УДК 547.633.6

CONTRIBUTION TO THE KNOWLEDGE ABOUT COLOURISTIC PROPERTIES OF SOME XANTHENE DYES

© 2000 A.V.El'tsov*, D.V.Samoylov*, N.O.Mchedlov-Petrossyan

Acid-base and tautomeric equilibria of Fluorescein nitro derivatives are highly sensible to the number and position of nitrogroups in a molecule. Xanthene dyes with nitrogroups in 2 and 7 positions form anionic lactones responsible for lowering of colour intensity. Dyes with such nitrogroups demonstrate high mobility of tautomeric equilibriua quinonoid anion $\rightleftharpoons$ lactone anion at environment change from water to micellar solutions of colloidal surfactants. 4,5-dinitro derivatives are similar to halogen derivatives and don't form anionic lactones. Processes following pH change are not restricted to reversible prototropic transformations: under action of cold alkali 4,5-dinitro derivatives form deep-coloured intermediates bearing partially cleaved pyran cycle. This reaction is easily reversible under action of acid or heating.

Most of xanthene dyes were obtained as early as the end of 19-th century. But they still draw an interest due to their bright colours ranging from yellow to bluish violet and relative commercial availability.

In 3-rd edition of Colour Index International [1] thirty xanthene dyes are included: sixteen are considered as Acid ones, four as Mordant, eighteen as Solvent (particularly for cosmetics) and five (as aluminium salt) as Pigment ones. Some of them are applied as photosensitizers, although their structure allows to simultaneously use them as Acid.

Three registered xanthene dyes contain nitrogroups in molecules: Solvent Orange 16 (CI 45396), Solvent Dye (CI 45395) and Acid Red 91 (45400). Attention is drawn by crimson colour of the latter. This dye is considered in CI and Chemical Abstracts as individual substance of structure (III) and a method of its synthesis consisting in nitric acid action upon 4,5-dibromofluorescein (X = Br, Y^1 = Y^2 = H, Z = H; see scheme 1) in sulphuric acid is given. We synthesized and purified Acid Red 91 in accordance with recommended method [2]. From the chromatographic data it follows that product obtained in this way in fact is a mixture of two substances. They are 4,5-dibrom-2,7-dinitrofluorescein (III) and 4,5-dibrom-2-nitrofluorescein (IV), the latter being dominating. It turned out that dye (III) can be synthesized mostly by nitration under more drastic nitration conditions and the dye (IV) can be obtained predominantely with shortage of nitric acid [3]. As it was shown in the work devoted to HPLC of commercial Merck sample of Acid Red 91 [4], this dye comprised a mixture of three substances, one of them being main. As judged from chromatographic data and electronic spectra this stainer has a structure of 4,5-dibrom-2-nitrofluorescein (IV). There was no evidence of formation of 4,5-dibrom-2,7-dinitrofluorescein (III) and of 2,7-dibrom-4,5-dinitrofluorescein (II) from Eosin by nitration, as noted [5], but instead of this the oxidative destruction of chromophore occurs. Dye (III) was prepared by action of bromine upon 2,4,5,7-tetranitrofluorescein in boiling acetic acid, 15% by-products being formed involving three components. The high-purity substance (II) was obtained by bromination of 4,5-dinitrofluorescein in aqueous alkali [3].

According to the 3-rd edition of CI information about «Solvent dye» (CI 45395) this dyestuff was to be obtained by direct nitration of Fluorescein and it was attributed to the structure of 2,7-dinitrofluorescein (X = H, Y^1, Y^2 = NO_2, Z = H) (Ia). But well before it was stated [2] that Fluorescein forms 4,5-dinitrofluorescein (I) by direct nitration and in CI this structure corresponds to the dye Solvent Orange 16 (CI 45396). So the dyes (CI 45395) and (CI 45395) chemically represent themselves as 4,5-dinitrofluorescein (I) indeed.

Depending on medium acidity Fluorescein dyes may exist in cationic (a), neutral (b,c,d), mono- (e,f) and dianionic (g) forms. Presence of three acid-base centres in their molecules is responsible for complex system of their prototropic equilibria. Carboxygroup in ortho-

*St-Petersburg State Technological Institute (Technical University), 198013, St-Petersburg, Moskovskiy pr., 26

