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INFLUENCE OF TETRABUTYLAMMONIUM BROMIDE AND SODIUM BROMIDE ON ACID-BASE PROPERTIES OF THYMOL BLUE IN WATER-ETHANOL MEDIUM**E.A. Reshetnyak, A.I. Rysukhina, N.N. Kamneva, K.V. Goloviznina**

For the first time the values of two acidity constants K_{a1} and K_{a2} of the sulfophthalein indicator thymol blue in water and water-ethanol (mass fraction of ethanol is 50%) solutions with and without addition of tetrabutylammonium bromide and a background electrolyte NaBr were determined. Spectrophotometry was chosen as a method of investigation and potentiometry was used to check the pH value in the solutions. It was found that the influence of tetrabutylammonium bromide on the pK_{a2} values (compared with aqueous solutions) of thymol blue in water and water-ethanol solutions correlated in sign with the effects that took place in micellar solutions of cationic surfactants for this indicator. Changes in the pK_{a1} value did not exceed a measurement error.

Keywords: thymol blue, acidity constant, water-ethanol solution, tetrabutylammonium bromide, background electrolyte, spectrophotometry, potentiometry.

Introduction

Thymol blue (2,2'-dimethyl-5,5'-diisopropylphenolsulphophthalein, TB) is an acid-base indicator, that is sufficiently studied and commonly used in analytical and physical chemistry practice. Thymol blue, along with other dyes, is used as a spectroscopic probe for investigating of medium effects [1-7]. It is known that transition from water to non-aqueous solvents, either to micellar solutions or similar media, causes a shift of protolytic equilibrium or leads to changes in values of the indicators (K_a) acidity constants. The value $\Delta pK_a = pK_a(\text{medium}) - pK_a^w(\text{water})$ is a quantitative characteristic of an influence of the indicator microenvironment in the chosen medium.

Different indicator systems based on dye solutions or sorbents with immobilized dyes are used as an express method to determine the pH of aqueous media; acid-base papers are best known to consumers [8,9]. Indicator papers that work in a "wide" pH range are prepared using water or water-alcohol solutions of indicator mixtures. These solutions can contain thymol blue. To improve the stability of immobilized indicators in sorbents, tetrabutylammonium bromide (TBAB) was added to the solutions of dyes [9]. The presence of a quaternary ammonium salt can cause a shift in the color transition of the indicator. A preliminary research into the indicator's behavior in the solution in the chosen conditions is necessary for prediction of acid-base properties of the dye in the sorbent phase.

The indicator thymol blue has two color transitions characterized by two acidity constants K_{a1} and K_{a2} . The schemes of protolytic equilibria are shown in Fig.1 ([4]). A molecule of an acid is red in color, hydroanion – yellow, anion – blue one.

A standard method of spectrophotometric determination of acidity constants is mostly used for investigation of acid-base properties of dyes under various conditions [10]. If the dissociation equilibrium of the indicator's acid form is represented by the equation $HR \rightleftharpoons R + H^+$, the formula for calculation of the logarithmic acidity constant is as follows:

$$pK_a = pH + \log \frac{A - A_R}{A_{HR} - A} \quad (1)$$

where A_R and A_{HR} are absorbances of conjugated forms of the indicator at a fixed wavelength, A – absorbance of the solution containing both the forms; the pH value of the solutions is determined by the potentiometric method.

In Table 1, some examples of the experimentally estimated values of the second acidity constant of thymol blue in aqueous micellar solutions of cationic surfactants at different values of ionic strength of the solutions (I) are collected. These results confirm regularities summarized in the literature [1,6,7]: the indicators' pK_a values decrease in the presence of micelles of cationic surfactants as compared with the values in water and increase when a background electrolyte is added to the micellar medium (references on the influence of TBAB on pK_{a1} and pK_{a2} of thymol blue were not found).

