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LETTERS TO THE EDITOR

Chemical and Physical Processes and Accompanying Tautomeric Transformations

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Tautomeric composition is an objective characteristic of a particular sample of a substance capable of tautomeric transformations and existing under specific conditions [1]. The external influence may shift tautomeric equilibrium, and the resulting number and nature of the tautomers contributing to the test substance may be changed. Chemical reactions of substances are usually accompanied by a shift of the tautomeric equilibrim. The study of reactions without taking the equilibria into account can result in serious errors. Such errors we detected, for example, in studies of ionization, protonation, complexation, and esterification of hydroxyanthraquinones. The use of anthraquinones as reagents for analysis of metals [2] or boron [3] is based not on their reactions, but on the accompanying shifts of tautomeric equilibria.

We noted that the change in the tautomeric composition can accompany not only chemical reactions, but also the physical processes. We have shown this by the example of different methods of preparation of aqueous solutions of an industrially important for the chemistry of dyes substance, known as 1,4,5,8-tetraamino-9,10-anthraquinone.

The study of the electron absorption spectra (EAS) showed that in the ethanol solution this substance is in fact a dynamic equilibrium mixture of 4,5,8,9-tetraamino-1,10-anthraquinone (**I**) and tautomeric 4,8,9-triamino-10-hydroxy-1,5-anthraquinone-5-imine, 8,10-diamino-5,9-dihydroxy-1,4-antraquinonediimine, and the conformers of 1,4,8-triamino-5-hydroxy-9,10 -anthraquinon-10-imine and 4,8-diamino-5,9-dihydroxy-1,10-antraquinonediimine, whose amino group in position 4 is not bound by an intramolecular hyd-rogen bond with the neighboring carbonyl group. The 1,10-quinoid structure of amino forms was revealed in the other α-amino-substituted anthraquinones [4].

1,4,5,8-Tetraamino-9,10-anthraquinone is poorly soluble in water, and a special technique is used to obtain its aqueous solutions. The EAS of its aqueous solution depends strongly on the method of preparation of the solution and its concentration. The EAS of a solution prepared by dissolving small crystals contains only π_l,π^*-band at 570 nm. The EAS of a solution obtained by filtering depends on the concentration: At the concentration of 4×10^{-5} M two π_l,π^*-bands, at 550 and 585 nm, at 2×10^{-5} M a maximum at 585 nm and two shoulders at 550 and ~600 nm, at 1×10^{-5} M a maximum at 570 nm and fuzzy shoulder at ~600 nm are observed [5]. The correlation analysis of these bands showed that these λ_{max} values are linearly related to the corresponding values of solutions in ethanol.

$$\lambda_{max}(\text{water}) = (0.4831 \pm 0.0155)\lambda_{max}(\text{ethanol}) + (278.0 \pm 9.5)\ \text{nm}.$$

Number of tautomers N = 4, the correlation coefficient $r = 0.9990$, the standard deviation $s = 1.0$ nm.

This relationship has helped to clarify the position of the long-wavelength shoulder at 590 nm. It follows from this pattern that in the tautomeric equilibria of the amine in both amphiprotic solvents, ethanol and water, the same tautomers are involved. The band at 585 nm belongs to the amine **I**, and the other three π_l,π^*-bands, to the related tautomeric imines. This assignment of the bands is confirmed by the correlation with the values of the sums of σ^A-constants of substituents assumed for anthraquinones. Thus, the differences in the EAS of aqueous solutions of the substance is related to the methods of preparation of solutions and their concentration as a result of changes in their tautomeric compositions.

Another known example is connected with irradiation of solutions of 2-amino-1-phenoxy-9,10-anthraquinone (**II**) in nonpolar solvents, which leads to its photoisomerization into 2-amino-9-phenoxy-1,10-anthraquinone (**III**), and the evaporation of the obtained solutions is accompanied by the reverse formation of the of 9,10-quinoid compound (**II**) [6]. Evidently these processes should be regarded as a shift of tautomeric arylotropic equilibrium **II** ↔ **III**.

Currently, the correlation analysis of EAS is the most reliable among the physicochemical methods of determining the tautomeric composition of a substance, because an adequate and sensitive response of EAS to the tautomeric transformations has been shown by a lot of examples. The use of other physicochemical methods for this purpose should be developed in future. The results obtained by different methods allow us a formulation of some general conclusions that should be considered in the study of substances capable of tautomeric transformations.

(1) It follows from the classical concept of tautomerism that the substance capable of tautomeric transformations is not an individual compound, but a dynamic equilibrium mixture of tautomers. The structure of the substance cannot be reflected only by the structural formula.

(2) There are conditions in which the tautomeric equilibrium is almost completely shifted towards one of the tautomers. If the structure of substance implies the possibility of tautomerism, then necessarily there are conditions in which it appears. If the tautomerism is not detected, it means that these conditions are not found.

(3) Competition between different types of tautomeric transformations possible for a substance may lead to the dominance of one type over the other, in different ways under different conditions.

(4) The separate measurements of different samples of substance in different conditions by different methods cannot refute the possibility of the existence of tautomers with certain structure. If they lead to different results, we must look for the cause of differences, but not arbitrarily declare the unreliability of one of them.

(5) If a second physicochemical method cannot detect tautomeric structures found in the same sample under identical conditions by the first method, this only means that the sensitivity of the second method is not sufficient to solve the problem.

(6) The study of the properties of any substance capable of tautomeric transformations is correct only when the tautomeric composition of the samples is simultaneously tested.

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