The Binding Constants of Eu and Th with Humic Materials

A. A. Helal, S. M. Khalifa, and G. A. Mourad

Hot Labs Center, Atomic Energy Authority, Cairo, Egypt

Received July 22, 2004

Abstract—The binding constants for Eu and Th fulvate complexes were measured by the solvent extraction technique. For comparison, the binding constant for the Eu humate complex was also investigated. The measurements were carried out radiometrically using $^{152,154}$Eu and $^{234}$Th. The results indicate that, in case of fulvic acid, one parameter, $\beta_1$, was required to fit the binding as a function of carboxylate concentration. With humic acid, Eu$^{3+}$ formed 1 : 1 and 1 : 2 complexes, and two parameters, $\beta_1$ and $\beta_2$, were required. In both cases, the strength of binding increased with $pK_a$ and degree of ionization of the ligands and with the valence of the metal ions.

Naturally occurring fulvic acid (FA) and humic acid (HA) are known to be strong complexing agents to metal ions in the environment. As natural polyelectrolytes, humic compounds are heterogeneous mixtures possessing many types of acidic functional groups that can bind with cations in aqueous media. There are two types of metal fulvate and humate complexation: electrostatic binding due to polyelectrolyte effect and inner-sphere complexation including chelation. As pointed out by Rashid [1], FAs are low-molecular-weight humic compounds. They are weakly aromatized, poorly condensed compounds with a preponderance of aliphatic side chains. As compared to HAs, FAs are less polymerized. They are generally enriched in oxygen-containing functional groups. Therefore, they are soluble in both acids and bases. FAs are believed to form more readily than the corresponding HAs [2]. Once formed, FAs probably undergo condensation reactions to form more complex HAs.

An important characteristic of a metal fulvate or humate complex is its binding constant (BC) characterizing the affinity of the cation for the ligand. Numerical values of BCs for metal fulvate and humate complexes would be of considerable value in predicting the behavior of radionuclides, trace elements, and toxic heavy metals in soils and sediments. As reviewed by Monsallier et al. [3], many experimental procedures have been used for the measurements of BCs such as solvent extraction (SE) [4], gel permeation chromatography [5], UV spectroscopy [6], ion exchange [7], laser-induced photoacoustic spectroscopy [8], time-resolved laser fluorescence spectroscopy [9], ultrafiltration [8, 10], and dialysis [7, 11]. Depending on the method, the results vary considerably.

According to Takamatsu and Yoshida [12], there are two difficulties in determining the BCs of metal fulvate and humate complexes, one related to determining concentrations of humic compound as complexant, and the other related to procedures for measuring the actual BCs. The average molecular weight, the maximum complexing ability, and the number of titratable functional groups have been used to represent the concentration of humic compound as complexant. Because of variations in the physicochemical characteristics of the humic compounds and the different methods used to measure the BCs, the reported constants have no consistency [1]. SE is a suitable method for radionuclide investigation since it allows measurements at tracer level concentrations. Although extensive use has been made of the SE (and other methods) for determining BCs of metal humate complexes, little application has been made in studies of metal complexes of FAs. In particular, data on lanthanides and actinides are limited. In this work, the BCs of $^{152,154}$Eu and $^{234}$Th with FA, and the BC of $^{152,154}$Eu with peat HA were determined using the SE technique.

EXPERIMENTAL

Chemicals and materials. The chemicals used were of analytical purity. Di(2-ethylhexyl) hydrogen phosphate, HDEHP, used in the SE was obtained from Union Carbide and purified according to Peppard et al. [13]. FA was isolated from the agricultural soil of Orman garden, an old garden located at the West Bank of Nile river in Cairo, Egypt. The HA is isolated...
THE BINDING CONSTANTS OF Eu AND Th WITH HUMIC MATERIALS

from a sample of peat. The HA was extracted and purified by the method described by Gunasekara and Xing [14]. The FA was extracted and purified by the standard method [15].

**Tracers.** The radiotracer $^{152,154}$Eu was prepared locally by neutron activation of Eu$_2$O$_3$ in the Egyptian reactor (ARE-RR-1). $^{234}$Th was separated from natural uranium by an SE system using 30% TBP in benzene [16]. The radiochemical purity of $^{234}$Th and $^{152,154}$Eu was checked by measuring the respective $\gamma$-ray spectrum with a Ge(Li) detector using a multichannel analyzer. The $\gamma$-emissions of both tracers were counted with a NaI(Tl) well counter of ORTEC type.

**Procedures.** The FA and HA samples were characterized by elemental analysis, potentiometric titration, and visible spectroscopy. The acid–base behavior of FA and HA was determined at an ionic strength $\mu$ of 0.1 M by direct titration [17]. The absorption in the visible region was measured using a Shimadzu 160A recording spectrometer.

For the SE experiments, the organic phases consisted of toluene containing HDEHP. Because of the precipitation problems encountered when contacting HA solutions with organic phase [16], the latter was preequilibrated several times against equal volumes of the corresponding buffer solutions before use. This preequilibration was continued until no $\mathrm{pH}$ change was observed in the fresh aqueous phase. The aqueous phases were prepared by using the suitable buffer solutions for the desired $\mathrm{pH}$s. These buffer solutions also contained the necessary quantity of NaClO$_4$ to make the total $\mu 0.1$ M.

Primary distribution experiments were performed to evaluate the time needed for equilibration for each of the ligands. For both Eu$^{3+}$ and Th$^{4+}$, the results obtained showed that the equilibrium is reached within 2.5 h in case of FA and 1.5 h in case of HA. A working solution of FA or HA was prepared by dissolving ca. 0.1 g in 10 ml of 0.1 M NaOH with overnight stirring under $\mathrm{N}_2$. The solution was titrated to the desired $\mathrm{pH}$ with 0.1 M HClO$_4$ and diluted to 100 ml with the suitable buffer solution [4] of the same $\mathrm{pH}$. Aliquots of this working solution were diluted with the buffer to obtain solutions of varying HA concentrations. The free humate concentration (in g-equiv l$^{-1}$) was determined by multiplying the concentration (g-equiv g$^{-1}$) and by the degree of ionization corresponding to the $\mathrm{pH}$ of the investigation.

Five milliliters of each phase and 10 $\mu$l of the tracer were added to 20-ml glass scintillation vials coated with silicon compounds [18] to minimize the adsorption of activity by the vial wall. Five milliliters of the buffer solution, without FA or HA, was used as a blank for each experiment. The vials were vigorously shaken in a thermostated shaker at room temperature ($25\pm1\,\text{C}$) for the suitable time, then they were centrifuged and the phases separated and centrifuged before removing aliquots for counting. The remainder of the aqueous phases was used to measure the final $\mathrm{pH}$s and the final HA concentrations in HA experiments.

**RESULTS AND DISCUSSION**

The elemental analysis of FA and HA samples indicated that the ratios of C, O, H, N and S are 51.0, 38.2, 4.4, 2.8 and 3.6% for FA and 48.5, 41.7, 5.4, 1.2 and 3.2% for HA. The higher atomic ratios O/C and H/C of HA than FA may reflect larger amounts of COOH and show that aliphatic C may be more abundant in FA.

Figures 1 and 2 give the potentiometric titration curves and the first derivatives for FA and HA samples. The curves have double inflections and, in general, they are similar to those obtained from weak acids. The first derivatives indicate that each sample has two maxima, which implies two kinds of ionizing functional groups. This phenomenon has been ex-