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Spectrophotometric and theoretical studies of the protonation of Allura Red AC and Ponceau 4R

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ABSTRACT

The acid-base properties of Allura Red AC and Ponceau 4R azo dyes were investigated by spectrophotometric, potentiometric and tristimulus colourimetry methods. Ionization constants of the functional groups were also found in aqueous solutions of the dyes. It was discovered that the wavelength of the maximum light absorption of Allura Red AC and Ponceau 4R solutions does not change significantly over a wide pH range. As a result, spectrophotometric methods yield little information for assessing the acid-base properties of the dyes. It was shown with a help of the tristimulus colourimetry method that it is possible to determine the ionization constants of the functional groups of the dyes even when there is significant overlap of the absorption bands of the acid-base forms. The basic spectrophotometric characteristics of the main forms of Allura Red AC and Ponceau 4R in water and organic solvents were calculated. The molar absorbance coefficients of azo forms were shown to increase as the dielectric permittivity of the solvent increases. It was determined that in aqueous solution the dyes exist in the azo form over a wide range of acidity – pH 2–12 for Allura Red AC (λ_{max} = 505 nm; $\varepsilon_\lambda = 3.1 \cdot 10^4$ dm^3 mol^{-1} cm^{-1}) and 1–13 for Ponceau 4R (λ_{max} = 510 nm; $\varepsilon_\lambda = 1.7 \cdot 10^{-4}$ dm^3 mol^{-1} cm^{-1}). The most probable protonation/deprotonation schemes were theoretically determined for Allura Red AC and Ponceau 4R using DFT calculations.

1. Introduction

Synthetic dyes are a class of food supplements. They are used to give food an attractive appearance as well as to compensate for the loss of the natural colour of food after processing and storing. Red food colourants, such as Allura Red AC (E129) and Ponceau 4R (E124), are synthetic azo dyes. Their chromophore properties are based on the presence of an azo group, which is connected to the auxochrome hydroxy and methoxy groups through aromatic π-system rings. These dyes are used to colour drinks, food, cosmetics and pharmaceuticals.

A significant range of research has investigated the toxicological properties of these dyes and their metabolites, and it has been established that they are potentially dangerous for human health [1–3], although there is no common point of view on whether Allura Red AC is genotoxic. Allura Red AC and Ponceau 4R dyes are forbidden in the United States; however, they are permitted in the European Union [4]. Therefore, the development of highly sensitive and selective analytical methods for determining colourants Ponceau 4R and Allura Red AC in food is an urgent task.

The status of the analytical chemistry of food dyes is summarized in a review article [4]. The source describes chromatographic [5], spectrophotometric [6] and voltammetric [7] methods for identifying azo dyes that do not always meet modern standards. An important analytical aspect is the establishment of the physical, chemical and acid-base characteristics of dyes in a solution. For example, the dissociation constant value (pK) is the basis for

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