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THE YELLOWNESS INDEX USE FOR THE ACID-BASE EQUILIBRIUM STUDY IN XYLENOL ORANGE AQUEOUS SOLUTIONS

The possibility of the yellowness index use for the acid-base equilibrium study and ionization constants determination in dyes solutions is studied. It is shown that the yellowness index is suitable for the set task. Its use enables a more reasonable mathematical apparatus algorithmization, automation, simplification and in comparison with the existing approaches of the chemical chromaticity method and classical physico-chemical methods.

Key words: yellowness index, acid-base equilibrium, ionization constants, coordinates of color, xylene orange.

1. Introduction

The aim of study is to establish the dyes physicochemical and acid-base characteristics of the reagents that are realized in the solutions with a broad values change of acidity or solvents. Also there is the determination of ionization constants (**pK**) and the spectral characteristics of individual reagents states or forms. The knowledge of pK values provides a basis for understanding of the chemical reactions between the compound of interest. Additionally, they play a major role in acid-base titrations, complex formation and various analytical procedures. Also, the pK values of a compound influence many characteristics such as its reactivity, spectral properties (color). Consequently, several publications were devoted to the determination of pK experimentally and theoretically [1, 2].

Nowadays interest in the chemical chromaticity (**CC**) method (tristimulus colorimetry method) has grown very much. The CC method approaches have been applied to create test methods [3], to assess the food quality [3, 4], as well as to study acid-base equilibrium in organic dyes solutions and analytical reagents [3, 5]. It is recommended to use a saturation (**S**) function and its derivative – the specific color discrimination for ionization constants determination in the dyes solutions [3, 6]. Yellowness Index is the indicator that describes the color change of the sample from white to yellow, and is calculated from the array of spectrophotometric data. Its calculation is methodologically simpler and easy to automatize. The yellowness index is used to assess the textile and food industries quality [5-8]. In this study we investigated the possibility of a more informative yellowness index (Y_I) use for acid-base equilibrium study and ionization constants determination.

2. Material and methods

2.1. Apparatus

Acid-base equilibrium in dyes solutions was studied by the UV/VIS-spectroscopy and chemical chromaticity methods using a spectrophotometer SF-56 (OKB

«LOMO-Spektor», St.-Petersburg, Russia) in the wavelength range 380-780 nm in quartz cuvettes with the thickness of the absorbing layer 1 cm. The medium's acidity was controlled by pH meter I-130 («ZIP», Gomel, Belarus).

2.2. Reagents

Xylenol orange (Merck) (**XO**) was chosen as a dye, whose functional – analytical groups are characterized by the reliably determined pK (table 1). The initial XO solution with 10^{-3} M concentration was made by sample dissolution ($m = 0,1682$ g) in 250 ml of distilled water. Solutions with lower concentrations were prepared by dilution of initial solution. The medium acidity was created by sulfuric acid and sodium hydroxide.

Table 1

Xylenol orange ionization constants

№	Group	Method				
		Potentiometry [9, 10]		Spectrophotometry [9]		CC [11]
1	–SO ₃ H	-	-	-1,74	-	-1,73
2	=OH ⁺	-	-	-1,09	-	-1,10
3	–COOH	-	-	0,76	-	0,70
4	–COOH	2,06	2,00	-	-	1,12
5	–COOH	2,16	2,74	-	2,60	2,53
6	–COOH	3,56	4,49	-	3,70	3,05
7	–OH	7,34	7,50	6,46	6,40	6,31
8	≡NH ⁺	9,68	10,30	10,46	8,40	10,45
9	≡NH ⁺	12,61	12,00	12,28	12,20	12,38

2.3. Procedures

The necessary medium acidity was created for pK determination. It was provided by putting the dye's aliquot of solution into the 50 ml flask. The obtained solutions absorption spectrum were registered and coordinates of color XYZ were calculated from the array of spectrophotometry data. Parameter Y_i was calculated by formulae:

$$Y_i = \frac{100(1,28X - 1,06Z)}{Y}$$

where Y_i – yellowness index; X, Y, Z – coordinates of color in the CIEXYZ color space.

