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## The study of the speciation of uranyl-sulphate complexes by UV-VIS absorption spectra decomposition

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Uranyl-sulphate complexes are the most significant U(VI) species in acid solutions containing sulphate ions. The study of their properties is of practical significance for characterisation of solutions used in underground uranium ore leaching and following remediation of leaching sites. At low pH values, the speciation of U(VI) mainly depends on its total concentration [UVI] and sulphate ions concentration [SO<sub>4</sub><sup>2-</sup>]. As absorption UV-VIS spectra of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub> solutions were found significantly depend upon the ratio  $\lambda = [\text{SO}_4^{2-}] / [\text{UVI}]$ , the spectrophotometric method for closer study of U(VI) - SO<sub>4</sub><sup>2-</sup> complexes speciation was used.

Studied solutions were of constant uranium concentration [UVI] = 5·10<sup>-2</sup> mol·L<sup>-1</sup>. Required values of the  $\lambda$  ratio were adjusted by proper additions of Na<sub>2</sub>SO<sub>4</sub> solution and varied from  $\lambda = 0$  up to  $\lambda = 20$ . Constant pH value pH = 2 was maintained by the additions of either HNO<sub>3</sub> or NaOH solution of negligible volume. Absorption spectra were recorded using UV/VIS spectrophotometer CARRY 100 within the wave-length range 190 –900 nm.

The following U(VI) species were considered under conditions given: UO<sub>2</sub><sup>2+</sup>, UO<sub>2</sub>SO<sub>4</sub> (aq), UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup> and UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>4-</sup>. As the most pronounced effects of the  $\lambda$  ratio value changes on the spectra revealed at wave-length between 380 and 500 nm, these parts of spectra were used as a database for the identification of individual U(VI) species and for determination of their individual spectra by deconvolution of the experimental spectrum. Proposed simple deconvolution method needs to estimate relative amounts of individual species, preliminary. Stability constants from NEA database and SIT method of activity coefficients calculation at high ionic strength were used for this purpose. The spectrum of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> solution without Na<sub>2</sub>SO<sub>4</sub> ( $\lambda = 0$ , pH = 2) was considered to be individual spectrum of pure UO<sub>2</sub><sup>2+</sup> specie. Absorbance data following from it and calculated relative amounts of all four species for each  $\lambda$  value were taken as the basic set of input data for deconvolution. Then, the absorbance of each of the three remaining species (UO<sub>2</sub>SO<sub>4</sub> (aq), UO<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub><sup>2-</sup>, UO<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub><sup>4-</sup>) at given wave length can be find by solving the system of three linear equations involving experimental data from three spectra of different  $\lambda$  ratio. The disagreement of spectra calculated from different triplets of experimental spectra can be caused either by experimental errors, or by incorrect estimation of relative amounts of individual species. Thus, presented method can be helpful even for estimation of accuracy of stability constants and SIT activity coefficients used in speciation calculations.

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