Calculation of the Parameters of the Mutual Effect of Ligands the Au(III)–Chloride Ion–Bromide Ion Complexation System

A. G. Kudrev

Institute of Chemistry, St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia

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Abstract—Published experimental curves of spectrophotometric titration of the system Au^{3+}–Cl^-–Br^- under the conditions of stepwise formation of mononuclear mixed-ligand complexes $AuCl_{4-n}Br_n^-$ are analyzed. A new matrix method is applied to calculating the constants of ligand substitution in the inner sphere of the central ion with fixed coordination sites. The suggested approach allows reduction of the number of variables in least-squares optimization of the titration curves, without impairing the accuracy of the description. The model of formation of square-planar complexes $[MY_{4-n}X_n]$ (n = 0–4) includes three independent variables $\bar{K}$, ω_{cis}, and ω_{trans} ($\bar{K}$ is the equilibrium constant of substitution of the first ligand, and ω_{cis} and ω_{trans} are corrections for the mutual effect), instead of four constants of stepwise substitution. The parameters of the substitution of chloride ion by bromide ion in the inner coordination sphere of Au(III) were calculated using the suggested approach.

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