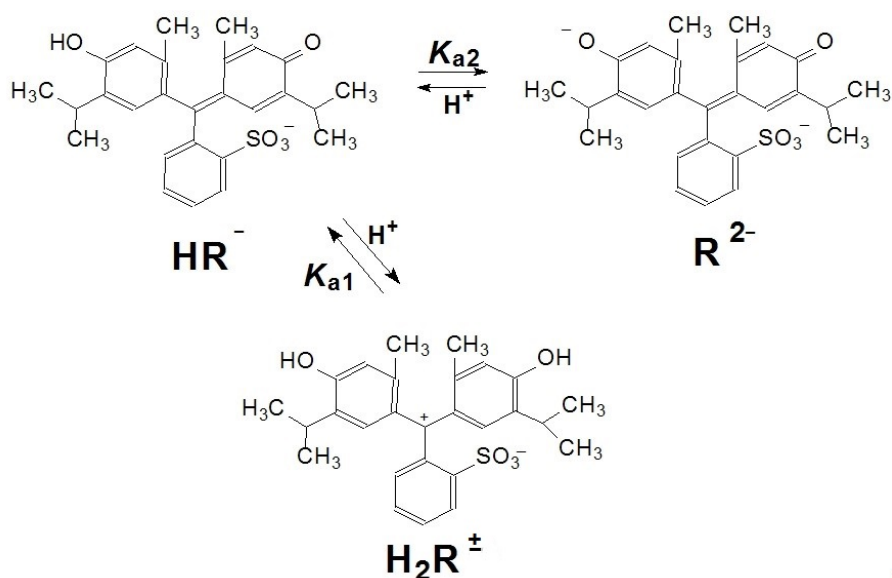


Figure 1. The scheme of protolytic equilibria of thymol blue.

Table 1. Values of the indices of the second acidity constant of thymol blue in water micellar solutions of cationic surfactants.

Surfactant	Conditions				pK_{a2}
	$c(\text{surfactant}), \text{mol/dm}^3$	Background electrolyte	$I, \text{mol/dm}^3$	$t^\circ\text{C}$	
cetyltrimethyl-ammonium bromide	0.003	KBr	0.011	20	8.90 [2]
	0.003	KBr	0.05	20	9.30 [2]
	0.01	NaBr	0.05	20	9.15 ± 0.05 [4]
	0.01	—	not stabilized	25	8.73 ± 0.03 [4]
	0.002	NaBr	0.05	25	9.60 [5]
ditetradecyldimethyl ammonium bromide	$5 \cdot 10^{-4}$	NaBr	0.01	25	8.90 ± 0.06 [6]
gemini 16-4-16 surfactants	$5 \cdot 10^{-4}$	NaBr	0.05	25	9.60 [6]
cetylpyridinium chloride	0.003	KCl	0.05	25	8.83 [1]
cetyltrimethyl-ammonium chloride	0.003	KCl	4.0	25	10.47 [3]

*In water solutions $pK_{a2} = 9.2$ ($I = 0$, [1,11]); 9.01 ($I = 0.01$, [11]); 8.90 ($I = 0.1$, [11]).

It is known that an increase in pK_{a2} i.e. a decrease of acid strength, is supposed to be observed when water is replaced by an organic or water–organic medium. Thus, pK_{a2} of thymol blue reaches the value of 13.1 in water–ethanol solution (91 mas % fraction of ethanol) [1].

The aim of this work was to investigate the influence of tetrabutylammonium bromide on acid-base properties of the indicator thymol blue in water and water–ethanol solutions (mass fraction of the alcohol 50%) in the presence of background electrolyte NaBr.

Experimental

Materials

In the present work, the chemicals were reagent or extra pure grade, all the solutions were prepared using distilled water. Stock solutions of thymol blue ($\sim 2 \cdot 10^{-4} \text{ mol/dm}^3$) and TBAB (0.10 mol/dm^3) were prepared by dissolution of exactly weighed amounts in ethanol (96 mas % fraction). Aqueous of 1.00 mol/dm^3 NaBr solution was prepared using exactly weighed amount.

The values of $\text{pH} < 3.3$ in the working solutions were maintained by HCl additions, pH from 4.0 to 5.5 by an acetate buffer, from 6.0 to 8.0 by a phosphate buffer, from 8.2 to 10.5 by a borate buffer,

pH > 11 by NaOH solutions. The stock solution of alkali was prepared from a saturated NaOH solution using CO₂-free water and was kept protected from the atmosphere.