position to the node carbon atom allows closing of lactone ring, leading to ring-chain tautomerism. Protolytic and spectral properties of halogen derivatives of Fluorescein have been studied most thoroughly [6–10]. Substituents have a considerable influence upon the basicity of protonation centres and thus determine the state of tautomeric equilibria of neutral and monoanionic forms. Monoanions of dyes with acceptors in xanthene nucleus exist mainly in phenolate form (f). On the other hand, monoanions of Fluorescein and derivatives with acceptors in phthalic acid fragment exist exclusively in carboxylate form (e). Zwitter–ionic form (b) was observed only for the latter dyes in aqueous solutions.
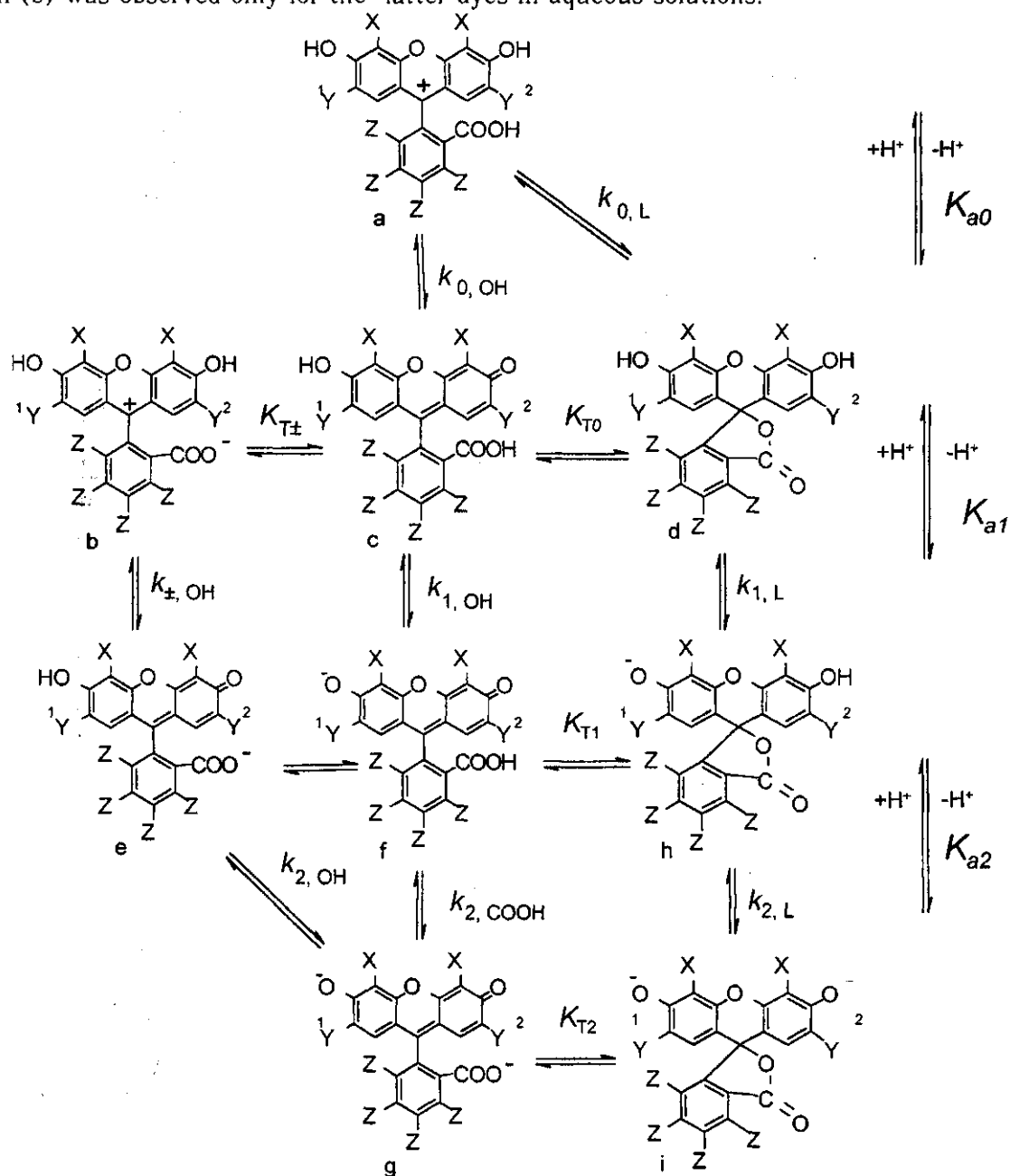
Scheme 1.

Fluorescein: X = Y^1 = Y^2 = Z = H; Eosin: X = Y^1 = Y^2 = Br, Z = H;
(I): X = NO$_2$, Y^1 = Y^2 = H, Z = H; (II): X = NO$_2$, Y^1 = Y^2 = Br, Z = H ;
(III): X = Br, Y^1 = Y^2 = NO$_2$, Z = H; (IV): X = Br, Y^1 = NO$_2$, Y^2 = H, Z = H
(V): X = Y^1 = Y^2 = NO$_2$, Z = H.

The values of molar absorptivities for dianions (g) with X = Y^1 = Y^2= H, Br, I and monoanions (f) with X = Y^1 = Y^2 = Br, I in maximum of electronic spectrum (in the region

490–530 nm) in aqueous and alcoholic solutions reach $\varepsilon_{max} = (88-112) \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. The ε_{max} values of monoanions are in average by 10–15% lower than those of dianions. Just these two forms are regarded as the dyes. This value can be taken as maximum for chromophore system of ionized hydroxyxanthene (ε_i^{hxs}). Neutral quinonoid structures (c) absorb in region 430–450 nm and they are characterised by low ε_{max} : $(10-30) \cdot 10^3$ $l \cdot mol^{-1} \cdot cm^{-1}$. This value can be considered as maximum for non−ionized hydroxyxanthene (ε_n^{hxs}). A little difference was observed between spectrum of carboxylate quinonoid monoanions (e) and neutral quinonoid structures (c) because carboxygroup almost does not effect the spectrum due to absence of conjugation between phthalic fragment and xanthene nucleus which are non−coplanar to each other. In analogy spectra of zwitter−ions (b) are similar to those of cations. Neutral lactones (d) possess no absorption in visible region due to disturbance of conjugation in xanthene chromophore as a result of sp^3−hybridization of node carbon atom. The systems of protolytic equilibria of Phenolphtalein and xanthene dyes are alike due to the similarity of their structures. Therefore it is convenient to approach protolytic equilibria of Fluorescein derivatives in connection with Phenolphtalein dyes. The lowering of dianion ε_{max} in water−organic mixture was observed for the latter at rising concentration of ethanol and methanol [11,12]. Addition of a polar aprotic solvent (DMSO, acetone) had exerted reverse effect [12]. The phenomena observed were explained by existence of tautomeric equilibrium between coloured quinonoid forms of a type (g) and colourless lactone of type (i). That was the basic argument in favour of existence of such lactones (i). Structures formed were not carbinols (which also are colourless), as the rate of fading is independent of concentration of hydroxyl−ions, and equilibrium was established practically instantaneously. The existence of the neutral forms of Fluorescein and Phenolphthalein in DMSO as lactone (d) is proved by IR spectroscopy [13]. Reasoning from this it is possible to construct the most general formal scheme of protolytic equilibria of Fluorecsein dyes, by including anionic lactones (h) and (i).

The mentioned meanings of ε_{max} correspond to the mixture of tautomeric forms with different spectral properties. Shift of tautomeric equilibrium along with solvent variation results in changes of these values and thus they cannot be considered as constants characterizing a certain chromophore structure. Consequently, these are formal values in fact (ε^{form}).

Experimental

Absorption spectra of dye solutions in 50% (by mass) aqueous ethanol were measured using SF−46 instrument (of USSR origin). pH measurements were performed on P 363−3 potentiometer and pH−121 pH−meter with ESL−43−07 glass electrode and Ag/AgCl reference electrode in a cell with liquid junction. Standard aqueous buffer solutions (pH 1.68, 4.01, 6.86, 9.18) were used for cell calibration. The pH values, corresponding to the proton activity standardized to the infinite dilution in the used mixed solvent ($pa^*_{H^+}$), were calculated according to equation: $pa^*_{H^+} = pH_{instr} - 0.20$ [14], where pH_{instr} is instrumental measured pH.

