Sulfonephthalein dyes. I.
## Spectrophotometric study of xylenol blue and bromoxylenol blue using colorimetric systems

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Acid-base equilibria of xylenol blue and bromoxylenol blue were studied spectrophotometrically in the visible radiation region. Electronic absorption spectra of both the indicators were measured in the range of their colour transitions and the colour changes were specified by calculating the courses of colour transition curves in chromaticity diagrams $CIE-xy$, $CIE-uv$ and in a complementary chromaticity diagram Q_xQ_y. Colorimetric data were used for calculation of partial dissociation constants of the indicators. Utilizing a uniform colour space $CIE-UVW$, the sight sensitivity to small colour differences in visual analytical methods was also studied. Advantages of application of tristimulus colorimetric systems in the study of acid-base indicators are discussed.
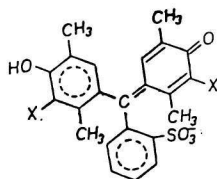
1. X = H, p-xylenol blue;
2. X = Br, bromoxylenol blue.

Scheme 1

Recently, an increased number of chemical indicators recommended for various titration methods have been reported in the chemical literature. The description of their colour transitions is usually only verbal and, with regard to subjective estimates of different authors, not exactly comparable. Chromaticity systems CIE (see *e.g.* [1]), required by many states as obligatory standards of the objective specification of colours, have seldom been applied till now to solve the problems of analytical chemistry, compared with other scientific branches. Colour transitions in the $CIE-xy$ chromaticity diagram were for the first time reported by *van Wyk* and *Clark* [2] for three acid-base indicators. *Reilley* with co-workers [3] worked out a complementary chromaticity system for the specification of colour changes of chemical indicators.

The tristimulus colorimetric systems can successfully be utilized for the study of chemical indicators. We would like to demonstrate our experiences on an example of

two acid-base indicators, *p*-xylenol blue and bromoxylenol blue (Scheme 1). In the group of sulfonephthalein dyes but a little attention has been paid to these indicators and they have not been studied spectrophotometrically as yet.

Experimental and results

Reagents, instrumentation, and measurements

Xylenol blue

A commercial preparation (*ca.* 17 g; Lachema, Brno) was dissolved in 5% $NaHCO_3$ (300 ml), the solution was filtered and the filtrate boiled with activated charcoal. The hot solution was again filtered and precipitated with small quantities of diluted (1 : 5) hydrochloric acid. The precipitate was filtered off, washed with diluted HCl and ether, and finally dried at 60°C. Contrary to the dark-brown commercial product with a strong odour, the obtained substance was violet, without odour of *p*-xylenol.

Bromoxylenol blue

Xylenol blue (*ca.* 10 g) was dispersed in glacial acetic acid (100 ml) and bromine (10 ml) was gradually added under stirring while the suspension was kept cold [4]. When the bromination was finished, the mixture was let stand for 60 min and then filtered through a fritted disk. On diluting with water the filtrate turned into a yellow-orange suspension that was let stand overnight. Afterwards the precipitate was filtered off, repeatedly washed with small quantities of diluted HCl, and dried at 50°C.

The purity of both the indicators was checked by the ascending paper chromatography on Whatman No. 1 paper. Systems of butanol—acetic acid—water (4 : 1 : 1) or saturated ammonia—acetone (1 : 5) or 5% acetic acid turned out to be convenient mobile phases. None of these systems proved any marked impurities on chromatograms. Results of the elemental analysis were also in the range of required precision.

Stock solutions of the indicators were prepared by dissolving the xylenol blue (0.04385 g) or bromoxylenol blue (0.07510 g) in water (500 ml). Britton—Robinson buffer solutions with ionic strengths adjusted to the constant value $I = 0.2$ by addition of sodium perchlorate were used for measurements. Acidic solutions of xylenol blue were measured in HCl/NaCl buffers.

A spectrophotometer VSU-1 (Zeiss, Jena) was applied in spectrophotometric measurements. Its function was checked by measuring the standard solutions of potassium chromate, ammonium cobalt(II) sulfate, and copper sulfate [5]. A precision pH-meter OP-205 (Radelkis, Budapest) equipped with glass and saturated calomel electrodes was used for pH measurements. The measuring cell was calibrated by standard buffer solutions of the conventional activity scale of pH.