Apparatus

Absorption spectra of dye solutions were measured using KFK-3 and HITACHI U-2000 apparatus against water or water-ethanol reference solutions in 1 cm cuvette. The pH values of working solutions were determined by the potentiometric method using either a compensation scheme with uncertainty of ±0.3 mV at (25.0±0.1) °C or pH meter-millivoltmeter pH-121 at room temperature. An Ag/AgCl electrode EVL-1M3 was chosen as a reference electrode and a glass electrode ESL-43-07 as an indicator one. Calibration of the optical path cell was carried out with standard aqueous buffer solutions. A correction $\Delta = -0.2$ units was applied for measured pH values of water-ethanol (50% mass fraction) solutions [12].

Procedure

The concentration of thymol blue was determined more precisely by spectrophotometric method taking into account the exact value of the molar absorptivity of the indicator in water solutions $\epsilon_{\max} = 3.6 \times 10^4 \text{ dm}^3/(\text{mol} \times \text{cm})$ [1].

Water-alcohol solutions of the indicator (50 mas % fraction of ethanol) with fixed pH and ionic strength values were prepared in a flask with a volume capacity of 10 ml. Necessary volumes of the base solutions were placed into the flask using pipettes in the following order: TB solution, 96 % ethanol, TBAB solution, NaBr solution, and then made up by an aqueous buffer solution. Concentration of the indicator in all the solutions was $3.0 \times 10^{-5} \text{ mol/dm}^3$, and that of TBAB: 0.01 or 0.002 mol/dm³. The fixed value $I = 0.05 \text{ mol/dm}^3$ was maintained by adding the background electrolyte NaBr. The value of ionic strength was determined by the concentration of the components of buffer solutions or HCl in case of absence of the TBAB and NaBr salts.

Results and discussion

The scheme of acid-base conversion of thymol blue in ethanol and water-ethanol-solutions is supposed to be the same as in water (Figure 1, [1]).



It is well known that in a strongly acidic medium (pH < 0), the zwitter-ion H₂R[±] is readily protonated forming cation H₃R⁺ (fixed by sight and spectroscopically) [1,13]. Different authors report the pK_{a1} value to be about 1.6. Based on this value, pH range from 0.7 to 3.5 was chosen for studying zwitter-ion dissociation to hydroanion. The contribution of the equilibrium concentration of H₃R⁺ ion to total concentration of the indicator can be neglected in this acidity range [13].

Absorption spectra of the three forms of the indicator at different pH values in water (without TBAB and NaBr) and water-ethanol solutions (with TBAB and NaBr) are shown in Figures 2 and 3. Absorption spectra of the dye were similar to those obtained in other tested systems. The values of the wavelength in maxima of the absorption bands of all the forms (λ_{\max} , Table 2) are shifted insignificantly into a long wavelength spectrum band by 4-11 nm in water-ethanol solutions as compared with the water ones. This shift is typical for colored particles when a polar solvent is replaced by a less polar one; the value of $\Delta\lambda_{\max}$ also characterizes the medium effect [1].

For the experimental evaluation of the indicator's acidity constants under different conditions, the wavelengths were chosen where the light absorption of the dye strongly depends on pH: λ_{\max} of the zwitter-ion when studying the first step of dissociation and λ_{\max} of the anion R²⁻ when evaluating the second acidity constant.

Examples of the titration curves of water-ethanol solution of the indicator by hydrogen chloride solutions and alkali are shown in Figure 4. For calculating every logarithmic acidity constants according to Eq. 1, 8-10 experimental points on the sloping part of the curves were chosen. Averaged values are presented in Table 2.