Synthesis and identification of all substances have been described earlier [3]. Spectrophotometric determination of pK_a values was carried out in 1−5 cm length cell and at dye concentrations (C) $(1.36-1.63) \cdot 10^{-5}$ M (25 °C). Phosphate, acetate and borate buffers and HCl solutions were used to provide suitable $pa^*_{H^+}$ in all solutions, the ionic strength of buffer systems being maintained constant (0.05 M). In pentyl alcohol Veronal buffers were used. All reagents were analytical−grade.

Spectra of neutral and dianionic forms were measured directly under conditions of domination of the corresponding form. The pK_{a1} and pK_{a2} values as well as monoanions spectra were

calculated by processing experimental absorbance (D) vs. $\text{p}a^*_{\text{H}^+}$ (Fig.1) by iteration method [15]. Absorbance dependences of averagely 18 solutions at 4–6 most informative wavelengths were used. For the calculation of thermodynamic values of $\text{p}K_a$ represented in Table 1 Debye–Hückel equation for ions activity coefficients was applied. The ionic parameter was assumed to be equal to 5 and activity coefficients of molecules were assumed to be unity.
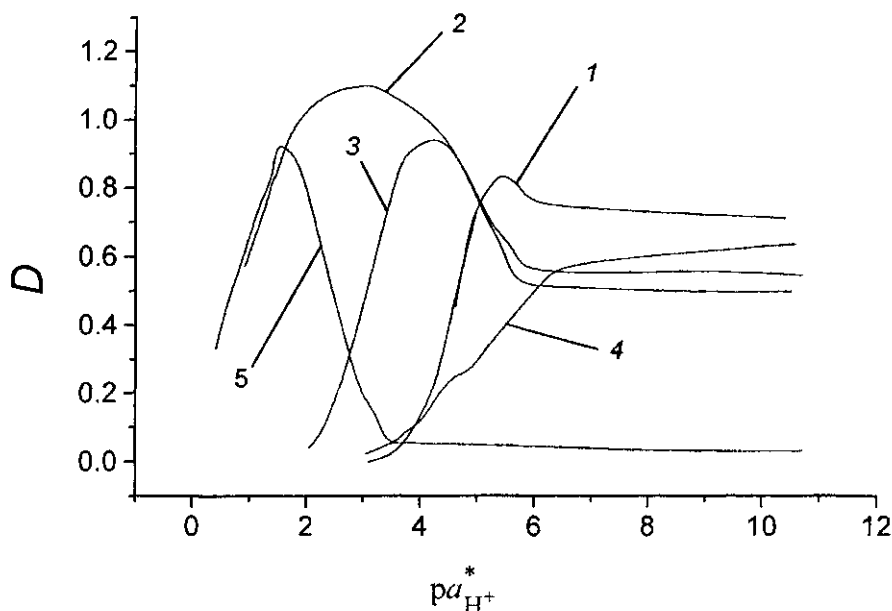

Fig. 1. Dependences of D vs. $\text{p}a^*_{\text{H}^+}$ for substances (I)-(V) in 50% aqueous ethanol at ionic strength 0.05M. 1 – (I), λ anal 515 nm, 2 – (II), λ anal 520 nm, 3 – (III), λ anal 560 nm, 4 – (IV), λ anal 535 nm, 5 – (V), λ anal 510 nm.

Results

We have applied the proposed scheme and spectral data for halogen derivatives to study Fluorescein nitro derivatives. Protolytic equilibria of dyes (I–V) were examined spectrophotometrically in 50% (by mass) aqueous ethanol. As a result the parameters of acid–base and tautomeric equilibria ($\text{p}K_a$ and $K_{\text{T}i}$, respectively) of these substances were determined and monoanions' spectra which are beyond direct observation were obtained (Fig. 2, 3). As mentioned before [13], for some dyes the fraction of these forms in a solution does not exceed 30%. It turned out to be impossible to estimate the (very low) values of the $\varepsilon^{\text{form}}$ of the neutral forms for the majority of dyes due to their limited solubility in the chosen solvent. As judged from the absence of bands corresponding to anions (compare the data in Fig. 2 and Fig. 3) spectra of dyes (I, III-V) in acetic acid (Fig. 3) represent the mixture of their neutral forms (c, d).

Since a certain kind of a spectrum was attributed to each coloured tautomeric form [16], a set of the dominant forms have been chosen for each substance on the basis of the experimental and calculated spectral data (Fig. 2, Table 1). On the analogy of Phenolphthalein derivatives [11, 12] and neutral lactones (d) of Fluorescein derivatives, the lactones of a type (h) and (i) should be colourless. Therefore the absorption of dianions of Fluorescein nitro derivatives in visible region is determined only by structure (g), and for monoanion – only by structure (f). For substance (II) the spectral curves 5a, 5b (Fig. 2) give an estimate of tautomers (f) and (g) spectra, accordingly. Using this line of reasoning, the neutral form of substances studied can absorb in visible region, even if it partially exists as quinoid (c). This form has a spectrum close to the spectrum of the neutral form of Eosin (Fig. 3, curve 6), which exists in water to a certain extent as such a tautomer [10]. Thus the spectra and the $\varepsilon^{\text{form}}$ values given in Fig. 2 and in Table 1 indicate that