Spectrophotometric measurements

Xylenol blue exhibits two colour transitions. Its neutral solutions are yellow, on acidification they turn into purple; this colour change corresponds to protonation of the quinoid oxygen [6]. The result is a symmetric molecule with its absorption band shifted towards longer wavelengths. On the other hand, in alkaline solutions a symmetric resonance structure arises by splitting off of a proton from the hydroxyl group; alkaline solutions of the indicator are blue.

Bromoxylenol blue shows but one colour transition in aqueous solutions, from yellow to blue, corresponding to deprotonation of the phenolic hydroxyl. Owing to the influence of electronegative substituents in o-positions to hydroxyl groups this colour transition is shifted to the region of lower pH values compared with xylenol blue.

Wavelengths of maxima of the light absorption and positions of isosbestic points are together with other data listed in Table 1.

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Table 1

Absorption maxima and complementary chromaticity coordinates of solutions of xylenol blue and bromoxylenol blue

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Indicator	Form	λ_{max} [nm]	Isosbestic point λ [nm]	Complementary coordinates		K_λ	(λ, nm)
				Q_x	Q_y		
p-Xylenol blue	H_2I	547		0.281	0.510	0.785	(550)
	HI^-	437	489 (390)	0.158	0.107	1.005	(440)
	I^{2-}	596	492	0.430	0.451	1.014	(600)
Bromoxylenol blue	HI^-	438	500	0.157	0.104	0.991	(440)
	I^{2-}	618		0.454	0.411	1.016	(620)

Colour transitions in the CIE—xy chromaticity diagram

Absorbance A_λ of a solution of the two-coloured acid-base indicator is a function of its absorption coefficients

$$A_\lambda = -\log T_\lambda = [a_{HI}(1 - \delta) + a_I \delta] c_I d, \qquad (1)$$

where T_λ is the spectral transmittance, a_{HI} and a_I are the absorption coefficients of both forms of the indicator involved in the equilibrium $HI \rightleftarrows I + H^+$, d is the length of the light path, c_I is the total concentration of the indicator and $\delta = [I]/c_I$ is the concentration fraction of the deprotonated form I.

Any colour is specified in the colorimetric space $CIE-XYZ$ by a vector $\bar{R}$, components of which X, Y, Z (in general R) are calculated by a summation of the products in the region of wavelengths of the visible radiation (weighted ordinate method) [1, 11]. Since a space diagram is unpractical, the diagram on a plane section of the colorimetric space, *i.e.* the $CIE-xy$ chromaticity diagram is used. Coordinates in this diagram (in general r) are calculated as

$$r = R/(X + Y + Z). \qquad (2)$$

The tristimulus coordinates are supplemented by a relative luminance value Y, these data being quite sufficient to specify a colour hue.

From one curve of the spectral transmittance one point in the chromaticity diagram is obtained by calculation. If all the points representing different hues in the course of the colour transition of the indicator are connected we obtain the so-called colour transition curve characterizing unambiguously and objectively the colour change.

Fig. 1. A section of the $CIE-xy$ chromaticity diagram with outlined curves of the colour transition.

1., 2. xylenol blue, $c = 8.77 \times 10^{-3}$ mg ml^{-1}, $d = 10.00$ mm; *3.* bromoxylenol blue, $c = 1.502 \times 10^{-2}$ mg ml^{-1}, $d = 19.99$ mm.
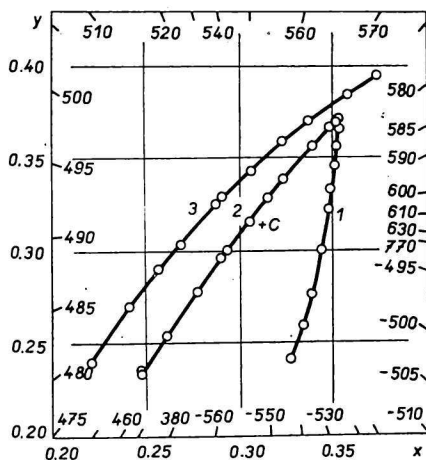
We employed the results of the spectrophotometric measurements and calculated the colour transition curves of xylenol blue and bromoxylenol blue. They are shown in a section of the $CIE-xy$ chromaticity diagram in Fig. 1; values of the dominant wavelengths are also written on the diagram to ease the orientation. The colour of the wavelength on the perimeter of the xy diagram intersected by the line connecting the given point with the point of the CIE standard source C is a certain approximation of the colour hue of the measured solution. For the non-spectral purple colours so-called complementary wavelengths are used, differentiated by a negative sign. The description of a colour change of indicators is completed by the course of a change of the relative luminance shown in Fig. 2.
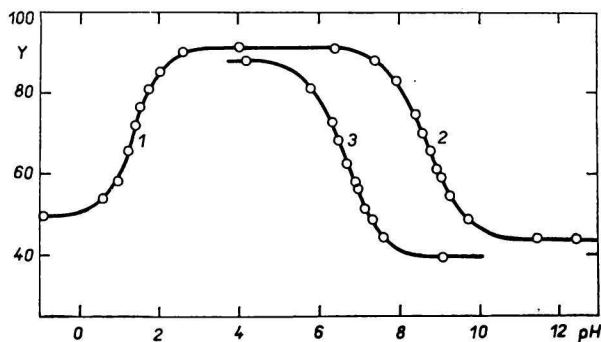

