SOLVATOCHROMISM OF SOME FOOD AZO DYES

In the current study the solvatochromic properties of such food azo dyes as tartrazine, sunset yellow FCF and carmoisine were described. It was shown that with an increase in the dielectric permittivity of the solvent, a bathochromic shift of the absorption band maxima of azo dyes is observed, which corresponds to the $\pi \rightarrow \pi^*$ electronic transition. It has been established that the values of the molar absorptivities of the dominant acid-base form of azo dyes in organic solvents almost linearly ($R \approx 0.90-0.92$) increase with an increase in their dielectric permittivity. It is noted that there is a weak correlation ($R = 0.70-0.80$) between the position of the absorption maximum of the dye and the value of the Hansen parameter.

Keywords: spectrophotometry, solvatochromism, carmoisine, sunset yellow FCF, tartrazine.

INTRODUCTION

Dyes play a significant role in the food industry, and the quality of food is closely related to organoleptic characteristics. The food systems industrialization in the food processing industry has increased with the use of various additives such as food colors, preservatives, stabilizers and sweeteners. Water-soluble dyes are used in beverages, confectionery, bakery, dairy products, etc. Water-insoluble dyes are used for coloring food, pharmaceutical, and cosmetic products containing fats and oils (tablets, lozenges, lipsticks, soaps, shampoos, etc.). Natural dyes are unstable and easily decompose, while synthetic ones give an intensive color to food and are stable during storage [1]. Nevertheless, the expenses related to their production are significantly lower in comparison with natural dyes obtaining. These benefits have encouraged manufacturers to use synthetic dyes, despite the abundant evidence that they have a negative impact on human health. Food dyes can cause serious disorders and diseases: nausea, headache, wound, lung cancer, hyperactivity, anemia [2], and also affect sense of vision, skin, mucous membranes, etc. Based on the foregoing, it becomes necessary to control the content of these dyes in food. For this purpose, various physicochemical methods are used: spectrophotometry [3], chromatography [4], micellar extraction [5], and a number of others. Among all variety of food dyes, the largest group is azo compounds (AC). Azo compounds chromophore properties and ability to participate in almost all known chemical reactions and processes give rise to special attention. The AC reactivity is associated with the azo group $\text{–N= N–}$ presence in their structures, as well as the nature and position of different functional groups ($\text{–OH, –COOH, –NH}_2$, $\text{–SO}_3\text{H}$, etc.) in the structural fragments of the molecule.
For detailed study and practical use of food dyes it is necessary to manipulate their basic physicochemical and chemical-analytical characteristics in solutions of different types, more specifically it is important to study their spectral-luminescent and solvatochromic properties. As a follow-up to previous studies on the ionic-molecular state of food dyes in solutions [6-10], this work is devoted to the study of solvatochromism of tartrazine (TAR), sunset yellow FCF (SY) and carmoasine (CAN).

**Chemicals and apparatus**

The parent solutions of the TAR, SY and CAN with a concentration of $1 \times 10^{-3}$ mol/dm$^3$ were prepared by dissolving a precisely weighed portion of the reagent in methanol. We used aprotic (chloroform, ethyl acetate, butyl acetate, tetrahydrofuran, 1,4-dioxane, acetonitrile, methylbenzene, dimethylsulfoxide, dimethylformamide), amphiprotic (methanol, 2-propanol, 2-butanol, 3-methylbutan-1-ol (triethylamine) organic solvents, that, if necessary, were additionally purified by distillation. All used reagents were of analytical grade.

Spectrophotometric measurements were carried out on a SF-56 (OKB “LOMO-SPECTR”, St. Petersburg, Russia) and Specord S600 (Analytic Jena) spectrophotometer in the wavelength range 380-780 nm in quartz cuvettes or with an optical probe with an optical path length of 10 mm (Hellma Analytics). The pH of the solutions was controlled by an ESL-63-07 pH glass electrode together with EVL-1M3 silver chloride reference electrode; and recorded on a potentiometer (I-160).

In the solvatochromism study, $0.04 \text{ cm}^3 1 \times 10^{-3}$ mol/dm$^3$ of dye methanol solution, 5 cm$^3$ of an organic solvent were placed into graduated test tubes with ground-glass stoppers, mixed and the absorption spectra were recorded in quartz cuvettes ($l = 1$ cm) using a spectrophotometer (SF-56) or an optical probe.

**RESULTS AND DISCUSSION**

The acid-base properties of these dyes were studied in detail earlier, and much less attention was paid to their spectral characteristics. The absorption spectra of investigated dyes aqueous solutions are shown in Fig. 1. In the absorption spectra of CAN and TAR, one absorption band is observed with absorption maxima at 520 and 425 nm, respectively. In the case of SY, there are an absorption band with a maximum at 480 nm and a shoulder at 400-410 nm in the absorption spectrum.

