SUPRAMOLECULAR INTERACTIONS INVOLVING DYE IONS IN AQUEOUS SOLUTIONS: THE INFLUENCE OF PHYSICO-CHEMICAL ENVIRONMENTAL FACTORS

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The self- or dissimilar association of dyes in solutions is one of the most important phenomenon which are widely used in modern biotechnologies, new materials and scientific area. At the same time this association has a significant influence on spectral and even structural properties of a solution [1]. The study of various properties of complex molecules which exist in the not only individual state in solution is complicated by different types of intermolecular interaction and this is the reason why studies on association permit a deeper understanding of their intermolecular processes. This investigation was aimed to reveal the main factors (such as structural characteristics of counter ions, the charge, presence of ionic surfactants), governing the formation and stability of dissimilar ionic associates:

1. Systematic research of association with participation of ionic forms of dyes has been offered by use of the "model" dyes and ions. These dyes were chosen from dyes belonging to different classes: pinacyanol, astrafloxin, rhodamine 110, tetrabromophenylfluoron; colourless ions: tetrabutylammonium, tetraphenylarsonium, tetraphenylborate. The "cation + anion" association was treated in terms of the equilibrium model.

2. A method of pre-experimental estimation of the stability was proposed. It is based on experimental (K_{as} values) and simulated (the association energy, molecular diagrams) data. The routes of ΔG^o estimation of counter ions have been shown with the help of the data on association "standard" ions such as tetraphenylarsonium or tetraphenylborate. The constancy of $\Delta G^o(Ct^+)$ and $\Delta G^o(An^-)$ contributions have been analyzed on a basis of experimentally obtained K_{as} values for associates of different structure. The satisfactory agreement between theoretically predicted values K_{as} and their experimental values is observed.

3. To determine the structural properties of dyes, semiempirical and nonempirical quantum-chemical methods were used, which make it possible with the using of molecular diagrams, to draw conclusions concerning the reactability of one or another fragment of a molecule. Each method gives its set (often different from other sets) of molecular parameters. However, it is important that the results of calculations (electron density, length and order of bonds, valence angles, etc.) of dyes and associates may differ substantially. By quantum-chemical methods it was found that formation of stable associates is accompanied by an essential isolation of energy. The high values of K_{as} ($10^5 – 10^{12}$ l·mol^{-1}) may indicate the formation of contact ionic associates.

References:

1. Shapovalov S.A. Association processes with the participation of dyes in solutions: Thermodynamic and equilibrium characteristics of nanosystems. – Riga : Academic Publishing of European Union, OmniScriptum Publishing group, 2020. – 114 p. – ISBN: 978-620-2-92204-3.