anions of substances (III–V) comprise a mixture of tautomers including colourless lactones of the types (h) and (i).
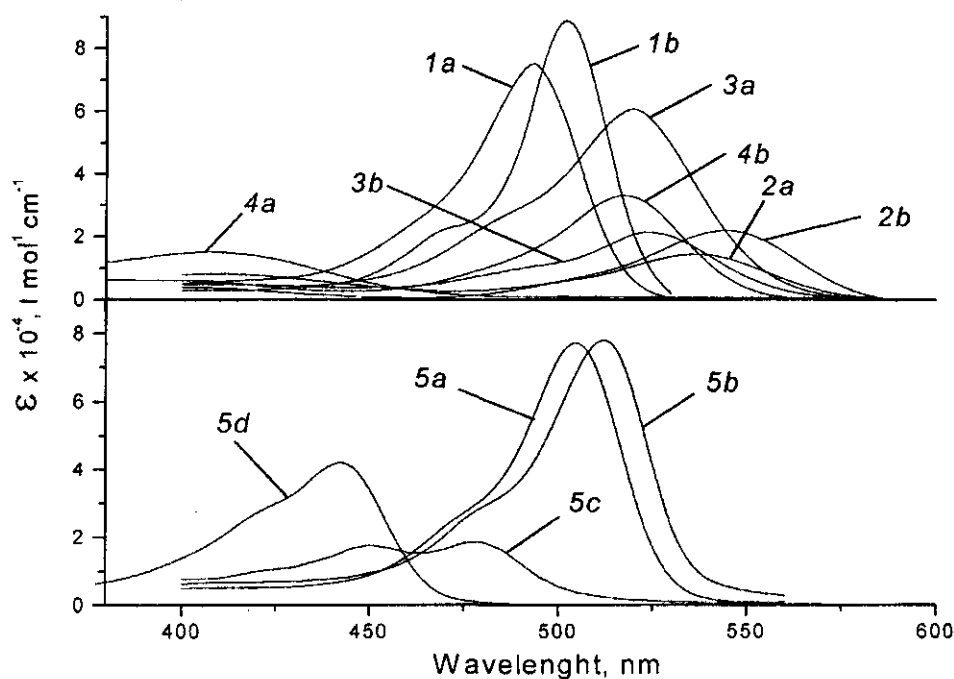

Fig. 2. Absorption spectra at $pa_{H^+}^*$ 6.9 of dianions (g, i) (1a-5a) mixture and calculated spectra of monoanions (f, h) (1b-5b) of substances (I) – 1a, 1b; (III) – 2a, 2b; (IV) – 3a, 3b; (V) – 4a, 4b; (II) – 5a, 5b; 5c – mixture of neutral forms (c,d), 5d – cation of substance (II). Spectra in 50% aqueous ethanol, as a rule at ionic strength 0.05 M (5c – at 5 M H_2SO_4, 5d – at 18 M H_2SO_4).
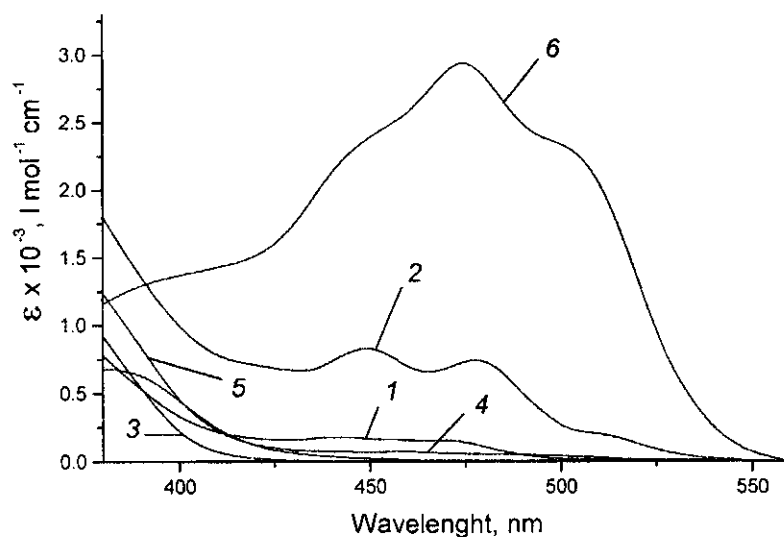

Fig. 3. Absorption spectra of Fluorescein nitro and bromo derivatives in acetic acid 1 – (I), 2 – (II), 3 – (III), 4 – (IV), 5 – (V), 6 – Eosin.

Table 1. Thermodynamic ionization constants and spectral characteristics of dyes (I – V) anions in 50% (mass) aqueous ethanol (25 °C)

Dye	Ionization constants		Long-wave absorption maxima of mono- and dianions: λ_{max}, nm ($10^{-3}\varepsilon_{max}$, $l \cdot mol^{-1} \cdot cm^{-1}$)	
	pK_{a1}	pK_{a2}	Dianion	Monoanion
Fluorescein	6.82	7.66	495 (88.5)	455 (34.3) [a]
Eosin	3.46	5.98	520 (99.6)	530 (84.0)
4,5-Dinitrofluorescein (I)	5.36±0.16	5.0±0.2	493 (76)	503 (93)
4,5-Dinitro-2,7-dibromo-fluorescein (II)	1.12±0.02	5.33±0.04	— [b] 505 (80)	— [b] 514 (81)
4,5-dibromo-2,7-dinitro-fluorescein (III)	3.39±0.04	5.15±0.08	410(8.3); 536 (14.4)	≈400(4.0); 543 (22)
4,5-dibromo-2-nitro-fluorescein (IV)	4.31±0.04	6.19±0.03	410(5.1); 519 (61)	410(5.1); 525 (21.5)
2,4,5,7-tetranitro-fluorescein (V)	1.4±0.2	2.38±0.11	407(15.1); 515 (≈1)	400(6.2); 516 (34)

Note: a) Fluorescein monoanion has structure (e). b) No evident band.

Since absorption band at ca. 515 nm in 50 % aqueous ethanol is practically not observed for tetranitro compound (V), it is possible to conclude, that this substance demonstrates the greatest propensity to formation of lactonic anion (i). Absorption bands of 2,4,5,7-tetranitrofluorescein in 400-410 nm region (Fig. 2) can be attributed to the isolated xanthene nucleus parts, whose spectrum is similar to that of 2,6-dinitrophenolate–ion. Bromonitro derivative (III) is inclined to lactonization to a less degree. On the contrary, judging from the spectra, dianions of substances (IV), (I) and especially (II) (isomeric to (III)) exist mainly as quinonoid structure (g) in the given mixed solvent. As for monoanions in the 50% ethanol the decrease in ε^{form} in relation to water in the range of 500–530 nm is also observed, their existence as lactones (h) is quite probable. Practically complete achromaticity of neutral forms in this solvent testifies the domination of lactone (d) for all studied substances, except substance (II).

