

Uranyl surface speciation on silica particles studied by TRLIL spectroscopy

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The mobility of contaminants in the environment is controlled by their adsorption onto solid materials. The adsorption reactions itself depends strongly on solution chemistry parameters as for instance pH or ligand concentration. A powerful tool to study uranyl complexation is the time-resolved laser-induced luminescence (TRLIL) spectroscopy as (i) it allows working at trace level concentrations and (ii) the obtained bi-dimensional luminescence data permit the identification of a complex on the bases of two independent parameters (its spectrum and its lifetime). Several authors (Kohler *et al.*, 1996; Waite *et al.*, 1994) have used the hypothesis of the existence of different uranyl surface complexes to explain the adsorption plateau. The principal aim of this work was to find out whether we could prove the existence

of several surface complexes by TRLIL spectroscopy.

Experimental

In the present study the sorption of uranyl ions to amorphous silica has been studied in the presence of atmospheric CO₂. Two sample series were prepared in the pH range 4 to 9 and at two uranyl concentration levels (1 and 0.1 μM). TRLIL spectroscopy was used to (i) describe quantitatively the total sorbed uranyl concentration following the wet chemical approach of Brina and Miller, 1992 (phases were separated by filtration < 0.45 μm), (ii) identify the different complexes at the silica-water-interface and (iii) determine their concentrations as the luminescence intensity is linearly related to the concentration of the emitting complex.

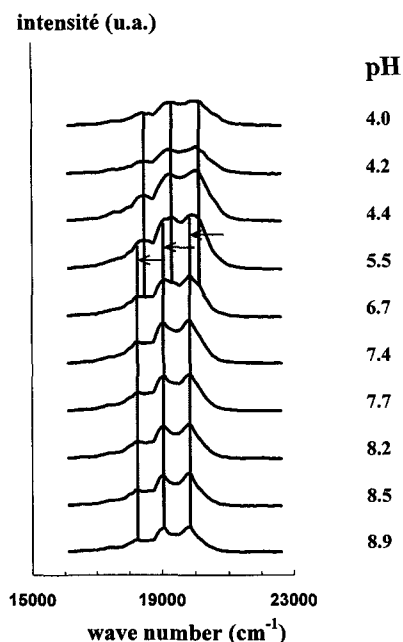


FIG. 1. Spectra of aerosil-uranyl-suspensions ($c_p = 1 \text{ g dm}^{-3}$, $[\text{UO}_2^{2+}] = 1 \text{ }\mu\text{M}$).

Results

Two luminescent uranyl surface complexes have been identified in the pH range 4 to 9. Both complexes could be differentiated:

by lifetimes (low pH: $170 \pm 25 \text{ }\mu\text{s}$; high pH: $360 \pm 50 \text{ }\mu\text{s}$) and

by uranyl emission spectra (250 cm^{-1} spectral 'red' shift between the low pH and high pH spectra, Fig. 1).

A quantitative speciation diagram could be obtained exploring three independent data sets: the spectra at both uranyl concentration levels and the decays of the series at 1 μM uranyl.

A gap between the experimentally determined sorbed concentration and the sum of the concentrations of the two luminescent complexes was observed between pH 8 and 9. This gap was interpreted as the presence of a carbonate-containing non-luminescent ternary surface complex (Fig. 2). Bernhard *et al.* (1996) reported the complexation with carbonate quenching the luminescence and therefore leading to no measurable signal at 1 μs after the laser pulse. The same found Kato *et al.* (1994) who could not detect a

