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HYDROLYSIS OF URANIUM(VI) AT VARIABLE TEMPERATURES

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The hydrolysis of U(VI) has been a subject of extensive studies. Hydrolysis constants for numerous species, $(\text{UO}_2)_m(\text{OH})_n^{(2m-n)^+}$ where $m = 1 – 4$ and $n = 1 – 9$, have been reported. However, the majority of the data are for the temperature of 20 to 25 °C with only a few studies covering the range of elevated temperatures. Besides, there have been only a few calorimetric studies on U(VI) hydrolysis at 25 °C, but no calorimetric studies at other temperatures. The scarcity of hydrolysis constants at elevated temperatures and the absence of enthalpy data at variable temperatures result in high uncertainty in evaluating the temperature effect on the hydrolysis of U(VI), a process of critical importance in radionuclide migration in the environment. In the present work, the hydrolysis constants for U(VI) in 0.1 mol kg$^{-1}$ tetraethylammonium perchlorate were determined at variable temperatures (10 - 85 °C) by potentiometry. Under the experimental conditions ($C_{\text{HA}}/C_{\text{U}}$ ranging from 4 to –2), the (2, 2) and (3, 5) species, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3(\text{OH})_5^+$, were found to be dominant. As the temperature was increased from 10 °C to 85 °C, the hydrolysis constants for the reactions of $m\text{UO}_2^{2+} + n\text{H}_2\text{O} \rightarrow (\text{UO}_2)_m(\text{OH})_n^{(2m-n)^+} + n\text{H}^+$ were found to increase by two and five orders of magnitude for the (2, 2) and (3, 5) species, respectively. The enthalpy of hydrolysis at variable temperatures was measured by titration microcalorimetry. These results are discussed in conjunction with the data on the hydrolysis of other actinide cations and the data on the complexation of U(VI) with other ligands.