It is possible to write down a set of equations, which are the complete mathematical description of this model of all equilibria:

$$pK_{a1} = pk_{1,OH} + \lg(1 + K_{T0}) - \lg(1 + K_{T1}) = pk_{1,L} + \lg\left(1 + K_{T0}^{-1}\right) - \lg\left(1 + K_{T1}^{-1}\right) \qquad (1)$$

$$pK_{a2} = pk_{2,COOH} + \lg(1 + K_{T1}) - \lg(1 + K_{T2}) = pk_{2,L} + \lg\left(1 + K_{T1}^{-1}\right) - \lg\left(1 + K_{T2}^{-1}\right) \qquad (2)$$

where $k_{1,OH} = a_{H^+}^* [i]/[c]$; $k_{1,L} = a_{H^+}^* [h]/[d]$; $k_{2,COOH} = a_{H^+}^* [g]/[f]$;

$k_{2,L} = a_{H^+}^* [i]/[h]$; $K_{T0} = [d]/[c]$, $K_{T1} = [h]/[i]$, $K_{T2} = [i]/[g]$.

Proceeding from the given equations, the constants of tautomeric equilibrium quinonoid ⇌ lactone (K_{Tj}), were estimated as:

$$K_{Tj} = \left(\varepsilon_{n,i}^{hxs} - \varepsilon^{form}\right) / \varepsilon^{form}, \qquad (3)$$

for K_{T0} calculations the ε_n^{hxs} value instead of ε_i^{hxs} (for K_{T1} and K_{T2}) was used. ε^{form} was measured directly for neutral and dianionic forms and calculated for monoanionic ones. One could calculate all parameters included into eqn. (1,2) but some of them are just formal values in fact because not all of corresponding tautomeric forms are formed in significant concentration for considered substances.

Discussion

Let's consider substituents influence on a location of a maximum long-wave absorption band of quinoid double charged anions (g) of nitro derivatives in 50 % aqueous ethanol. From

data given in Table 1 for dianions of di- and mononitro derivatives one may consider that consecutive introduction of nitrogroups to 2 and 7 positions of Fluorescein molecule results in bathochromic shift of a maximum of the long-wave absorption band by 20 nm for each nitrogroup. Comparing in pairs spectra of dianions of dinitro derivative (I) and of dibrominated substance (II), as well as of Fluorescein and Eosin, one may conclude that the bromine atoms in the same positions cause similar in character but weaker colour deepening than nitrogroups ($\Delta\lambda_{max}$ 8 nm).

Using 4,5-dinitrofluorescein as an example one can observe, that such nitrogroups contrary to 2,7-nitrogroups insignificantly influence the position of a long-wave absorption band maximum of dianion (g): a hypsochromic shift makes 2 nm with reference to Fluorescein. On the other hand the introduction of bromine atoms in positions 4 and 5 results in bathochromic shift of dianion long-wave absorption band by 15 nm compared with Fluorescein. The occurrence of bromine atoms in positions 2 and 7 in this structure enhances effect and results in total bathochromic shift of the specified band by 25 nm.

Comparing in pairs Eosin with dibromo derivative (II) and isomeric substance (III) with tetranitro derivative (V) makes it evident that the replacement of bromine by nitrogroup in positions 4 and 5 results in hypsochromic shift of an absorption maximum of dianion (g) by 15 and 21 nm, correspondingly, though the total shift relative to Fluorescein is still bathochromic (10 and 20 nm correspondingly). It is curious, that the hypsochromic shift following introduction of nitrogroup in the position conjugative to phenolate group is observed for the first time. In case of 2,4,5,7-tetranitrofluorescein (V) a combination of the specified hypsochromic effect of nitrogroups in positions 4,5 with a bathochromic effect of the same substituents in positions 2,7 gives total bathochromic shift of a long-wave absorption band maximum of dianion by 20 nm relative to dianion of Fluorescein. It is clear that nitrogroups in 2 and 7 positions exert the major influence upon location of long-wave absorption band of Fluorescein nitro derivatives.

For single-charged phenolate monoanions (f) of nitro derivatives shifts of long-wave absorption band maxima in relation to Eosin monoanion are nearly the same as corresponding $\Delta\lambda_{max}$ of dianions in relation to Eosin dianion. Substance (V) is an exception since hypsochromic shift of absorption band maximum of its monoanion is slightly lower than that of dianion (5 nm vs.14 nm). Consequently, influence of nitrogroup position upon the shift of long-wave absorption band maximum in electronic spectra of quinoid anions is almost independent of the value of their charge.

