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Spectrophotometric Study of the Interaction between Americium(III) and Humic Materials*

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Actinides in all oxidation states (III, IV, V and VI) would form strong complexes with natural organics like humic and fulvic acids [1]. Hydrolysis (oxidation state IV) and carbonate complexation (oxidation states V and VI) would usually dominate over the formation of organic complexes in the pH and carbonate concentration ranges of most sub-surface waters. For trivalent actinides, however, humate complexation could be predominant, and the effects on actinide transport properties in the environment for example would be most pronounced for this oxidation state. This has been confirmed in several studies of americium sorption and mobility in geologic systems in the presence of humic materials [2–5]. A study of the formation of americium complexes with humic and fulvic acids of various origins (groundwater, surface water, lake sediments and soil), using a spectrophotometric technique, is presented in this paper.

Experimental

Absorbance spectra were recorded (at 470–530 nm, 10 cm cells, with a Cary 17 D instrument) for americium solutions (2.48×10^{-5} M or 3.10×10^{-5} M in 0.10 M $NaClO_4$ with 0.005 M NaAc, pH 4.65) in the presence of humic materials. Five different humates were used at concentrations between 0 and 60 mg/l:

(a) Fulvic acid from a deep groundwater (Fjällveden, Sweden); FA–GW [6].

(b) Fulvic acid from a surface water (Bersbo, Sweden); FA–SW [7].

(c) Humic acid from a surface water (Bersbo, Sweden); HA–SW [7].

(d) Humic acid from a lake sediment (Lake Bradford, Florida); HA–LB [8, 9].

(e) Humic acid from a soil (available from Aldrich); HA–A [10].

The recovery of the humic materials, their purification and characterization are described elsewhere [6–10].

All work with americium, including recording of the spectra, was performed in a glove-box at 20 ± 1 °C and in the presence of air.

Results and Discussion

Absorbance spectra for the five systems are given in Fig. 1. The characteristic absorbance peak for americium(III) at 503.1 nm is displaced in the presence of humates, and a new peak appears at 504.8–505.5 nm. The presence of an isosbestic point indicates that only one new species is formed in the system.

Conditional formation constants have been calculated on the assumption that the new peak represents a 1:1 complex (AmA) and that no other species (except Am^{3+}) have to be considered. The absorbance A in the system would be given by

$$A = \epsilon_0 a + \epsilon_1 b \qquad (1)$$

where a and b are the concentrations (mol/l) of Am^{3+} and AmA, respectively and ϵ the corresponding molar extinction coefficients. The ratio

$$A/(a + b) = \epsilon \qquad (2)$$

would give ϵ_0 and ϵ_1 for $b = 0$ and $a = 0$, respectively. The formation of the complex AmA is given by

$$\beta = b/[a(mC - b)] \qquad (3)$$

where m = total concentration of humate (g/l) and C = capacity of the humate (eq/g). For a given ratio of a/b and with a known value for C the corresponding value for m can be calculated as a function of β.

Figure 2 gives values for ϵ according to eqn. (2), as measured at the wave length corresponding to the 1:1 complex of the system. Calculated formation constants giving the best fit to experimental data, Fig. 2, are given in Table I, as well as capacities and formation constants for americium–humate complexes given in the literature.

The spectra indicate the formation of a single 1:1 complex. This may merely represent a certain type of bonding between americium and the humics, and no further conclusions concerning the nature of the complex can be drawn solely from the present data. However, no second type of complex is indicated, corresponding to what is denoted as a 1:2 species in the literature [9, 11, 12]. Possibly, the americium/humate concentration ratio is too high for such species to be formed.

