Application of Direct Calorimetry in Studies of Intermolecular Interactions in Solutions of Linear and Cyclic Oligopyrroles

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In this work dissolution enthalpies of ligands, salts and metallocomplexes of linear and cyclic olygopyrroles are considered. For their determination we used a precision dissolution calorimetry method. In the experiments carried out at 298.15 K, not polar (benzene), electron-donor (pyridin, dimethylformamide) and proton-donor (chloroform, 1-propanol) solvents were investigated as solvating environments taking into account the compounds solubility and opportunities of a calorimetric method. It was found, that processes of dissolution of ligands and dipyrrolylmethene salts and biladienes-a,c in not polar benzene and associated proton-donor 1-propanol are endothermicthat that may be caused, as a rule, by high energy of a crystal lattice, polarity of molecules of hydrobromides (which can show properties of weak electrolytes in organic solvents), solvent association (1- propanol), and the absence of appreciable power contributions from specific solvatation. The dissolution exotermicity rises essentially for ligands in proton donor solvents, and for their salts in electron-donor solvents owing to solvatation contributions caused by the acid-basic interactions. The correlations obtained on the basis of the calorimetric experiment data are discussed. Besides the features of dissolution, solvatation, porphyrins and their metallocomplexes with d-metals additional coordination processes, in case of alkyl-substituted tetraphenylporphin are considered separately. Influence of peripheral assistants and the nature of the central ion of metal on enthalpy characteristics of the given processes is analyzed. For alkyl-substituted tetraphenylporphin and their complexes a dissolution enthalpies in cyclohexane were received, that has allowed to estimate the sovation contribution from π-π-interactions of porphyrin with benzene. For example this contribution for tetra(3,5-di-tert-butylphenyl)porphin is 37.8 kJ/mol.