We have performed quantum-chemical calculation of dianions of isomeric substances (II) and (III) using AM1 method realized in program HyperChem 5.01. As it turned out, xanthene nucleus in both structures is planar, but dihedral angles between its plane and phthalic fragment (76°) and nitrogroup (54°) in structure (II) differ from those in structure (III): 94° and 28°, respectively. The HOMO configuration and dipole moments of ground states (12 D) are repeated despite of differences in geometry of carbon skeleton and substituents position in xanthene nucleus (Fig.4). Consequently the changes in molecule electronic configuration following the excitation are responsible for difference between electronic spectra of quinoid dianions (g) of these dyes. As appeared this difference emerges indeed in passing of dianions of dyes (II) and (III) from ground to Franck-Condon excited state, which is presented in Fig. 5.
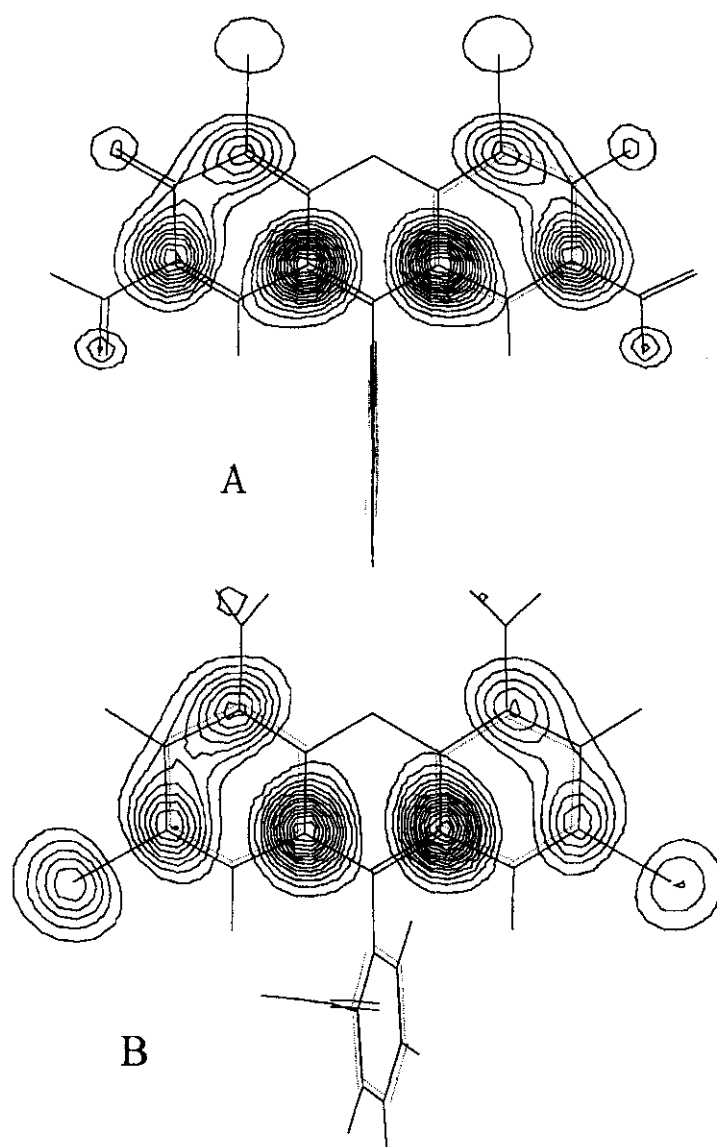
Fig. 4. HOMO configuration of substances (III) – A and (II) – B. The cross-section of squared wave function by the plane parallel to xanthene nucleus at distance 1.5Å from it is shown.
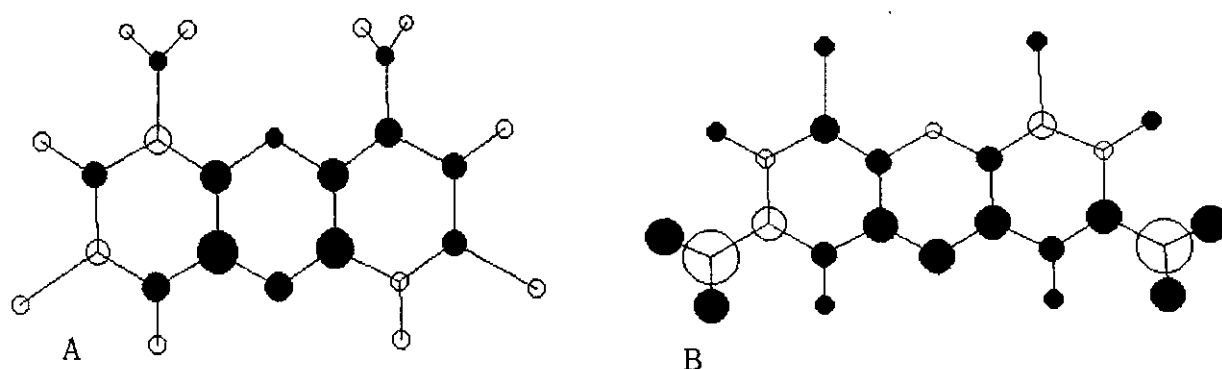

Fig. 5. Diagrams of net charge redistribution over atoms of dianions (g) of dyes (II) – A and (III) – B at excitation to Franck-Condon excited state. (Phthalic acid fragments not shown). The squares of circles are proportional to the values of net charge changes. Black – negative change, white – positive.

As stated earlier [11,12], the relationship between the tendency of Phenolphtalein dianion to lactonization and of tautomeric equilibrium mobility manifests itself on solvent variation.

The less stable are quinonoid anions (g), the more mobile is the equilibrium. By means of spectral data for isomeric nitrobromo compounds (II) and (III) in 50% aqueous ethanol we have shown that nitrogroup position influences the relative stability of quinoid (g) and lactonic (i) dianions. The mobility of tautomeric equilibrium of neutral form of Fluorescein becomes obvious when medium is changed from water to micellar solutions of colloidal surfactants. In so doing tautomeric equilibrium has been shifted towards lactonic structures of (d) type through the variation of pseudophase nature [16]. Surfactants of all types display insignificant influence on absorption spectrum of nitrobromo compound (II) dianion (Fig. 6A) which coincides with earlier observations for dianions of Fluorescein halogen derivatives which are not inclined to lactonization [16]. It testifies that in this case mobility of the equilibrium does not even reveal itself and solvatochromic effect takes place [17] proving high stability of quinonoid dianion (g) of this compound. On the other hand the character of spectrum variation of isomeric bromonitro compound (III) in solutions of all three surfactant types (Fig. 6B) is governed by regularity noted for Phenolphtalein derivatives: tautomeric equilibrium of this dye is mobile and the dye is inclined to lactone formation.
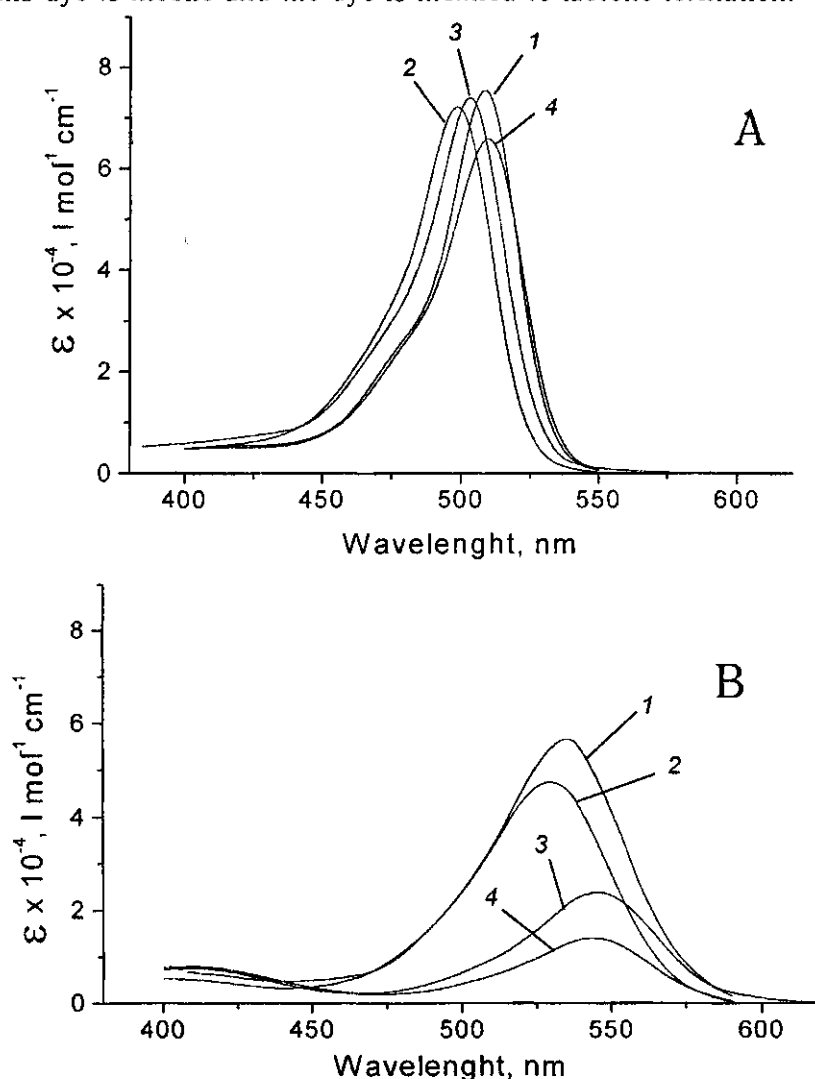