Fig. 2. The dependence of the relative luminance on pH. Solutions of xylenol blue *(1, 2)* and bromoxylenol blue *(3)*.

Colour transitions in the complementary chromaticity diagram $Q_x Q_y$

The complementary diagram $Q_x Q_y$ differs from the diagram $CIE-xy$; instead of transmittance T_λ, values of absorbance A_λ are used to calculate the tristimulus components of R, and thus to avoid their exponential dependence upon the concentration of the

dye in the solution. The complementary coordinates Q_x, Q_y calculated by a formula ana-logous to eqn (2) are then determined only by the course of absorption coefficients de-pendent on the wavelength; they are physical constants in character.

The re-calculation of the complementary coordinates, Q_r, to the $CIE-xy$ diagram is enabled by eqn (3)

$$r = G_r - J(Q_r - G_r) - J^2(Q_r - G_r + Q_r^d) = G_r - J\,V_r - J^2\,W_r. \qquad (3)$$

The only quantity dependent on concentration is the so-called optical concentration of the dye in solution, J

$$J = E\,c_I\,d = K(X_c + Y_c + Z_c). \qquad (4)$$

The source of light is substituted by the "grey" point G_r. The complete definitions of the symbols used in eqns (3) and (4) together with derivations of the mathematical relations are reported in [3].

One of the advantages of the complementary colour diagram is the facilitation of calculations of any point in the course of the colour transition from the data of hues of the limiting forms of the indicator involved in the equilibrium. Analogously to eqn (1) it holds

$$J = J_{HI}(1 - \delta) + J_I\,\delta = [E_{HI}(1 - \delta) + E_I\,\delta]\,c_I\,d, \qquad (5)$$
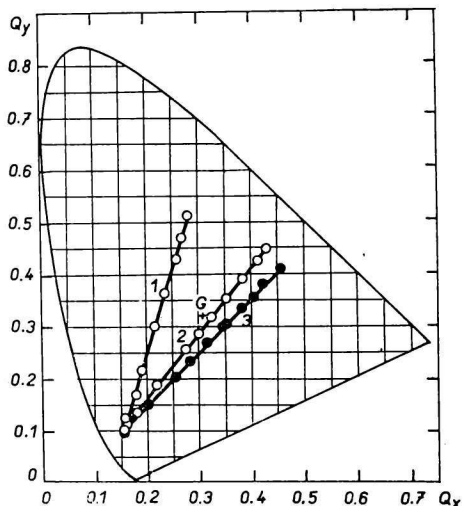
and for the calculation of coordinates

Fig. 3. The complementary chromaticity diagram Q_xQ_y and straight lines of the colour transition.
Xylenol blue, the transition in acidic (1) and alkaline (2) regions; bromoxylenol blue, the transition in alkaline region (3); achromatic "grey" point (G).
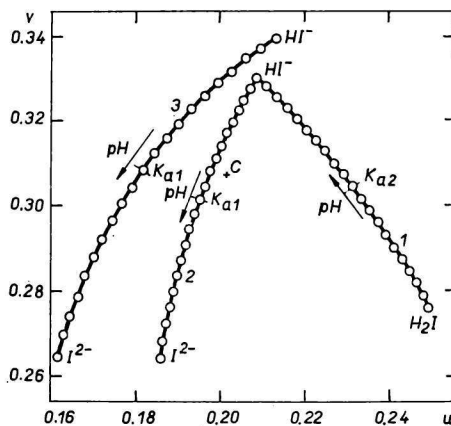
Fig. 4. The course of curves of the colour transition of xylenol blue (1, 2) and bromoxylenol blue (3) in the $CIE-uv$ uniform chromaticity-scale diagram.
All the distances between two neighbour-ing colour points represent equal differ-ences in the value of the concentration fraction, $\Delta\delta = 0.05$.

