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Complex Formation of Europium and Low Molecular Weight Carboxylic Acids

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Rare earth elements (REEs) have been widely used in various high technology industries. As a result, REEs are discharged into the environment. Recent studies show that REEs of anthropogenic origin are present in in the aquatic environment, suggesting that REEs are contaminants of emerging concern. It is essential to assess the complex formation of REEs with organic matters since speciation of REEs is determining for their fate, transport and biotoxicity. This study investigated the complex formation of europium (Eu), a commonly used REE, with low molecular weight carboxylic acids, including citric acid (Cit), succinic acid (Suc) and malic acid (Mal), that are ubiquitous in the ecosystems and daily life. Equilibrium stability constants at 25°C and ionic strength of 0.15 mol/L were determined by potentiometric titration and Hyperquad2008. Contributing binding sites of ligands were evaluated by the stability constants and confirmed by electron spray ionization-mass spectrometer (ESI-MS). Results indicate that the complexation capacity was Cit>Mal>Suc, and complexes formed as 5-member chelates, 6-member chelates, and 7-member chelates, respectively. Under conditions simulating typical river water, Eu exists in soluble species throughout all pH and it forms various species with citric acid, such as $EuCitH^{+}$, $EuCit^{0}$, $EuCit_2^{3-}$, and EuCit(OH)-. The dominant species with malic acid is $EuMal^{+}$, while there is no complex formation between Eu and succinic acid. Complex formation with inorganic ligands, such as hydroxyl ion (OH^{-}) and carbonate ion (CO_3^{2-}) were assessed as well.