3. Results and discussion

3.1. Effect of the medium acidity

The absorption spectra of XO in aqueous solution were studied by various the medium's acidity. Figure 1 (parts **a** and **b**) shows the changes in the absorption spectra of XO.

Figure 1 shows the changes in the absorption spectra of XO. As can be seen from fig. 1 (**a**) in the acidic medium XO has absorption bands at 430 – 460 nm (curves 2, 3),

505-515 nm (curve 1) and absorption band with maximum at 670 ± 10 nm (curve 4). Increasing the concentration of OH-groups in the solution contributes to formation of new acid-base forms of XO.

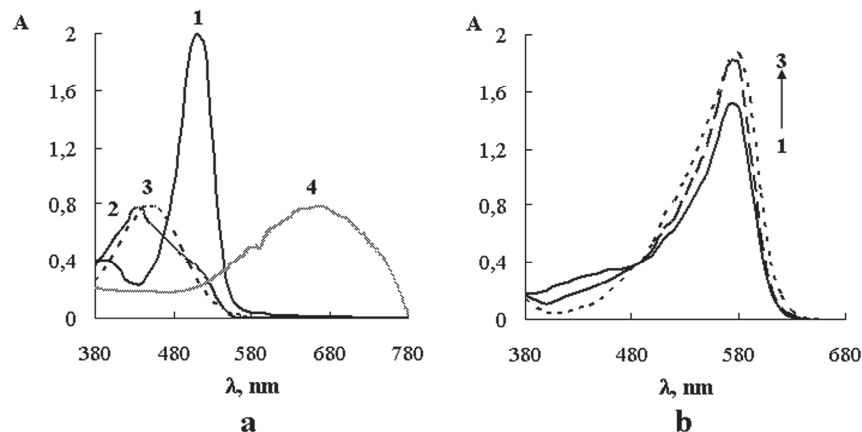


Fig. 1. The electronic absorption spectra of the xlenol orange solution in acidic (part a: 1 – 18M H_2SO_4 medium, 2 – pH 1, 3 – pH 3, 4 – pH 5) and alkaline (part b: 1 – pH 8, 2 – pH 10, 3 – pH 13) media.

They are characterized by isosbestic point at 490 nm and absorption maxima at 575 nm (fig.1 b, curves 1-3). The observed changes in the absorption spectra are explained the acid-base equilibria in XO solution. Each balance describes appropriate pK values.

3.2. Determination of pK values

We studied the possibility of the yellowness index use for determining the dye pK values. Figure 2 shows the Y_I dependence of the medium acidity.

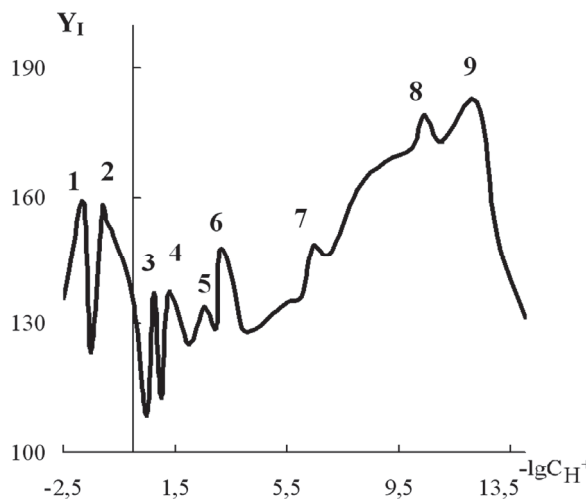


Fig. 2. The Y_I dependence of the xlenol orange solution on the medium's acidity

It is known that for an absolutely white body – $Y_I = 0$, for yellow and red ones – $Y_I > 0$; for blue and green ones – $Y_I < 0$. The fracture's points on the curve of Y_I values dependence from pH corresponds to the areas of transition from one form to another. The corresponding values $-\lg CH^+$ are received by finding the coordinates of each peak, which are numerically equal to the values of the XO pK in solution. The formation of 9 peaks confirms the presence of 9 values of pK (table 1) for different molecule forms of the XO in the solution, each of which is characterized by specific Y_I values, whose sign indicates the solution reagent color in a wide range of medium's acidity. The graphic dependence analysis (fig. 2) points to the existence of ten differently charged forms of XO in solution, which depend on the medium acidity and are in dynamic equilibrium; each of which is characterized by pK value (table 2).

