately for MnCl₂-NaCl mixtures and for NaCl solutions of approximately the same total chloride concentrations. All

spectra were corrected for the background absorption of the cell and the solvent by subtracting the absorption of the cell filled with water at the respective temperatures. The background absorption was measured before and after each experiment to eliminate the effects of window etching. Total manganese concentrations were determined by atomic absorption and chloride ion concentrations were analysed by ion chromatography.

Manganese chloride solutions absorb both in the visible and UV regions. Visible transitions are of the d-d type and have very low intensity. *Ab initio* calculations show that [MnCl(OH₂)₅]⁺ and [MnCl₂(OH₂)₄]⁰ have a number of distinct UV transitions with oscillator strength > 0.1 This makes distinction of these complexes possible by means of UV spectrophotometry. One of the difficulties of this study was strong charge-transfer-to-solvent absorbance of chloride ion which red shifts with increasing temperature, hiding absorbance of manganese species at temperatures above 300°C. Thus, an accurate correction for the actual chloride absorbance is required. A mathematical model of chloride absorbance was constructed taking into account the non-linear behaviour of the absorbance as function of

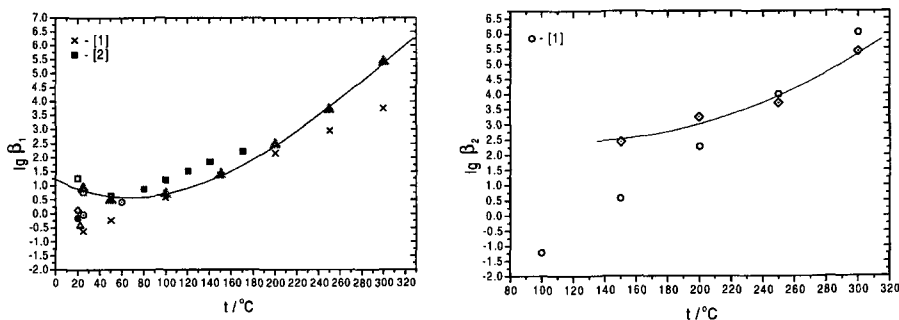


FIG. 1.

concentration. The number of absorbing species in a specific wavelength interval was determined by rank analysis of the absorbance matrix. Since the measured absorbances and concentrations are subject to experimental errors, the problem of finding of molar absorptivities is ill-posed and in many cases, the overdetermined system of linear equations at each iteration as well as the hessian of the objective function are ill-conditioned. To deal with these difficulties, our algorithm extensively uses ideas of Tikhonov's regularization of ill-posed

problems to establish a stable solution. The preliminary results of our study are shown on Fig. 1, where lines correspond to our data.

References

- [1] Gammons, C.H. and Seward, T.M. (1996) *Geochim. Cosmochim. Acta*, **60**, 4295–311.
- [2] Wheat, C.G. and Carpenter, R. (1988) *J. Sol. Chem.*, **17**, 467–80.