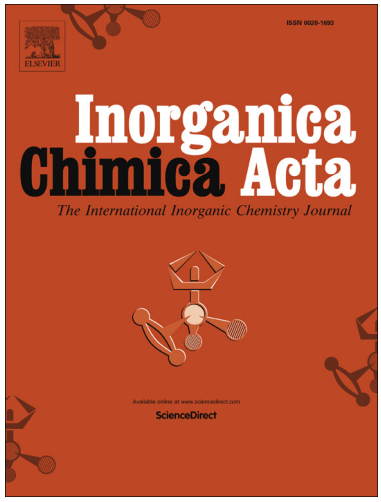

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Stability Constants for Zirconium(IV) Complexes with EDTA, CDTA, and DTPA in Perchloric Acid Solutions

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Keywords: Zirconium(IV), EDTA, CDTA, DTPA, Stability Constant, Specific ion Interaction Theory

Abstract

We quantified the stability constants of Zr(IV) with ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetic acid (EDTA), *trans*-1,2-diaminocyclohexane-*N*,*N*,*N'*,*N'*-tetraacetic acid (CDTA), and diethylenetriamine-*N*,*N*,*N'*,*N''*,*N''*-pentaacetic acid (DTPA) in 0.75-1.00 mol·L^{-1} $HClO_4$ with 1.00 mol·L^{-1} total ionic strength using a liquid-liquid extraction technique. The data indicated the formation of ubiquitous 1:1 complexes, but also newly reported 1:2 metal-ligand complexes. The 1:1 complexes were identified as $Zr(EDTA)^0$ ($\log_{10}\beta_{101} = 27.9 \pm 0.1$), $Zr(CDTA)^0$ ($\log_{10}\beta_{101} = 29.6 \pm 0.2$), and $Zr(DTPA)^-$ ($\log_{10}\beta_{101} = 35.3 \pm 0.3$), and the newly identified bis-complexes as $Zr(EDTA)_2^{4-}$ ($\log_{10}\beta_{102} = 54.4 \pm 0.2$), $ZrH_4(CDTA)_2^0$ ($\log_{10}\beta_{142} = 58.5 \pm 0.5$), and $ZrH_8(DTPA)_2^{2+}$ ($\log_{10}\beta_{182} = 70.3 \pm 0.4$). The quantification of the stability constants described above required determining acid dissociation constants for EDTA and DTPA at varied ionic strength at 25.0 ± 0.1°C by potentiometric titration, and the Specific ion Interaction Theory (SIT) model was used to correlate the acid dissociation constants with ionic strength. The resulting thermodynamic constants at zero ionic strength from this analysis for EDTA were: $pK_{a3}° = 2.21 \pm 0.06$, $pK_{a4}° = 3.21 \pm 0.06$, $pK_{a5}° = 6.76 \pm 0.09$, and $pK_{a6}° = 10.27 \pm 0.03$, and for