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Thermodynamic and Kinetic Parameters of Cerium(IV) Complexes with Some Dicarboxylic Acids

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We present some generalizations of the classical thermodynamic methods for studying the complex formation to determine along with formation constants also the redox-decay rate constants of complexes with cations in an unstable oxidation state, and the rate law of numerous redox processes for which the rate-determining step is the decay of such intermediate complex. These generalized methods are applied to a comparative study of cerium(IV) complexes with some dicarboxylic (oxalic $H_2 Ox$, malonic $H_2 Mal$, succinic $H_2 Suc$, and glutaric $H_2 Glut$) $H_2 L$ acids at the ionic strength $I = 2$, pH 0.4-1.6 of a sulfate medium, and 20.0^0c with the aid of spectrophotometry and pH potentiometry. The region of existence, composition of the cerium(IV) complexes, ligand speciation, the thermodynamic parameters of formation, and the kinetic parameters of their redox decomposition are determined for these complexes on the sulfate background. The rate law for the redox process that occurred in these studied systems is derived on the basis of calculated constants and the set of all the chemical and algebraic equations describing the rapid preequilibria and way out of these preequilibria within the investigated systems. The quantitative process model is also created. The existence of the direct linear correlations between the logarithms (i) of the intracomplex redox decay rate constant k_1 (s^{-1}) and complex formation constant K_1 (mol dm^{-3}), (ii) K_1 and $H_2 L$ first dissociation constant $K(1,a)$ (mol dm^{-3}), as well as (iii) observed rate constant k_obs (mol^{-1}) $dm^3 s^{-1}$) for the cerium(IV) $H_2 L$ oxidation and $K(1,a)$. It is shown that the first correlation can be treated as a kinetic manifestation of the chelate effect (an increase in $logk_1$ with a greater $logK_1$) in the series of complexes $[CeOHGlut]^+$, $[CeOHSuc]^+$, $[CeOHMal]^+$, and $[CeOHOx]^+$. Two other correlation equations/their equivalent forms can be interpreted as analogs of the Brønsted equation well known in organic chemistry. They can be applied to describing the reactions of complex formation and the oxidation of organic compounds by variable-valence metal ions in the coordination chemistry.

Biography

Olga Voskresenskaya is a Senior Scientist at the Joint Institute for Nuclear Research (JINR) in Dubna, Russia. Originally from Western Siberia, she graduated from and completed her postgraduate work in the Chemistry Department of the oldest university in Siberia, Tomsk State University. There she specialized also in theoretical physics at the Physics Department and worked at the Siberian Physical-Technical Institute of the same university. Dr. Voskresenskaya continued her mathematical education at the Ural State University in Yekaterinburg and received there a Masters's Degree in Mathematical Physics. Thereafter, she received a Ph.D. in Theoretical Physics at the JINR, where she has been staff member since 1994. The main directions of her current research activities are equilibrium and nonequilibrium thermodynamics of quasistationary states as well as mathematical models in the field of theoretical physics and physical chemistry.

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