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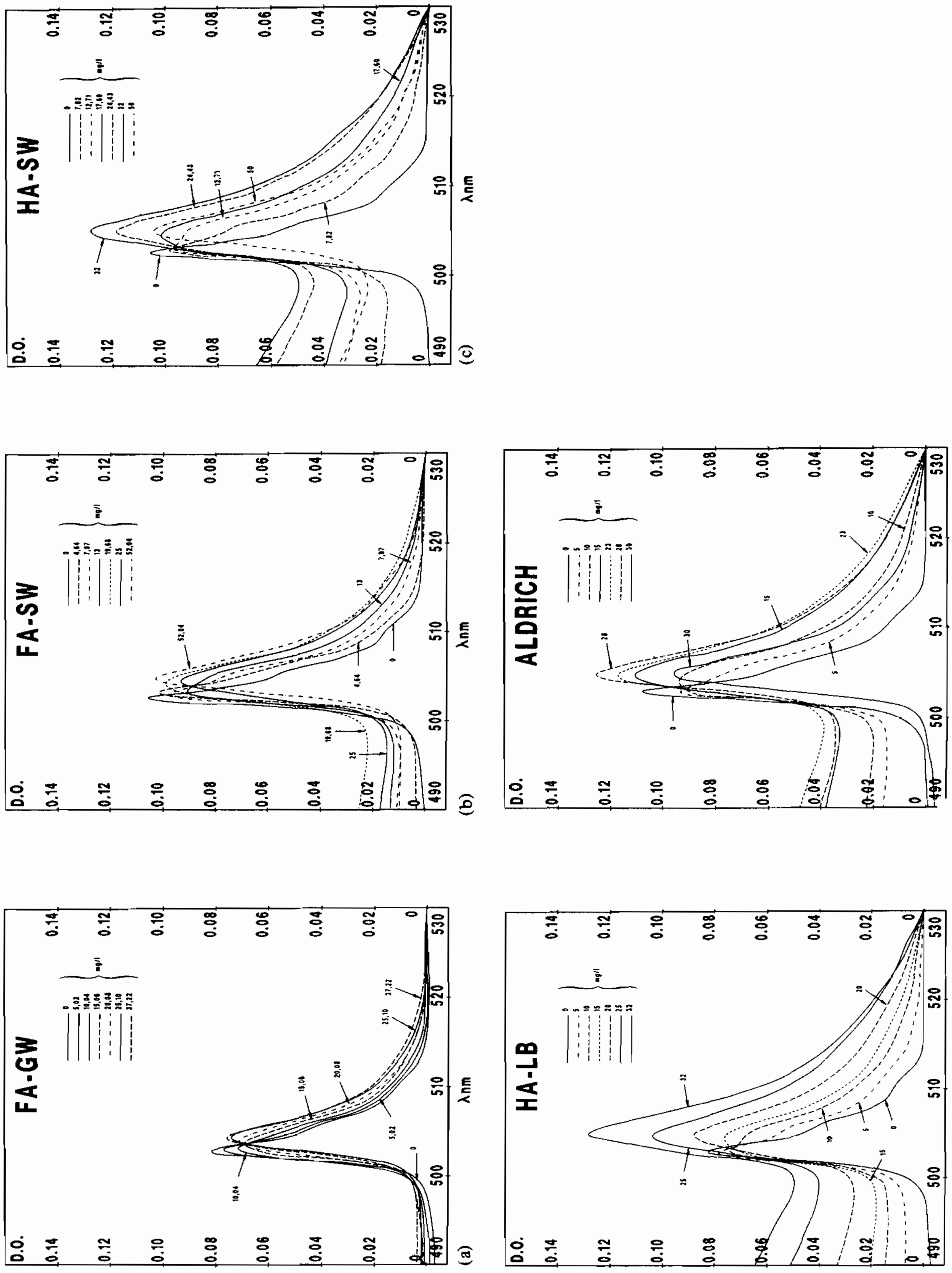

Fig. 1. Absorbance spectra for americium in the presence of humics.

