EFFECT OF INTERLIGAND INTERACTION ON THE COMPLEX STABILITY

Zamaljutin V., Podzorov A., Rukk N., Mikhailov V., Skrjabina A., Poljakova T.

M.V. Lomonosov Moscow State Academy of Fine Chemical Technology (MITHT), Vernadsky av., 86, Moscow, 119571, Russian Federation. Tel. 8(495)9368912, e-mail: roukkn@inbox.ru

The thermodynamic model [1] developed for quantitative estimating cooperativity in supramolecular polymetallic assemblies has been applied to monometallic coordination complexes with neutral and anionic ligands and CN = 4, 6, as well as to octahedral complexes with bidentate ligands. Reference data for zero ionic strength have been used [2, 3]. The model takes into consideration the interligand interactions by introducing the u^{LL} parameter into the Bjerrum equation:

$$\beta_n^{ML} = C_n^m (f^{ML})^n (u^{LL})^{\frac{n(n-1)}{2}} ,$$

where : f^{ML} – parameter which describes the metal–ligand interaction; *m* = CN; C_n^m – the number of combinations from *m* for *n* for monodentate ligands; C_n^m = 12, 30, 24 for *n* = 1, 2, 3, respectively, for octahedral complexes with bidentate ligands. Optimized parameter values for both models have been calculated by means of a least-squares fit in application to lg*βn*.

It was demonstrated that consideration of the interligand interactions in the overwhelming majority cases essentially, up to complete agreement with the experimental data, improves the formation constant description as compared with the Bjerrum model. Practically for all systems $u^{LL} < 1$, that is the negative cooperativity takes place.

References

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