The effect of organic solvents on the spectrophotometric characteristics (solvatochromism) of the investigated dyes was studied for the dominating forms of azo dyes in solution. To interpret the results obtained and evaluate the effect of the solvent type, we used various parameters characterizing their macrophysical properties, and, first of all, the dielectric constant, borrowed from [11]. With an increase in the dielectric constant of the solvent, a bathochromic shift of the absorption bands maxima of azo dyes is observed, which corresponds to the $\pi \rightarrow \pi^*$ electronic transition. An analysis of the obtained results allows us to conclude that the values of the molar light absorption coefficients of the dominant acid-base form of azo dyes in organic solvents almost linearly ($R=0.90-0.92$) increase with an increase of their dielectric constant (Fig. 2).
It should also be noted that the position of the maximum correlates ($R = 0.70-0.80$) with the value of the Hansen parameter associated with the density of intermolecular interaction of azo dyes with a solvent in the case of the formation of hydrogen bonds [12]. It should be noted that for the studied dyes, the solvatochromic shifts are insignificant and do not exceed 15 nm.

**Fig. 1.** Absorbance spectra of azo dyes aqueous solutions; $l = 1$ cm, $C = 5 \cdot 10^{-5}$ M.

**Fig. 2.** The influence of solvent nature on molar absorptivity of Carmoisine (a) and Tartrazine (b) (the dots on the graphs correspond to the listed solvents).
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CONCLUSIONS

Thus, as a result of this work, the solvatochromic properties of such food azo dyes as tartrazine, Sunset yellow FCF and carmoazine were studied. It is shown that with an increase in the dielectric constant of the solvent, a bathochromic shift of the absorption band maxima of azo dyes is observed, which corresponds to the $\pi \rightarrow \pi^*$ electronic transition. It has been established that the values of the molar light absorption coefficients of the dominant acid-base form of azo dyes in organic solvents almost linearly (R≈0.90-0.92) increase with an increase of their dielectric constant. It is noted that there is a weak correlation (R = 0.70-0.80) between the position of the absorption maximum of the dye and the value of the Hansen parameter.

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СОЛЬВАТОХРОМИЯ НЕКОТОРЫХ ПИЩЕВЫХ АЗОКРАСИТЕЛЕЙ

В данной работе изучены сольватохромные свойства таких пищевых азокрасителей как тартразин, желтый «Солнечный закат» и кармоазин. Показано, что при увеличении диэлектрической проницаемости растворителя наблюдается батохромный свдвиг максимумов полос поглощения азокрасителей, что соответствует π→π* электронному переходу. Установлено, что величины молярных коэффициентов светопоглощения доминирующей кислотно-основной формы азокрасителей в органических растворителях практически линейно (R≈0.90-0.92) возрастают с увеличением их диэлектрической проницаемости. Отмечено, что наблюдается удовлетворительная корреляция (R=0.70-0.80) между положением максимума поглощения красителя и величиной параметра Хансена.

Ключевые слова: спектрофотометрия, сольватохромия, кармоазин, желтый «Солнечный закат», тартразин.

СОЛЬВАТОХРОМИЯ ДЕЯКИХ ХАРЧОВИХ АЗОБАРВНИКІВ

На сьогоднішній день значну увагу приділяють вивченню харчових барвників, і в першу чергу таких, що мають синтетичне походження. Представлена робота є продовженням досліджень кислотно-основних та спектрофотометричних характеристик харчових барвників. Дану роботу присвячено вивченню сольватохромії ряду харчових азобарвників (тартразину, кармоазину та жовтого «Сонячний захід»). Особлива увага до азосполук обумовлена їх хромофорними властивостями та здатністю приймати участь майже у всіх відомих хімічних реакціях і процесах, що пов’язано з їх реакційною здатністю, яка пов’язана з наявністю в їх структурі азогрупи –N=N–, а також природою і положенням різних функціональних груп (–OH, –COOH, –NH2, –SO3H тощо) у структурних фрагментах молекул. Введення поверхнево-активних речовин або органічних розчинників може призводити до зміни не тільки кислотно-основних, а й спектральних властивостей (сольватохромія) переділених азобарвників. Вплив природи органічних розчинників досліджено на прикладі аптоніх (хлороформ, етилацетат, бутилацетат, тетрагідрофуран, 1,4-діоксан, акетоннітріл, метилбензол, диметилформамід, диметилсульфоксид, амілалкантовий спирт) та протонних (метанол, 2-пропанол, 2-бутанол, 3-метилбутан-1-ол) та протонних. Показано, що при збільшенні діелектричної проникності розчинника спостерігається батохромний зсув максимумів смуг поглинання азобарвників, що відповідає π→π* електронному переходу. Встановлено, що вели-
чини молярних коефіцієнтів світлопоглинання домінуючих кислотно-основних форм азобарвників в органічних розчинниках практично лінійно (R≈0.90-0.92) зростають зі збільшенням їх діелектричної проникності. Відзначено, що спостерігається задовільна кореляція (R = 0.70-0.80) між положенням максимуму поглинання барвника і величиною параметра Хансена.

Ключові слова: спектрофотометрія, сольватохромія, кармоазин, жовтий «Західний сонячний» тартразин.

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