$$Q_r = \frac{Q_{r,\mathrm{HI}} J_{\mathrm{HI}}(1 - \delta) + Q_{r,\mathrm{I}} J_{\mathrm{I}} \delta}{J_{\mathrm{HI}}(1 - \delta) + J_{\mathrm{I}} \delta} . \tag{6}$$

The colour transition accompanying a simple chemical equilibrium is represented in the complementary diagram $Q_x Q_y$ by a line connecting the points of limiting forms of indicator. In Fig. 3, transitions of xylenol blue and bromoxylenol blue are drawn. Complementary coordinates of the limiting forms of indicators are listed in Table 1.

Determination of dissociation constants

The complementary diagram $Q_x Q_y$ can also be employed in the study of equilibrium systems. For acid-base indicators, the determination of dissociation constants linked with their colour changes is of primary importance. However, the line of the colour transition in the diagram $Q_x Q_y$ has to be adapted so that equal distances between the points would correspond to equal changes in the value of the concentration fraction δ.

Reilley and *Smith* [7] obtained a linear relationship between the position of the complementary colour point and the ratio of concentrations of the present components by plotting the products $Q_x J$ against $Q_y J$. The negative logarithm of the dissociation constant is then estimated by a simple interpolation of pH values of two experimental points neighbouring the midpoint of the straight line.

A mathematical evaluation requires to substitute the ratio of equilibrium concentrations by a measurable quantity. In general, the dissociation constants of the partial dissociation step $H_i I \rightleftarrows H_{i-1} I + H^+$ can be written as

$$K_{ai} = \frac{[H_{i-1}I]\, a_{H^+}}{[H_i I]} , \tag{7}$$

which is a mixed constant since activities are considered for hydrogen ions while molar concentrations for other species. With regard to eqn (5) we obtain, after rearranging, a relationship convenient for calculations

$$pK_{ai} = pH - \log \frac{J - J_{H_i I}}{J_{H_{i-1}I} - J} . \tag{8}$$

Values of the optical concentration J are suitable for calculation in all cases where the colour transition is accompanied by a marked change of the relative luminance. This condition is realized for the majority of acid-base indicators. For unicolour indicators such procedure is most advantageous.

The numerical evaluation can be supplemented by the graphical solution of eqn (8), the measured pH values being plotted on abscissa and the values of $\log (J - J_{HI})/$

Table 2

Dissociation constants of xylenol blue and bromoxylenol blue

Indicator	Equilibrium	pK_{ai} ($I = 0.2$; $t = 25°C$)
p-Xylenol blue	$H_2 I \rightleftarrows HI^- + H^+$	$pK_{a2} = 1.17 \pm 0.05$
	$HI^- \rightleftarrows I^{2-} + H^+$	$pK_{a1} = 8.94 \pm 0.01$
Bromoxylenol blue	$HI^- \rightleftarrows I^{2-} + H^+$	$pK_{a1} = 6.98 \pm 0.01$

$/(J_I - J)$ on ordinate. The resulting straight line intersects the abscissa at the zero value of this logarithm and at the value of pH equal to the negative logarithm of the dissociation constant.

Such a procedure was employed in the determination of the partial dissociation constants of xylenol blue and bromoxylenol blue. The results are summarized in Table 2. Only the dissociation constant of xylenol blue corresponding to the colour transition in an alkaline region can be compared with the published values. *Cohen* [8] reported the value of its negative logarithm 8.6 as an approximation, without further specification of conditions. From a kinetic study of *Rose* and *Stuehr* [9] $pK_{a1} = 8.88$ may be calculated for the ionic strength 0.1 and the temperature 25°C.

Colour modification of transitions

The colour transition of any indicator can be modified by adding suitable inert dyes so that the solution would be grey at a certain pH value or the concentration ratio. To facilitate the selection of the inert dyes suitable for such modification, we defined in our previous communication [10] a coefficient K_λ that enables a simple calculation of the optical concentration J from the absorbances A_λ measured at the given wavelength λ. Tabulated values of the complementary tristimulus coordinates Q_x, Q_y and the coefficients K_λ of indicators and inert dyes can be utilized for calculations of the optimum composition of the modified indicator. The necessary values of the studied indicators are listed in Table 1.

