

Metal Complexation Studies in Low-Temperature, Acid-Sulphate Waters Using Mercury/Mercurous Sulphate Concentration Cells

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Acid rain associated with fossil fuel burning and smelting activities, and acid mine drainage from both coal and metal mining operations produce dilute to highly saline surface waters with very low pH's and high sulphate concentrations. In many acid-sulphate waters across a wide range of ambient temperatures, multivalent metals including Al, Fe, Zn, Cd, Co, Cu, Pb, etc., occur in solution in their fully oxidized, hydrated ionic forms, since hydrolysis is suppressed by the low pH's prevalent. In such environments, many potential organic ligands are fully protonated, and most solid surfaces are neutral or positively charged. Therefore, the mobility of multivalent cations in these environments is largely controlled by the dissolution rates and thermodynamic stabilities of clays, oxides and other solid phases of the metals of interest, and complexes of the hydrated metal ions with chloride and sulphate anions in solution. The ionic strengths of acid-sulphate waters are highly dependent on the bisulphate dissociation constant and the stability constants of metal-sulphate complexes, but the determination of these constants is highly dependent on the activity coefficient models chosen to interpret experimental results, which are themselves highly dependent on ionic strength. In order to circumvent this problem and provide quantitative and unambiguous metal sulphate complexation data for assessing metal ion mobility and bio-availability, we have developed a new potentiometric concentration cell consisting of matched mercury/mercurous sulphate electrodes, housed in separate compartments connected by a porous glass liquid junction. The electrodes are shown to exhibit Nernstian response, and thus the cell potential arises solely from the difference in sulphate anion activity between the test and reference compartments and a small liquid junction potential. Experiments with this cell are initiated by adding the same low-pH (ca. 1-3), high-sulphate (ca. 0.01 to 0.05 molal) solution to both compartments. This starting solution also contains high concentrations (0.1 to 5 molal) of an "inert" 1:1 electrolyte such as sodium trifluoromethanesulphonate (NaTr) to maintain a constant ionic strength. A near zero potential is established in a matter of hours, after which an acidic solution of the metal of interest, in sufficient NaTr to maintain approximately constant ionic strength, is titrated into the test compartment, with continuous monitoring of the cell potential until a constant value is obtained. Using such cells, we have conducted an extensive investigation of the complexation of Al(III), in which the

formation constants of the mono- and disulphate complexes have been determined in 0.3, 0.5 and 1.0 molal NaTr at temperatures of 10, 25 and 50 degrees centigrade. Our new results at 50 degrees centigrade are shown to be in excellent agreement with our earlier studies (Ridley et al., 1999), which involved both gibbsite solubility measurements and pH-titrations of aluminium sulphate solutions using our high temperature hydrogen-electrode concentration cells (HECC's). In the earlier study, we concluded that the HECC was not suitable for determination of aluminium-sulphate complexes at temperatures below about 50 degrees centigrade, due to the fact that bisulphate becomes an increasingly strong acid with decreasing temperature. Our new results also agree well with the low-ionic-strength conductance studies of Nishide and Tsuchiya (1969), but give constants that are much stronger than most other literature data. However we will show that most of the earlier literature results were adversely affected by inadequate activity coefficient models, and/or use of potentiometric cells insufficiently sensitive to the metal-sulphate reaction. We have also initiated studies of sulphate complexation with Zn(II), to obtain formation constants for the monosulphate complex at 25 degrees centigrade at 0.1 and 0.3 molal ionic strength approximately an order of magnitude weaker than the equivalent Al(III) monosulphate complex. Using this approach, we intend to investigate the sulphate complexes of the other metals listed above, provided that the metal ions do not induce rapid oxidation of Hg(I). Due to the long-term stability exhibited by these cells, they can also be used to investigate the dissolution and precipitation kinetics of metal sulphate solids more soluble than mercurous sulphate, using solution perturbation/relaxation techniques with continuous, in situ monitoring of the sulphate ion activity in the test solution.

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Nishide T & Tsuchiya R, *Bull. Chem. Soc. Japan*, **38**, 1398-1400, (1965).

Ridley MK, Wesolowski DJ, Palmer D & Kettler RM, *Geochim. Cosmochim. Acta*, **63**, 459-472, (1999).