Fig. 6. Absorption spectra of dianions (g, i) mixture of substances (II) - A and (III) - B in aqueous media at pH 6.9: 1 - water with no additives; with addition of: 2 - 0.016 M sodium dodecylsulphate, 3 - 0.003 M Cetyltrimethylammonium bromide, 4 - 0.01 M Brij 35.

The influence of nitrogroups position becomes clearly evident in comparison between compounds (I) and (IV). Insignificant variation in absorption spectra of these compounds at medium change from water to 50% aqueous ethanol (Fig. 7) does not allow to conclude that anions of these substances transform into the lactone form. Though the tendency of spectra variation following a further medium change to n-pentyl alcohol (Fig. 7) testifies that in the

considered pair of substances undoubted lactonization of dianon is observed only for dye (IV) bearing nitrogroup in position 2. Consequently the appearance of at least one nitrogroup in either 2 or 7 positions stabilizes lactionic dianions (i) in this solvent.
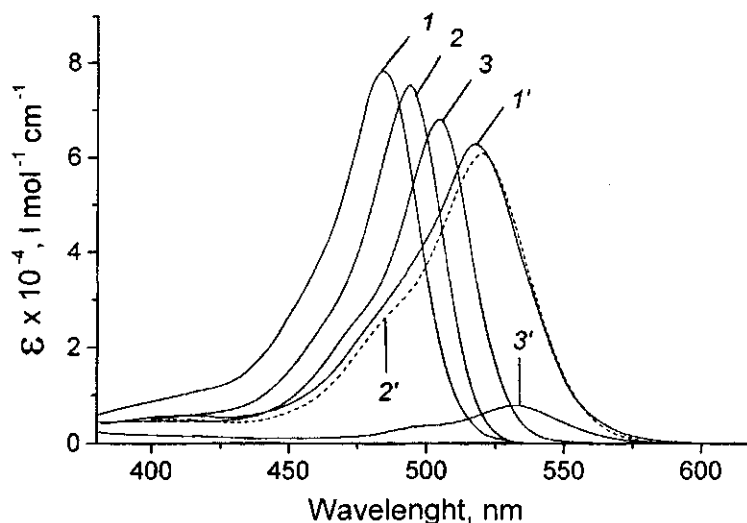

Fig. 7. Absorption spectra of dianions (g, i) mixture of substances (I) – (1-3) and (IV) – *(1'-3')* in in water pH ≈8.5 (1,1'), in 50% aqueous ethanol at pH 6.9 (2,2') and in n-pentyl alcohol + 4·10⁻⁴ M Veronal + 1.6·10⁻⁴ M BuONa (3,3').
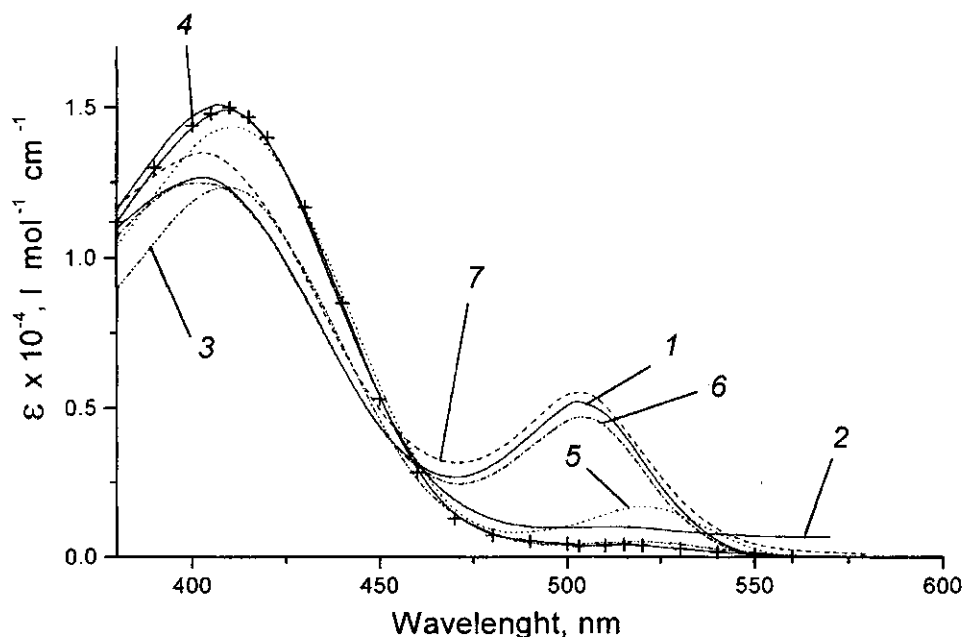

Fig. 8. Absorption spectra of 2,4,5,7-tetranitrofuorescein (V) dianions (g, i) mixture in different media: 1 – water, 2 – 50% aqueous ethanol, 3 – n-pentyl alcohol + 4·10⁻⁴ M Veronal + 1.6·10⁻⁴ M BuONa, 4 – 0.01 M Brij 35 in water, 5 – 0.003 M cetyltrimethylammonium bromide in water, 6 – 0.016 M sodium dodecylsulphate in water, 7 – 0.092 M sodium dodecylsulphate in water. In micellar media pH 6.9.

