Yu. A. ZHDANOV, O. E. SHELEPIN, K. N. BAGDASAROV, N. I. BUDNYATSKAYA

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Abstract

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Yu. A. ZHDANOV, O. E. SHELEPIN, K. N. BAGDASAROV, N. I. BUDNYATSKAYA

STUDY OF THE INDICATOR PROPERTIES OF 2-HYDROXYPERINAPHTHINDENONE

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In studying hydroxy derivatives of perinaphthindenone, we observed that a yellow aqueous-alcoholic solution of 2-hydroxyperinaphthindenone (I) in alkaline media changes color to a deep burgundy; upon acidification of the solution the yellow color returns. This made it possible to assume the presence of indicator properties in this oxyketone, in connection with which a study was begun of the absorption spectra of aqueous-methanolic solutions of I with various pH values from 1 to 14 in the region 320–620 mμ (Fig. 1). For this purpose a series of solutions was prepared with increasing pH values and with the same ionic strength, indicated in Table 1, and a constant concentration of 2-hydroxyperinaphthindenone equal to 0.0002 g-mol/l. The absorption spectra were recorded on an SF-4 spectrophotometer; the solutions were photometered in quartz cuvettes with an optical path length of 1.00 cm. The corresponding working solutions served as comparison solutions.

Table 1

pH values of buffer mixtures

pH	Buffer composition	Ionic strength
1.10	0.1N HCl	0.1
1.30	0.1N HCl + 0.1N NaCl	0.1
2.90	0.1N HCl + 0.1N NaCl	0.1
5.50	0.1N HCl + 0.1N NaCl	0.1
6.90	0.1N HCl + 0.1N NaOH	0.1
8.70	0.1N NaCl + 0.1N NaOH	0.1
8.95	0.1N NaCl + 0.1N NaOH	0.1
9.18	0.1N NaCl + 0.1N NaOH	0.1
9.30	0.1N NaCl + 0.1N NaOH	0.1
10.80	0.1N NaCl + 0.1N NaOH	0.1
12.88	0.1N NaOH	0.1

The curves constructed for the visible part of the spectrum agree well with the data available in the literature (1) on the positions of the maxima of the

Structural formulas I and II

Figure 1: Structural formulas I and II

Fig. 1 and Fig. 2

Figure 2: Fig. 1 and Fig. 2

methanolic solution of 2-hydroxyperinaphthindenone: 363 and 426 mμ (in our case 366 and 425 mμ).

Changes in the curves in the near ultraviolet with increasing pH are generally hypochromic, with an absorption maximum at $\lambda = 366$ mμ. In the visible region the character of light absorption becomes definitely dependent on the pH value. On going from acidic to alkaline media, a hypochromic shift of the absorption maximum at $\lambda = 425$ mμ is observed, reaching a minimal value at pH 14. Simultaneously with the hypochromism, as pH increases at $\lambda = 425$ mμ, strong hyperchromism occurs at $\lambda = 500$ mμ, reaching a limiting value at pH 14. Finally, at pH 9.18, in the region from 400 to 500 mμ, the optical densities of the solution form an almost straight line parallel to the abscissa axis and passing through the isosbestic point with coordinates $\lambda = 470$ mμ and $\varepsilon = 2880$. Apparently, there is a dependence between the magnitude of light absorption and the structure of the colored forms existing in acidic and alkaline media (^{2}).

(I) (II)

If I is taken to be the corresponding yellow acidic form of 2-oxyperinaphthindenone with an optical-density maximum at $\lambda = 425$ mμ, then the red alkaline form is, in our opinion, the chelate sodium salt II, which has an absorption maximum at $\lambda = 500$ mμ. The pure isolated sodium salt, burgundy in color, has the form of scaly crystals, which do not melt but char on heating, and is stable

Fig. 1. Light-absorption curves of 2-oxyperinaphthindenone in solutions with pH values:
a—1.10; —6.90; —8.95; —9.18; —12.88*

Fig. 2. Dependence of ε on pH at $\lambda = 425$ mμ (*a*) and at $\lambda = 500$ mμ ().
Point of intersection at pH 9.18

for a long time in a desiccator over fused alkali. When this salt is dissolved in alcohol, ether, and other solvents, the solutions acquire a yellow color, evidently as a result of partial hydrolysis of the salt by small amounts of water; with an excess of water the salt is hydrolyzed completely.

Thus, the salt can exist only in media with pH greater than the value $\mathrm{pH}_{1/2\,\mathrm{ind}}$. Since the alkaline form at $\lambda = 425$ mμ has a definite value of light absorption, and the light absorption of the acidic form at $\lambda = 500$ mμ likewise does not reduce to zero, the absolute values of light absorption should not be taken into account when calculating α_{ind}; and, in characterizing the absorption spectra of this two-color indicator with closely spaced maxima on the wavelength scale, one may note only the intensification of the red coloration with increasing pH and the intensification of the yellow coloration with decreasing pH. Accordingly, for the acidic and alkaline forms the relative light-absorption values ($\Delta\varepsilon$) were found by subtracting ε_1 from ε_{14} at the given wavelength.

$$\Delta\varepsilon_{425\,\mathrm{m}\mu} = \varepsilon_1 - \varepsilon_{14} = 5370 - 1860 = 3510,$$

$$\Delta\varepsilon_{500\,\mathrm{m}\mu} = \varepsilon_{14} - \varepsilon_1 = 3370 - 780 = 2590.$$

Analogous relative light-absorption values could also have been obtained by using, as comparison solutions, solutions with pH values corresponding to the minima of coloration at the given wavelengths. It is evident that $\Delta\varepsilon_{425\,\mathrm{m}\mu} \neq \Delta\varepsilon_{500\,\mathrm{m}\mu}$.

