



Interaction of uranyl with acetate in aqueous solutions at variable temperatures



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ABSTRACT

Increasing activities in the environmental management of nuclear wastes incite significant interest in the study of the interaction of actinides with organic matter in aqueous solution, especially at elevated temperature. The system U(VI)-acetic acid is studied in aqueous solutions at pH 2 in the temperature range from 15 °C to 55 °C by affinity capillary electrophoresis (ACE). The formation of two complex species $\text{UO}_2\text{CH}_3\text{COO}^+$ and $\text{UO}_2(\text{CH}_3\text{COO})_2$ is observed. Thermodynamic parameters (the molar Gibbs energy of reaction ($\Delta_r G_m$), the molar enthalpy of reaction ($\Delta_r H_m$) and the molar entropy of reaction ($\Delta_r S_m$)) are determined at fixed ionic strength of $0.05 \text{ mol} \cdot \text{L}^{-1}$ ($\text{NaClO}_4\text{-HClO}_4$) and calculated at 0 ionic strength with extended Debye–Hückel equation for the activity coefficients. Obtained results are compared with literature data.

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1. Introduction

The interaction of U(VI) with natural organic matter is of great interest. It deals not only with a fundamental knowledge, but also with the migration of U(VI) species in the environment and their distribution in the geosphere and biosphere [1–3]. Knowledge about the impact of natural organic matter on U(VI) migration is required for the long term risk assessment for nuclear waste repositories, for facilities of the former uranium mining and milling sites [4–7]. Humic acids are the principal components of humic substances, which are the major constituents of organic matter. Humic acids are characterized by heterogeneous structural and functional properties. They are composed of aliphatic and aromatic structural elements and a variety of different, mainly oxygen containing functional groups [4]. The most simple model substances for humic acids represent low-molecular short chain organic acids which can occur as humic acid building blocks and simulate their structure and functionality. The acetic acid is the smallest organic acid with a carbon chain.

Among the different geochemical processes, aqueous complexation can also control the transport behaviour of radionuclides. Moreover, the most probable transport media is aqueous phase

[6,8–11]. In this project we are interested in the complexation of U(VI) with acetic acid in aqueous solutions at various temperatures.

The interaction of U(VI) with acetic acid at room temperature has been studied in several projects. In paper [12] the data from these projects are reviewed. The three complex species of uranyl with acetate are evidenced (UO_2Ac^+ , UO_2Ac_2 and $\text{UO}_2(\text{Ac})_3^-$). The logarithms of the thermodynamic stability constants (β°) are $\log \beta^\circ_1 = 2.94 \pm 0.08$ [12], $\log \beta^\circ_2 = 5.50 \pm 0.15$ [12] and $\log \beta^\circ_3 = 7.25$ [13].

Very few papers are devoted to study of uranyl interaction with acetic acid at various temperature [14–18]. However, actually the increasing activities in the environmental management of nuclear wastes incite significant interest in the study of the chemistry of actinides in solution, especially at elevated temperature. Usually, potentiometric and calorimetric methods are used to determine the thermodynamic parameters. The most studies of U(VI)-acetate interactions are performed at high ionic strength (mostly at 1 M) [14,16–18]. To the best of our knowledge there is no the standard thermodynamic parameters communicated (the molar enthalpy ($\Delta_r H_m^0$), and the molar entropy ($\Delta_r S_m^0$) for complex formation reactions) at zero ionic strength.

In this project we study of uranyl interaction with acetic acid at various temperatures (from 15 °C to 55 °C) by means of affinity capillary electrophoresis (ACE). Affinity capillary electrophoresis methods are successfully used for the determination of stability constant values for different systems in the last years [12,19–40].

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This method attract attention due to a number of advantages, including high resolution, speed of analysis, low running costs, minimal sample consumption and aptitude for automation, among others [41]. The recent achievements in this field are reviewed [40,42,43]. Special review is devoted to the actinide speciation by capillary electrophoresis [41]. Due to the stability constants obtained from electrophoretic mobility measurements at different temperatures, the thermodynamic parameters can be determined. The values of stability constants, thermodynamic parameters, such as the molar Gibbs energy ($\Delta_r G_m$), the molar enthalpy ($\Delta_r H_m$), and the molar entropy ($\Delta_r S_m$) for complex formation reactions are calculated at ionic strengths of $0.05 \text{ mol} \cdot \text{L}^{-1}$ and extrapolated to zero ionic strength with aid of extended Debye–Hückel equation for the activity coefficients [44].

2. Experimental section

2.1. Chemicals and solutions

All chemicals used are of analytical reagent grade. The stock $\text{UO}_2(\text{ClO}_4)_2$ solution (0.1 M in 0.63 M HClO_4) is obtained by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (>99% FLUKA puriss) in 12 M HClO_4 (MERCK Suprapur) and evaporating the resulting solution to almost dryness on a sand bath. The residue is dissolved in concentrated HClO_4 and evaporated again. This last operation is repeated three times. The uranium concentration is checked by PERALS spectrometric measurements described elsewhere [45]. Glacial acetic acid ($\geq 99.99\%$) is supplied by Sigma–Aldrich. Concentrated perchloric acid (60% solution from Sigma–Aldrich) is diluted in water to the requisite concentration. The exact concentration is determined by acid–base titration with certified NaOH solution. Sodium perchlorate (99%) is provided by Merck. The impurity content in this chemical is low enough (Sulphate and chloride contents are at ppm level.) and does not have any impact on results obtained. Moreover the work is done with diluted solutions. The exact concentration of diluted solution is determined by gravimetric method. All solutions are prepared with deionised water (Millipore direct Q, $R = 18.2 \text{ M}\Omega$).