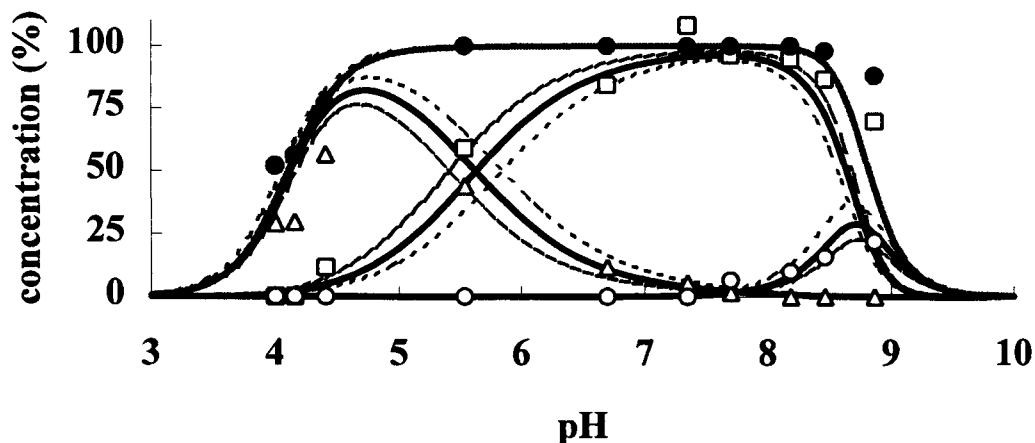


FIG. 2. Uranyl surface speciation on the bases of the spectra ($[UO_2^{2+}] = 1 \mu\text{M}$; \square , Δ , \circ and \bullet represent the lower and the higher protonated state; the carbonated surface species and experimental total sorbed concentration, respectively.)

luminescence signal of uranyl carbonate complexes in solution.

For both examined total uranyl concentration levels (1 and $0.1 \mu\text{M}$) the luminescence was characterised by similar spectra and lifetimes. Therefore we assumed the absence of surface uranium hydroxy-polymers.

Surface complexation modelling and conclusion

The luminescence based speciation results could be described within the constant capacitance model framework. The presence of the following three different mono-nuclear (1:1) surface complexes was assumed: two silica-uranyl-hydroxyl-complexes releasing 2 and 3 protons and one ternary silica-uranyl-hydroxyl-carbonato-complex releasing also 3

protons. All complexes are supposed to have bidentate structure.

References

- Bernhard, G., Geipel, G., Brendler, V. and Nitsche, H. (1996) *Radiochimica Acta*, **74**, 87–91.
 Brina, R. and Miller, A.G. (1992) *Anal. Chem.*, **64**, 1413–8.
 Kato, Y., Meinrath, G., Kimura, T. and Yoshida, Z. (1994) *Radiochimica Acta*, **64**, 107–11.
 Kohler, M., Curtis, G.P., Kent, D.B. and Davis, J.A. (1996) *Water Resources Research*, **32**, 3539–51.
 Schindler, P.W. and Gamsjaeger, H. (1972) *Kolloid Z. Z. Polym.*, **250**, 759.
 Waite, T.D., Davis, J.A., Payne, T.E., Waychunas, G.A. and Xu, N. (1994) *Geochim. Cosmochim. Acta*, **58**, 5465–78.

TABLE 1. Intrinsic constants (log K) for the silica surface speciation

Reactions			logK
$\equiv\text{Si}(\text{OH})_2 - \text{H}^+$	\rightleftharpoons	$\equiv\text{SiO}_2\text{H}^-$	-6.98
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} - 2 \text{H}^+$	\rightleftharpoons	$\equiv\text{SiO}_2\text{UO}_2^0$	-4.8
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} - 3 \text{H}^+ + \text{H}_2\text{O}$	\rightleftharpoons	$\equiv\text{SiO}_2\text{UO}_2\text{OH}^-$	-10.46
$\equiv\text{Si}(\text{OH})_2 + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3^0 - 5 \text{H}^+ + \text{H}_2\text{O}$	\rightleftharpoons	$\equiv\text{SiO}_2\text{UO}_2\text{OHCO}_3^{3-}$	-22.14

(Constant Capacitance Model; $c_p = 1 \text{ g dm}^{-3}$; $A_s = 169 \text{ m}^2 \text{ g}^{-1}$; $j = 7 \text{ F m}^{-2}$; $I = 0 \text{ M}$;
 $[\equiv\text{Si}(\text{OH})_2]_{\text{total}} = 0.51 \text{ mM}$; $[\text{H}_2\text{CO}_3^0]_{\text{free}} = 16.4 \mu\text{M}$; $[\text{H}_4\text{SiO}_4^0]_{\text{free}} = 0.9 \text{ mM}$; $[\text{UO}_2^{2+}]_{\text{total}} = 1 \mu\text{M}$).