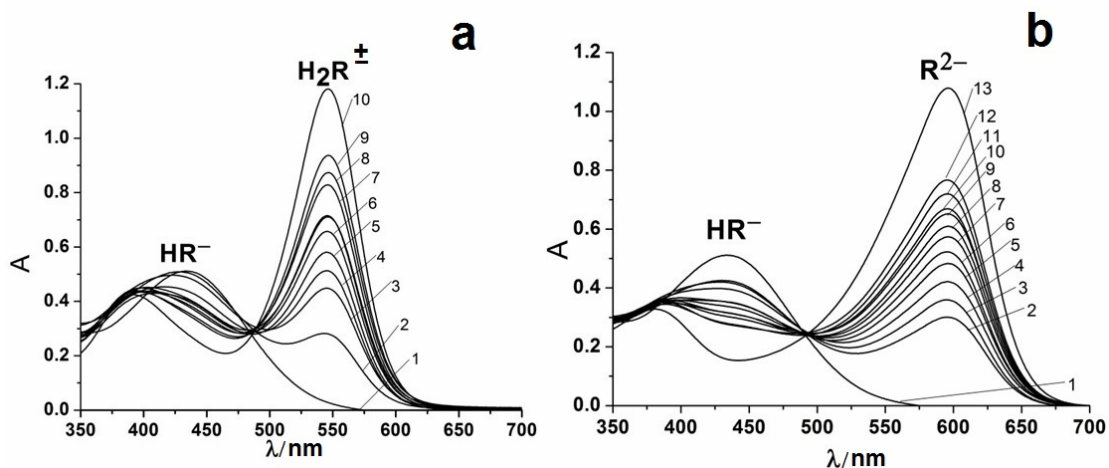


Figure 2. Absorption spectra of thymol blue at different pH values in water solutions with concentration of TB $3.2 \times 10^{-5} \text{ mol/dm}^3$:

a) pH: 1 – 5.00; 2 – 2.29, 3 – 2.00, 4 – 1.86, 5 – 1.74, 6 – 1.62, 7 – 1.57, 8 – 1.47, 9 – 1.28, 10 – 0.70.
 b) pH: 1 – 5.00; 2 – 8.63; 3 – 8.78; 4 – 8.85; 5 – 8.94; 6 – 9.05; 7 – 9.08; 8 – 9.20; 9 – 9.21; 10 – 9.26; 11 – 9.38; 12 – 9.43; 13 – 13.0.

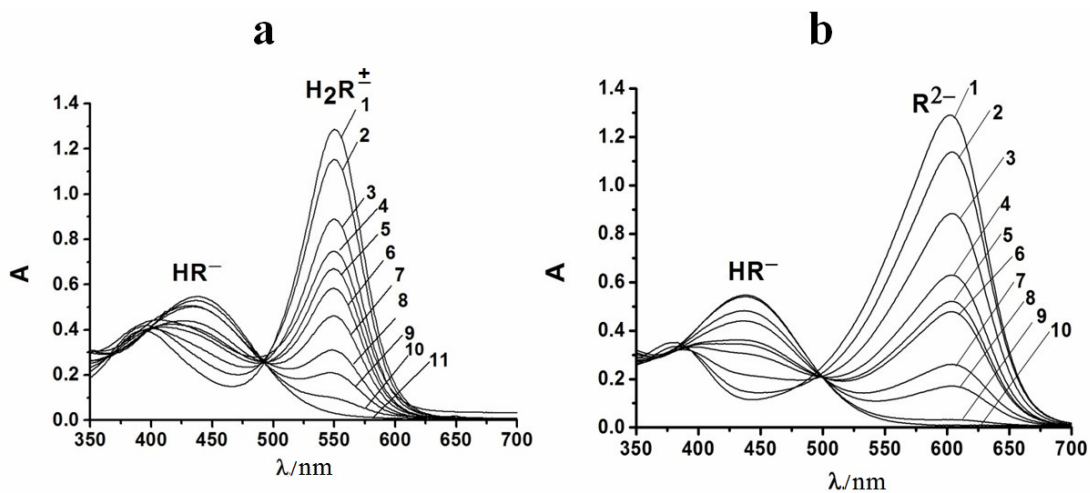


Figure 3. Absorption spectra of thymol blue at different pH values in water solutions with concentration of TB $3.2 \times 10^{-5} \text{ mol/dm}^3$, TBAB – 0.01 mol/dm^3 , NaBr ($I = 0.05 \text{ mol/dm}^3$):

a) pH: 1 – 1.00; 2 – 1.50, 3 – 1.68, 4 – 1.89, 5 – 1.96, 6 – 2.09, 7 – 2.27, 8 – 2.60, 9 – 2.79, 10 – 3.30, 11 – 5.00.
 b) pH: 1 – 13.00; 2 – 11.00; 3 – 10.80; 4 – 10.60; 5 – 0.43; 6 – 10.26; 7 – 10.01; 8 – 9.87; 9 – 8.94; 10 – 5.00.