2.2. Apparatus and software

Capillary Electrophoresis measurements. P/ACE system MDQ capillary electrophoresis instrument (Beckman Coulter, France) is used. The system is comprised of 0–30 kV high-voltage built in power supply, equipped with a UV–vis spectrophotometric diode array detector. UV direct detection at 200 nm is used in this work. A capillary (50 μm I.D., 363 μm O.D.) made from fused silica is obtained from Beckman Instruments and had a total length (L_t) of 31.2 cm and an effective separation length (L_d) of 21 cm. The capillary is housed in an interchangeable cartridge with circulating liquid coolant. The length of non-thermostated capillary inlet (L_{inlet}) is about 4.2 cm (about 20% of the effective separation length). The ambient temperature is about 20 °C. The data are obtained at the standard state pressure (0.1 MPa). Every measurement is repeated at least three times. Data acquisition and processing are carried out with Karat 32 software (Beckman Coulter, France).

All concentration and constant calculations are done with the EXCEL® and ORIGIN® software programs. The solver module program is used for fitting experimental points by least squares curve fitting.

pH measurements. A pH-meter GLP-21 (Crisin, France) and a combination electrode are used for pH measurements after calibration against NIST standards (4.01 and 7.00). An aliquot of solution is used for each measurement. The pH values of solutions is 2.00 ± 0.05 .

2.3. Procedure

The capillary is conditioned prior to use by successive washes with 0.1 M sodium hydroxide, deionised water and the buffer solution under study. It is rinsed for 2 min (at a pressure of 103.4 kPa) with the buffer between two runs and kept filled with deionised water overnight.

In order to avoid hydrolysis and/or polymerisation of the uranyl ion, that could potentially lead to the formation of additional species and/or to the modification of uranyl mobility values, we use the perchloric acid–sodium perchlorate aqueous solutions at pH 2.0 as background electrolyte (BGE). At such values and uranyl concentration of $1 \cdot 10^{-4} \text{ M}$, the contribution of hydrolysed and polymeric species to U(VI) is negligible [46]. The ionic strength (I) of BGE is $0.05 \text{ mol} \cdot \text{L}^{-1}$. The relative standard deviation estimated is less than 5%. The pH is controlled with pH-meter (see Section 2.2).

The normal polarity mode is applied (injection is performed at the positive end). The sample, containing only uranyl ions and the neutral marker, is injected in the capillary. The capillary contains BGE (perchloric aqueous solution at pH 2.0) with fixed concentrations of acetic acid. Sets of runs are then made for different concentrations of acetic acid (from 0 to $0.8 \text{ mol} \cdot \text{L}^{-1}$) in BGE. The separation voltage applied is 5 kV and the injection time (by a pressure of 3.45 kPa) is 4 s. This value of applied voltage is chosen to respect the Ohm's law. The current is about 40 μA and the input power is about 0.2 W. In these conditions we can estimate that the effect of Joule heating is insignificant in the thermostated part of capillary and the deviation from the desired temperature is $\leq 1^\circ \text{C}$ [19,47]. The separations are performed at constant forward pressure of 1.4 kPa.

2.4. Data treatments

2.4.1. Electrophoretic mobility determination

The electrophoretic mobility μ ($\text{cm}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}$) can be calculated by using the following expression:

$$\mu = L_t L_d \frac{1/t - 1/t_{\text{eof}}}{U}, \quad (1)$$

where L_t (m) is the total capillary length, L_d (m) is the length between capillary inlet and the detection window, U is applied voltage in V, t (s) is the migration time of the studied species, t_{eof} (s) is the migration time of dimethylsulfoxide (DMSO), used as a neutral marker for electroosmotic flow mobility determination.

In this work the hydrodynamic transfer of the sample through the non-thermostated inlet into the thermostated region of capillary is used to avoid the influence of non efficiently thermostated short inlet [23]. To calculate the ion mobility for this mode, expression (1) is modified. In this case L_d is no longer the length between the capillary inlet and the detection window, but is now the length between the position of the sample in the capillary thermostated zone and the detection window (L'_d). To find L'_d we measure the elution time of marker (DMSO), using only forward pressure. In this case we can write:

$$v_p = \frac{\pi d^2 L'_d}{4t_m}, \quad (2)$$

where v_p is volumetric flow rate (generated by forward pressure, m^3/s), d is the capillary diameter (m), t_m is the elution time of marker after the hydrodynamic transfer through the non-thermostated inlet (s). The L'_d can be calculated with aid of Poiseuille equation for laminar viscous and incompressible flow and the expression (2):

$$L'_d = \frac{\Delta P d^2 t_m}{32\eta L_t}, \quad (3)$$

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