Table 2

**Xylenol orange ionization constants installed by using the yellowness index
(n=3; P=0,95)**

№	Group	pK
1	$-\text{SO}_3\text{H}$	$-1,75 \pm 0,03$
2	$=\text{OH}^+$	$-1,10 \pm 0,03$
3	$-\text{COOH}$	$0,75 \pm 0,03$
4	$-\text{COOH}$	$1,25 \pm 0,03$
5	$-\text{COOH}$	$2,50 \pm 0,03$
6	$-\text{COOH}$	$3,10 \pm 0,03$
7	$-\text{OH}$	$6,41 \pm 0,03$
8	$\equiv\text{NH}^+$	$10,42 \pm 0,03$
9	$\equiv\text{NH}^+$	$12,35 \pm 0,03$

The results (Table 2) correlate with those presented in Table 1 literature data, which indicates that the results are reliable and the yellowness index use for the acid-base properties study and the establishment of the corresponding values of the dyes' molecules and organic analytical reagents pK are suitable.

The yellowness index use allows to simplify the calculations in comparison with the specific color differences parameter. The algorithm of pK definition with the specific color discrimination has the following form:

absorption spectrum – the color coordinates XYZ – the color coordinates LAB – the color saturation S – parameter specific color discrimination – the dependence identification of the $SCD = f(-\lg CH^+)$ – definition of the pK.

The algorithm is simplified by using the yellowness index:

absorption spectrum – the color coordinates XYZ – the yellowness index Y_I – the dependence identification of the $Y_I = f(-\lg CH^+)$ – definition of the pK.

4. Conclusion

Thus, the use of color characteristics of chemical systems in chemistry of dyes enhances the study of their acid-base equilibria. Also it should be noted that the chemical chromaticity method compared to other physico-chemical methods (spectrophotometry, potentiometry, etc.) provides more complete information about available and appropriate protolytic equilibria constants. As a result of our work we established the principal possibility of the yellowness index use for the acid-base equilibrium study and pK determination in the dyes solutions. The yellowness index allows to simplify and reduce the mathematical apparatus instead of the existing approaches of chemical chromaticity method and classical physico-chemical methods.

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ФУНКЦІЯ ПОКАЗНИКА ЖОВТИЗНИ ПРИ ДОСЛІДЖЕННІ КИСЛОТНО-ОСНОВНИХ РІВНОВАГ КСИЛЕНОЛОВОГО ОРАНЖЕВОГО У ВОДНИХ РОЗЧИНАХ

Резюме

Вивчено можливість застосування функції показника жовтизни для дослідження кислотно-основних рівноваг і визначення констант іонізації ксиленолового оранжевого у водних розчинах. Показано, що використання даної функції дозволяє спростити математичний апарат, алгоритмізацію та автоматизацію розрахунків, у порівнянні з існуючими підходами методу хімічної кольориметрії та класичними фізико-хімічними методами.

Ключові слова: показник жовтизни, кислотно-основні рівноваги, константи іонізації, координати кольору, ксиленоловий оранжевий.

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ФУНКЦИЯ ПОКАЗАТЕЛЯ ЖЕЛТИЗНЫ ПРИ ИЗУЧЕНИИ КИСЛОТНО-ОСНОВНЫХ РАВНОВЕСИЙ КСИЛЕНОЛОВОГО ОРАНЖЕВОГО В ВОДНЫХ РАСТВОРАХ

Изучена возможность применения функции показателя желтизны для исследования кислотно-основных равновесий и определения констант ионизации ксиленолового оранжевого в водных растворах. Показано, что использование данной функции позволяет упростить математический аппарат, алгоритмизацию и автоматизацию расчетов, в сравнении с существующими подходами метода химической цветиметрии и классическими физико-химическими методами.

Ключевые слова: показатель желтизны, кислотно-основные равновесия, константы ионизации, координаты цвета, ксиленоловый оранжевый.