

The investigation of zirconium(IV) citrates forming in aqueous solutions

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Abstract

System zirconium(IV) – citric acid was studied by potentiometric titration in combination with mathematic simulation for metal-to-ligand ratio 1 : 1, 2 : 3, 1 : 2 and 1 : 3 in argon media for the purposes of guarding by carbon dioxide. Composition, stability and speciation diagrams of zirconium(IV) citrates in aqueous solutions were calculated in software CPESP. It has been found that in equimolar ratio of Zr(IV) ions and ligand (H₄Cit in research system the tetranuclear species of the different deprotonation degree are formed from mononuclear cationic complex [ZrHCit]⁺. In the case of the two- or threefold citric acid excess the existence of mono and binuclear zirconium(IV) citrates were found out. In the case of citric acid twofold excess compared with Zr(IV) ions was demonstrated that mono and binuclear complexes with 1:2 and 2:4 metal-to-ligand ratio are formed, furthermore mononuclear bis (ligand) complexes are dominated in acid media but 2:4 species are found in neutral and alkaline media. The hydrolysis is concealed almost completely in the systems with threefold citric acid excess and in this situation 1:3 and 2:6 zirconium(IV) hydroxocitrates are not formed. A comparison of stability of titanium(IV) and zirconium(IV) citrates single-type composition testify that the values of titanium complexes stability constants far exceeds the zirconium species stability by the same degree of deprotonation. We suggested the optimal complexation schema in the Zr(IV) – citric acid system.

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