* In order to simplify the figure, the light-absorption curves corresponding to pH values 1.30; 2.90; 5.50; 8.70; 9.30; 10.80 have been omitted; to illustrate the nature of the changes in ε values as a function of pH, Fig. 2 gives their extreme values at 425 and 500 mμ.

When the absolute values of $\varepsilon_{\max}$ at different pH values are plotted on the graph optical density of the solution—pH value (Fig. 2), two curves are obtained, intersecting one another at the point corresponding to the isosbestic point in Fig. 1 with respect to the value of ε, i.e., the point of equal optical densities at all pH values. This point, found graphically by us, corresponds to pH 9.18 and, as is seen from the graph, is not $\mathrm{pH}_{1/2\,\mathrm{ind}}$ (2). The half-value indicator exponent can be found from the $\Delta\varepsilon$ values of two straight lines corresponding to the acid and alkaline forms, and lies on the curve at the point dividing this straight line in height into halves, i.e., $\mathrm{pH}_{1/2} = 8.8$; the vertical with pH value 8.8 (Fig. 2) passes through both of these points. Thus, the calculation of α can be carried out from either of the curves.

The dissociation constant of the indicator was calculated according to the following equations (3): $pK_a = pK_{\mathrm{ind}} - \lg f_{\mathrm{ind}}$;

$$-\lg f_{\mathrm{ind}} = \frac{0.508 z^2 \sqrt{I}}{1+\sqrt{I}}; \qquad I = \frac{1}{2}\sum cz^2;$$

$$pK_{\mathrm{ind}} = \mathrm{pH} + \lg\frac{1-\alpha}{\alpha};$$

$$\alpha = \frac{\Delta\varepsilon_{\mathrm{pH}}}{\Delta\varepsilon}, \qquad pK_{\mathrm{ind}} = \mathrm{pH}_{1/2},$$

where α is the fraction of the alkaline form at the given pH value. The results of calculating the above quantities from both curves are given in Table 2.

Table 2

Values of the degree and dissociation constant of the indicator at different pH values

pH	$-\lg f_{\text{ind}}$	$\lambda =$ 425 mμ: $\alpha' = 1 - \alpha$	$\lambda =$ 425 mμ: pK_{ind}	$\lambda =$ 425 mμ: pK_a	$\lambda =$ 425 mμ: K_a	$\lambda =$ 500 mμ: α	$\lambda =$ 500 mμ: pK_{ind}	$\lambda =$ 500 mμ: pK_a	$\lambda =$ 500 mμ: K_a
6.90	0.122	0.036	8.327	8.449	$3.56 \cdot 10^{-9}$	0.058	8.112	8.234	$5.83 \cdot 10^{-9}$
8.70	0.123	0.447	8.793	8.916	$1.21 \cdot 10^{-9}$	0.417	8.816	8.939	$1.15 \cdot 10^{-9}$
8.95	0.122	0.579	8.812	8.934	$1.16 \cdot 10^{-9}$	0.587	8.798	8.920	$1.20 \cdot 10^{-9}$
9.18	0.1226	0.716	8.778	8.900	$1.26 \cdot 10^{-9}$	0.793	8.598	8.721	$1.91 \cdot 10^{-9}$
9.30	0.1225	0.818	8.648	8.771	$1.70 \cdot 10^{-9}$	0.835	8.596	8.723	$1.92 \cdot 10^{-9}$
10.80	0.122	0.988	8.862	8.984	$1.04 \cdot 10^{-9}$	0.990	8.800	8.922	$1.20 \cdot 10^{-9}$

The obtained mean values $K_{a\,\text{av}}$ are $1.274 \cdot 10^{-9}$ (for $\lambda = 425$ mμ) and $1.476 \cdot 10^{-9}$ (for $\lambda = 500$ mμ) and are in good agreement with the value of K_a for the complex compound I with $SnCl_2$ in an aqueous-alcoholic medium of composition 2 : 1, which was determined by the photometric method of isomolar series. The instability constant of the complex was determined from the deviation of optical densities from the Bouguer–Lambert–Beer law upon dilution (4) and had the value $pK = 8.91$; $K_a = 12.305 \cdot 10^{-10}$.

The transition interval of the indicator color was determined by the method of direct and reverse titration of 0.1 N solutions of hydrochloric, sulfuric, and nitric acids with 0.1 N sodium hydroxide solution, measuring the pH of the solution at the moment of noticeable color change with an LP-58 potentiometer with a glass electrode. The titrated solution, of volume 10 ml, contained 2–3 drops of a 0.1% alcoholic solution of 2-hydroxyperinaphthindenone. With good agreement of the titration results, the pH interval of the indicator color transition is equal to 7.9–9.3. When 0.01 N acid solutions were titrated with 0.01 N alkali solution and back, the pH interval of the indicator color transition was 7.5–9.3. The mean pH value, 8.6 in the first case and pH 8.4 in the second, is situated sufficiently close to the point pH 8.8 obtained photometrically (Fig. 2).

The data presented testify to the satisfactory reversibility of the titration process and to the sensitivity of the indicator 2-hydroxyperinaphthindenone.

2-Oxyperinaphthindenone (I) was synthesized by the method of Fieser and Newton (5) and purified chromatographically by precipitation on activated alumina, followed by elution of the bright-yellow layer with absolute hexane. The substance obtained had a melting point of 180°.

Rostov-on-Don
State University

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Note: Figure translations are in progress. See original paper for figures.

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