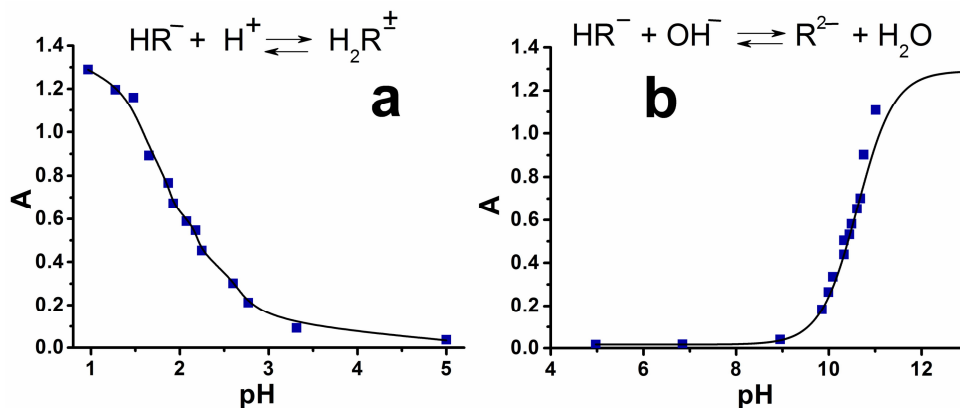


Figure 4. Spectrophotometric titration curves of water–ethanol solutions of thymol blue by HCl solution (a; $\lambda_{\text{max}} = 550 \text{ nm}$) and NaOH solution (b; $\lambda_{\text{max}} = 604 \text{ nm}$). (a, b: $c(\text{TB}) = 3.2 \times 10^{-5} \text{ mol/dm}^3$, $c(\text{TBAB}) = 0.01 \text{ mol/dm}^3$, $I = 0.05 \text{ mol/dm}^3$ (NaBr).

Table 2. λ_{\max} values of absorption bands of three forms of thymol blue and logarithmic acidity constants values of the indicator obtained under different conditions

Medium	Conditions			λ_{\max} , nm			pK_{a1}	pK_{a2}
	t , °C	c , mol/dm ³	I , mol/dm ³	H ₂ R [±]	HR ⁻	R ²⁻		
Water	25	—	0.001 – 0.05	546	430	596	1.76 ± 0.04	9.05 ± 0.02
	25	—	0.05 (NaBr)	546	430	596	1.77 ± 0.05	9.06 ± 0.02
Water : ethanol = 1:1 by weight	18-20	—	0.001 – 0.05	552	441	603	2.00 ± 0.15	9.45 ± 0.11
	25	—	0.05 (NaBr)	550	437	602	1.88 ± 0.09	10.06 ± 0.06
	18-20	0.001 (TBAB)	0.005 – 0.03	552	441	603	1.77 ± 0.05	8.30 ± 0.16
	25	0.01 (TBAB)	0.05 (NaBr)	550	437	604	1.80 ± 0.04	10.59 ± 0.06

Bishop [11] underlines that temperature fluctuation and the presence of background electrolytes in the solutions display negligible influence on the equilibria of dissociation of indicator molecules with a bipolar ionic structure (in particular, the molecular form of thymol blue). This statement is illustrated by the data in Table 2. The difference in the value of the first logarithmic acidity constant did not exceed a measurement error under all the studied conditions (confidence intervals for all of the mean values of pK_{a1} overlap), i.e., the pK_{a1} fluctuation is negligible.

The behavior of the logarithmic second acidity constant of thymol blue illustrates regularities discussed hereinabove. Stabilization of the ionic strength of the buffer aqueous solution of the indicator by adding the electrolyte NaBr ($I = 0.05$ mol/dm³) did not influence the constant value significantly. Having cationic surfactants properties, TBAB displays a greater influence on the shift of acid-base equilibrium than NaBr.