## Visual sensitivity to small colour changes

The colour quality of the transition of an indicator is an important factor for the visual observation of a titration. The primary question is the ability of an experimenter to perceive the colour change of the titrated solution and to compare it with the colour of a comparison solution, a standard, *etc*. An analogous role plays the visual sensitivity to small colour changes in a colorimetric determination of pH which is still used in many test laboratories.

An objective solution of this problem including physiological and psychological parameters is uneasy. In the $CIE-XYZ$ colorimetric space as well as in the $CIE-xy$ chromaticity diagram, equal linear distances in different places do not correspond to equal subjectively perceived differences of the colour percept, and reversely. The distance of two points in the xy chromaticity diagram is not itself sufficient for quantitative determination of the colour change.

In consequence of endeavours to express equal colour changes the xy diagram was usually linearly transformed into new coordinates. Czechoslovak Standard [11] adopted, in agreement with recommendation of CIE (1964), the uniform colour space UVW proposed by *Wyszecki* [12]. Coordinates in the plane section *i.e.* in the uniform chromaticity-scale diagram uv are derived through a transformation of the coordinates x, y [1, 11].

When the optical properties and the partial dissociation constants are known, it makes possible the detail calculations of the colour transition curves; the programmes for such purpose in the ALGOL language were recently published [13]. In Fig. 4 there are outlined the courses of the colour transition curves of xylenol blue and bromoxylenol blue calculated by a small computer Odra 1013 using a worked out programme. All the differences in the values of the concentration ratio δ of the neighbouring points are

Fig. 5. The dependence of the colour change perceptibility, $\Delta\delta/\Delta E$, on the value of the concentration fraction δ. The transition of xylenol blue in acidic (*1*) and alkaline (*2*) solutions; the transition of bromoxylenol blue (*3*).

$$\delta_i = [H_i\,l]/c_I$$
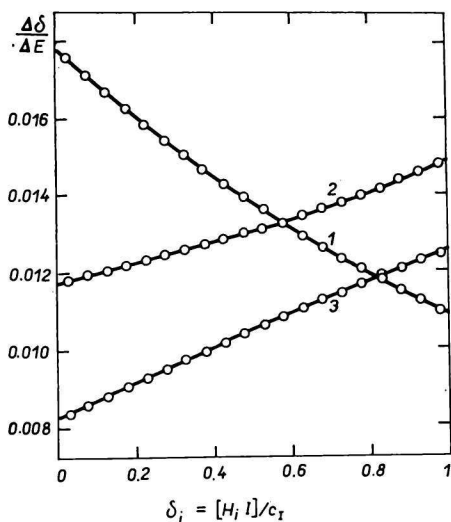
0.05, each distance representing also a certain value of the pH difference and the colour difference ΔE. The distance of two points, (U_1, V_1, W_1) and (U_2, V_2, W_2), in the colorimetric space UVW, characterizing a subjective difference in two colour percepts is calculated from an equation

$$\Delta E = [(U_1 - U_2)^2 + (V_1 - V_2)^2 + (W_1 - W_2)^2]^{1/2}. \tag{9}$$

Eqn (*9*) is valid in satisfactory degree for a realistic estimation of the subjective colour differences of two colour areas of equal size and shape, observed in white or light-grey field area by an observer photopically adapted to the used lighting, spectral composition of which is not much different from the average composition of daylight. Hence we may define for comparison of two solutions containing equal concentrations of the indicator, with regard to requirements of colour observations, so-called *colour change perceptibility* as a quantity which includes the properties of sight. This quantity may be regarded
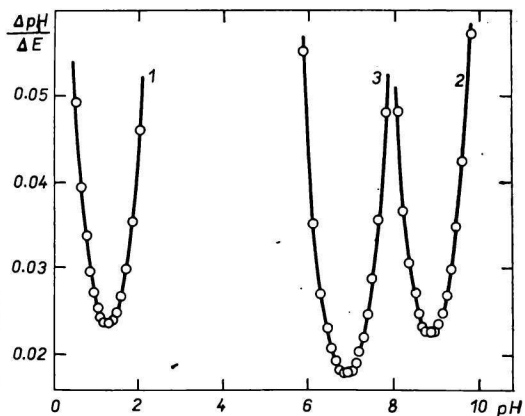

Fig. 6. The dependence of the colour change perceptibility, defined as $\Delta\mathrm{pH}/$ $/\Delta E$, on pH.
Solutions of xylenol blue (*1, 2*) and bromoxylenol blue (*3*).

e.g. as a change of the concentration ratio δ per a unit of the colour difference ($\Delta\delta/\Delta E$) or as a change of pH per a unit of the colour difference ($\Delta\text{pH}/\Delta E$). The graphic plots of this value are outlined in Figs. 5 and 6.

