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New Aspects of Complex Formation in the Gadolinium(III)–Citric Acid System in Aqueous Solution

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Abstract

The complexation of gadolinium(III) with citric acid in aqueous solutions was studied by pH-metric titration, proton magnetic relaxation, and mathematic simulation in the pH range 2.0–10 at [Gd3+]: [H4Cit] = 1:1, 1:2, 1:3 ([Gd3+] = 1.3, 2.6, 5.0, 10.0, and 20.0 mmol L−1). In the process of simulation, the equilibrium composition, a model obtained from previously known works and including mono- and bis-citrate complexes of gadolinium(III) was taken as a basis. In this work, it is shown that a satisfactory description of the experimental data set of two independent physico-chemical methods is achieved only with the additional inclusion of citrate complexes of gadolinium(III) with higher degree of protonation and some new polynuclear complexes. The complex [GdH4Cit]3+ with the molecular form of the citrate ligand, and the polynuclear complexes [Gd2(HCit)2]°, [Gd2Cit2]2-, [Gd6(OH)2Cit6]8-, [Gd6(OH)3Cit6]9- were first detected at the molar ratio of 1:1. At two- and three-fold excess of citric acid, mononuclear bis- and tris-citrate complexes with different degrees of protonation were found, and binuclear tetrakis- and hexakis-citrate complexes [Gd2(HCit)Cit3]9-and [Gd2(HCit)4Cit2]14- at the pH > 7.5. On the example of this manuscript, the importance of applying the NMR relaxation method for identifying polynuclear complexation in systems containing paramagnetic ions is shown.

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Keywords

citric acid, Complex formation, complexes stability, gadolinium(III), polynuclear complexation

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