The pK_{a2} value, as it was expected, increased from 9.05 to 9.45 when water solutions of thymol blue containing only the buffer were replaced by water–ethanol ones (when passing to a less polar solvent); adding the background NaBr salt for the ionic strength stabilization led to a subsequent increase in logarithmic acidity constant up to the value of 10.06. Adding of a comparatively small amount of the TBAB salt (0.002 mol/dm³) to water–ethanol solutions of the indicator decreased the pK_{a2} value from 9.45 to 8.30 (Table 2, the third line from the bottom). The sign of the effect is the same as in the cationic surfactants in the solutions of thymol blue (Table 1).

The background electrolyte NaBr being added to water-ethanol solutions containing TBAB were supposed to shift the equilibrium (3) to the side of hydroanion, which had to lead to the increase in the pK_{a2} value. Just this result was obtained in our study: stabilization of ionic strength of the solutions (0.05 mol/dm³) causes the increase in the pK_{a2} value from 8.30 to 10.59 (Table 2, the next-to-last line) even if TBAB concentration is increased five times.

Conclusions

The study of protolytic equilibria of the indicator thymol blue in water–ethanol (50% mass fraction) solutions with and without adding tetrabutylammonium bromide and sodium bromide confirmed the fact that the influence of the TBAB salt on acid-base properties of the dye is similar to the influence of micellar solutions of cationic surfactants. The decrease (comparing with water) of polarity of the medium and the presence of the background electrolyte NaBr caused the opposite in sign effects on the value of logarithmic second acidity constant comparing with the influence of TBAB. These factors did not affect the equilibrium of zwitter-ion dissociation to hydroanion of the indicator significantly – change in the pK_{a1} value did not exceed the measurements error.

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Е.А. Решетняк, А.И. Рисукина, Н.Н. Камнева, Е.В. Головизнина. Влияние тетрабутиламмоний бромида и натрий бромида на кислотно-основные свойства тимолового синего в водно-этанольной среде.

Для сульфоталеинового индикатора тимолового синего впервые определены значения двух констант кислотности K_{a1} и K_{a2} в водных и водно-этанольных (с массовой долей спирта 50%) растворах соли тетрабутиламмоний бромида с добавками и без добавок фонового электролита NaBr. Исследования проводили методом спектрофотометрии, значение pH в растворах уточняли потенциометрически. Установлено, что влияние соли тетрабутиламмоний бромида на изменение значения pK_{a2} тимолового синего в водных и водно-этанольных растворах коррелирует по знаку с эффектами, которые наблюдали для этого индикатора в мицеллярных растворах катионных поверхностно-активных веществ. Изменение величины pK_{a1} не превысило погрешности измерений.

Ключевые слова: тимоловый синий, константа кислотности, водно-этанольная среда, тетрабутиламмоний бромид, фоновый электролит, спектрофотометрия, потенциометрия.

О.О. Решетняк, А.І. Рисухіна, Н.М. Камнева, К.В. Головізніна. Вплив тетрабутиламоній броміду і натрій броміду на кислотно-основні властивості тимолового синього в водно-етанольному середовищі.

Для сульфоталеїнового індикатора тимолового синього вперше визначено значення двох констант кислотності K_{a1} і K_{a2} у водних і водно-етанольних (з масовою часткою спирту 50%) розчинах солі тетрабутиламоній броміду з добавками і без добавок фонового електроліту NaBr. Дослідження проводили методом спектрофотометрії, значення рН у розчинах уточнювали потенціометрично. Встановлено, що вплив солі тетрабутиламоній броміду на зміну значення pK_{a2} тимолового синього в водних і водно-етанольних розчинах корелює за знаком з ефектами, які спостерігали для цього індикатора в міцелярних розчинах катіонних поверхнево-активних речовин. Зміна величини pK_{a1} не перевищила похибки вимірювань.

Ключові слова: тимоловий синій, константа кислотності, водно-етанольне середовище, тетрабутиламоній бромід, фоновий електроліт, спектрофотометрія, потенціометрія.

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