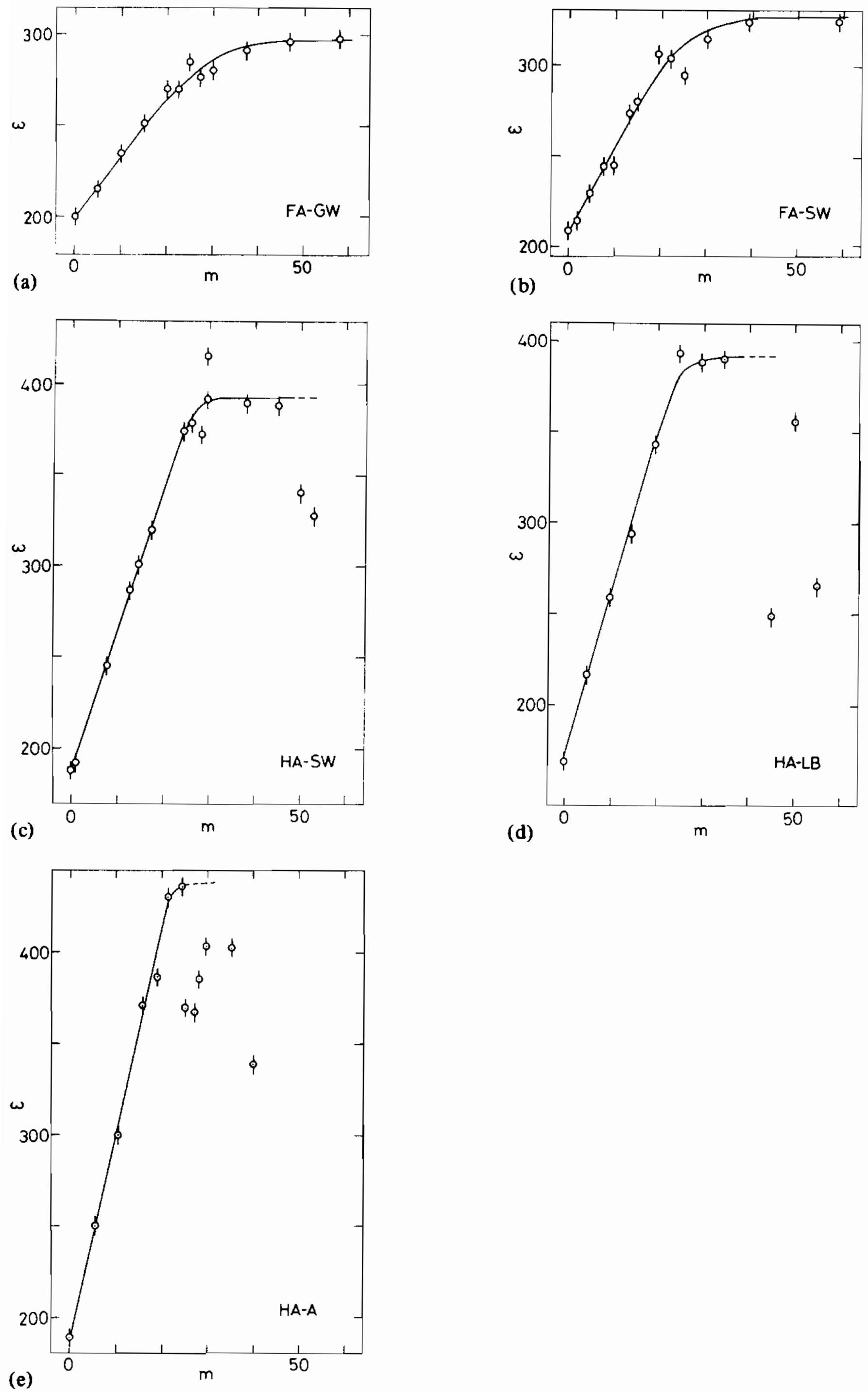

Fig. 2. Absorbance (ϵ) as a function of total humic concentration (m, mg/l) at the wave length corresponding to the formation of an AmA complex.

The formation of a colloidal fraction and subsequent precipitation with time of a visible solid phase take place when the concentration of humics is above the equivalence point. This is particularly the case for the high molecular weight humic acids HA–LB (M_r = 15 000) and HA–A (M_r > 50 000), while the fulvic acids remain as soluble species even at concentrations far above the equivalence point. Similar coagulation phenomena have previously been reported when humics in solution encounter

TABLE I. Formation Constants for AmA Complexes

Humate	Capacity[a] (meq/g)	log β (l/eq)	Reference
FA–GW	0.88	6.2 ± 0.2	this work
FA–SW	1.22	6.0 ± 0.2	this work
HA–SW	1.20	7.0 ± 0.2	this work
HA–LB	1.03	7.0 ± 0.3	this work
HA–A	(1.4)	(7.5)	this work
HA–LB		6.83[b]	11
HA–LB		9.26[c]	9, 12
HA (soil)		6.4[d]	13, 14

[a]Corresponding to a 1:1 complex. [b]Ion-exchange, pH 4.5, $I = 0.1$; given in l/eq. (H^+). [c]Solvent extraction, pH 4.65, $I = 0.1$; calculated from $\log \beta = 10.58\alpha + 3.84$; given in l/eq. ($H^+$). [d]Ion-exchange, pH 6.5, $I = 0.1$.

solutions of high americium concentrations [15]. However, the molar extinction coefficient for americium would set a lower concentration limit in spectrophotometric studies of the present type, and measurements can not be performed at significantly lower americium concentrations. Thus, the calculated formation constants rather represent minimum values since the observed ϵ_1 values corresponding to the 1:1 complex might be too low due to the formation of a colloidal humic fraction (*cf.* HA–LB and HA–A in Fig. 2).

The calculated conditional formation constants are in fair agreement with previously published data (Table I) considering the differences in experimental techniques and chemical conditions and also the fact that the formation constants are not given in the same units due to different definitions of the ligand capacities. In the present study, the concentrations of americium and humic materials are of the same order of magnitude, and complex formation is studied under conditions where all the added humate would be complexed by americium. Previously published studies, Table I, have been performed with americium at trace concentration levels. This could be one reason for the significant difference between the constants for the HA–LB systems.

Spectrophotometric studies of americium–humate complexation performed at lower americium concentrations (in the wavelength range 250–320 nm) are in progress.

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