With respect to the calculated values, the human eye proved to be a very accurate and sensitive instrument in differentiating colour hues. For example, at the start of the colour change of bromoxylenol blue even 1.7% of blue colour of the deprotonated form of the indicator may be distinguished from yellow colour of the comparison solution, if we take into account that an average worker can distinguish the difference in colour percepts of approx. two ΔE units and that the value of the colour change perceptibility $\Delta\delta/\Delta E$ in this region is equal to 0.00834. Thus the traditional assumption of the ratio of components being equal to 10 : 90 does not seem to be always justified, at least in the comparative titrations.

Some conclusions can be drawn also for colorimetric methods of pH determination, their precision is usually reported as ± 0.1, in the optimum case ± 0.05 pH unit. Also here it is possible to achieve more accurate results, namely in the close vicinity of the half of the colour transition. The result of the colorimetric determination of pH is therefore influenced first of all by carefulness in preparing a series of comparison buffer solutions.

The slope of the colour change of an indicator in visual titrations depends on the pH changes corresponding to the addition of a titrating agent near the equivalence. The pH change corresponding to the minimum addition near the equivalence can be calculated from the equilibrium constants on which the determination is based. The slope of the colour change of an indicator during the titration can also be estimated by means of photometric indication. If we know the corresponding $\Delta v/\Delta\text{pH}$ or $\Delta v/\Delta\delta$ values we consequently can define the colour change perceptibility of an indicator in titrations with a comparison solution by another way: as the addition of a titrating agent necessary for the unit change of the colour percepts between the titrated solution and the comparison solution, $\Delta v/\Delta E$.

We applied this procedure to chelatometric titrations with metallochromic indicators and our results verified a probable connection between standard deviations of the visual titrations and the perceptibility $\Delta v/\Delta E$. This quantity encompasses both the important factors influencing the range of titration errors, *i.e.* the slope and the quality of the colour transition of an indicator. However, a great attention has to be paid to the titration procedure [14]. Our results indicate a possibility to predict the errors of visual titrations on the basis of a quite objective evaluation of the colour changes of indicators.

Discussion

The application of tristimulus colorimetry proved to be a useful tool of the study of acid-base indicators. Together with spectrophotometric methods it can provide maximum information of their colour changes.

Traditional spectrophotometric methods can help us to verify the behaviour of an indicator in solutions, to find the position of the maxima of absorption bands, to determine equilibrium constants, and some other data. The colorimetric systems *CIE* enable a completely objective mathematical description of the colour percepts of the visually observed transitions of indicators, so that we do not have to rely on the verbal description only. For this objective evaluation, the *CIE — xy* chromaticity diagram is employed, in which each colour hue is unambiguously represented by the coordinates x, y and the relative luminance Y.

The application of the complementary chromaticity diagram Q_xQ_y affords some other advantages: it facilitates the determination of the partial dissociation constants, advantageous especially in studying subsequent equilibria [7]. The large range of practical application of the diagram Q_xQ_y is especially in calculations of the optimum additions · of inert dyes when modified indicators are to be prepared.

The sensitivity of sight to small colour changes of the indicator transition can be studied by means of the colorimetric systems of uniform colour scales $CIE-UVW$ or $CIE-uv$, which enable to define and calculate the colour change perceptibility. These quantities include precision of the receptivity of the colour change percepts and they are expressed in terms of the corresponding differences of the value of the concentration of one of the indicator forms or differences in pH and also in the consumption of a titrating agent. The colour change perceptibility thus characterizes the precision of the colorimetric methods of pH determinations or the visual comparison titrations.

The presented study of the two, till now neglected acid-base indicators, xylenol blue and bromoxylenol blue, demonstrates their behaviour in aqueous solutions. It was found similar to the related sulfonephthaleins, thymol blue and bromothymol blue. This enables practical applications of both the studied indicators.

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