



Protonation of Patented Blue V in aqueous solutions: theoretical and experimental studies

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Abstract. The acid-base properties of the Patented Blue V dye were studied by spectrophotometry and tristimulus colourimetry. The mechanism of protonation of Patented Blue V has been investigated with semi-empirical and DFT methods. The quantum chemical calculations of total energy defined the most stable isomer for each protonated form in water solution. In addition to thermodynamic parameters, the condensed Fukui function and molecular electrostatic potential were successfully used as reactivity descriptors for the determination of the most favorable site for protonation. Moreover, for the explanation of the structure of the most deprotonated form of the dye in highly basic medium, the weak intramolecular interactions were investigated with the reduced density gradient function. The semi-empirical calculations of absorbance spectra explained the changing of the colour of the dye for the different protonated states. It has been shown that the dominant form of the Patented Blue V was the electro-neutral form, and the molar absorptivity ($\epsilon_{639} = 1.06 \times 10^5 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) increases with the increase of the dielectric permittivity of the solvent. The replacement of polar solvents by less polar ones is causing a bathochromic shift of the absorption band of the dye, the value of which is correlated with the value of the Hansen parameter.

Keywords. Patented Blue V; ionization constants; tristimulus colourimetry; spectrophotometry; DFT calculations.

1. Introduction

Synthetic food dyes are used more often than natural ones to enhance the appearance of food by giving it artificial colour. The safety of these dyes is highly controversial and depends on nature and concentration; they may be allergens and carcinogens.¹ Food dyes, such as Patented Blue V (PBV), are widely used for dyeing alcoholic and non-alcoholic beverages, confectionery and pharmaceuticals. However, an important task is the establishment of the physical, chemical and acid-base characteristics of PBV in solution. The characteristic of the acid-base properties is a proton-transfer reaction equilibrium constant (pK_a).² In addition, pK_a is included in the adsorption, distribution, and metabolism (ADME) phenomena profile

along with other physicochemical properties that determine the major pharmacokinetic and pharmacodynamic parameters of molecules.^{2,3} The direction and intensity of protolytic process can be estimated by pK_a value. In turn, it makes possible to determine the state of acid-base equilibrium, charge, ratio of the ionic-molecular forms of the substance. To the best of our knowledge, despite the use of this dye, data on its acid-base properties are not described in detail. It might be due to the peculiarities of the PBV. The dye is a polyfunctional organic compound with functional groups that are similar in acidic properties and with overlapping absorption spectra of its equilibrium forms. In such cases, standard methods such as potentiometry and spectrophotometry are uninformative. In some ways, the use of various chemometric algorithms allows to achieve better results.⁴ Of equal interest is the use of tristimulus colourimetry approaches, which have proven themselves in the study

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