Since the only difference between cations (a) of isomeric substances (II) and (III) is position of substituents in relation to hydroxygroup, it is convenient to assume equal acidity ($pK_{0,OH}$) of these groups. But, as appeared, substance (II) completely turns into cation (a) in sulphuric acid just at H_0 −7.6, whereas dye (III) remains in form of colourless lactone (d) even at H_0 −8.6. Thus the difference in ability of these nitrocompounds for protonation clearly demonstrates high stability of neutral lactone (d) of substance (III) as compared with substance (II) in this medium, in agreement to the equation:

$$pK_{a0} = pk_{0,OH} - \lg(1 + K_{T_0}),\qquad(4)$$

This coincides with the relative stability of lactones in acetic acid (K_{T_0}).

Generalizing spectral data on neutral (d) and anionic (i) lactones stability of isomeric nitrocompounds (II) and (III) in 50% aqueous ethanol, in surfactant micellar solutions, as well as in acetic acid one may conclude that nitrogroups in 2 and 7 positions stabilize corresponding lactones. And on the other hand the same groups in 4 and 5 positions stabilize quinonoid structures (c) and (g).

It is convenient to compare antithetical effects of 4,5 and 2,7 nitrogroups upon the state of tautomeric equilibrium of dianions using tetranitrofluorescein (V) as an example. The mobility of tautomeric equilibrium of its dianionic form (g $\rightleftharpoons$ i) at medium variation is clearly shown in Fig. 8. Judging from spectra of dye (V) dianions in n-pentyl alcohol and micellar surfactant solutions the mentioned equilibrium is shifted toward the right in organic phase or micellar pseudophase.

Considering 2,4,5,7—tetranitrofluorescein it becomes evident that with nitrogroups in 2 and 7 positions the transformation of mono— and dianions to corresponding lactones (h, i) is further facilitated by the same groups in positions 4 and 5 but not hindered by them, as it can be concluded from comparison of substances (II) and (III). Thus presence of nitrogroups in 2,7—positions of xanthene nucleus appears to be a principal structural factor responsible for propensity of Fluorescein derivatives to closing of lactone cycle.

For Fluorescein nitro derivatives we made an attempt to calculate standard enthalpies of transition of neutral, mono— and dianionic quinonoids (c, f, g) to corresponding lactones (d, h, i) in vacuum. These values are considered as parameters characterizing total influence of all diversities between initial and resulting structures upon the process of lactone cycle formation. The entropy change was treated as constant since the same structure transformation was involved. Quantum—chemical calculations were performed by using the above mentioned technique. As it evidences from calculations (Table 2) for dianions the lactonization is in general a more energetically favourable process than for monoanions which is consistent with the experimental data ($K_{T1} < K_{T2}$). Good concordance is observed between ΔH(g$\rightarrow$i) values and tautomeric equilibrium constants for dyes dianions (K_{T2}), confirming the greater stability of tetranitrofluorescein (V) lactonic dianion (i). The high tendency to lactone (d) formation observed for all the neutral forms of compounds (I–V) is in good agreement with calculated ΔH(c$\rightarrow$d) values. Contradiction with calculations is observed only for substance (IV) whose monoanions are more inclined to lactonization than dianions as shown experimentally.

Table 2. Calculated standard enthalpies of formation (ΔH) kcal / mol of different acid-base tautomeric forms of Fluorescein nitro derivatives in vacuum

Forms / Compounds	c	d	f	h	g	i	Transformation		
							c $\rightarrow$ d	f $\rightarrow$ h	g $\rightarrow$ i
I	−58	−65	−135	−122	−124	−125	−7	13	−1
II	−50	−53	−124	−114	−114	−112	−3	10	2
III	−49	−54	−116	−116	−114	−126	−5	0	−12
IV	−57	−61	−125	−117	−111	−122	−4	8	−11
V	−43	−49	−132	−123	−128	−146	−6	9	−18

The pK_a and K_T values and spectral data obtained for dyes (I–V) allow to believe that on application of these dyes as «Solvent» (for cosmetics) the forms (c, d, f, h) are mostly presented in medium used, whereas under acid and mordant dyeing conditions forms (g, i) are dominating. Therewith the forms (c, f) are responsible for hue in the former case and forms (f, g) − in the latter. Intensity of colour is determined by state of equilibrium between coloured quinonoid (c, f, g) and colourless lactonic (d, h, i) forms. It is higher in polar aprotic solvents similar to acetone, DMSO, DMFA and lower in alcohols. Thus it may be thought that colour brightness of Acid Red 91 dye acceptable for acid dyeing is conditioned by spectral properties of exactly mononitro dye (IV) dianion (g), much less inclined to lactone formation than dinitro product (III), which is included in CI.

However the knowledge concerning absorption spectra of each form and medium acidity at which they exist doesn't permit to predict the hue and brightness of colour in commercial application. It is caused by difficulty in determining dye forms ratio in non-buffered organic media. Therefore it is reasonable to use buffered systems for exact reproducing of defined colours.

But the processes following pH change are not restricted to the reversible prototropic transformations. As early as 1902 it was noticed [2] that initially yellow alkaline solutions of 4,5-dinitrofluorescein (I) and 2,7-dibromo-4,5-dinitrofluorescein (II) gradually turned deep blue even cold, and under further action of hot alkali became colourless during several hours. Colour of 2,4,5,7-tetranitrofluorescein solution changed neither upon rising pH to 12 nor during standing at this pH for several days [3]. With regard to mentioned above lactonization tendencies it may be presumed that discrepancy in behaviour of these substances in alkaline solutions is due to existence of substances (I) and (II) in this medium predominately in quinonoid form (g), whereas 2,4,5,7-tetranitrofluorescein (V) exists mostly in lactonic form (i). These transformations may occur yet in hot solution of sodium carbonate and lead to poor reproducibility of resulting colour.

Upon the action of acetic acid on deep blue alkaline reaction mixture of dye (I) the orange precipitate yields. It is possible to isolate individual product from this solid, being distinguishable from initial substance in some properties. Judging from elemental analysis and H^1-NMR data this compound is a dye of Phenolphtalein group bearing partially cleaved pyran cycle – 2-[2,4-dihydroxy-3-nitrophenyl-(2-hydroxy-3-nitro-4-oxo-2,5-cyclohexadienylyden)-methyl]-benzoic acid (VI)

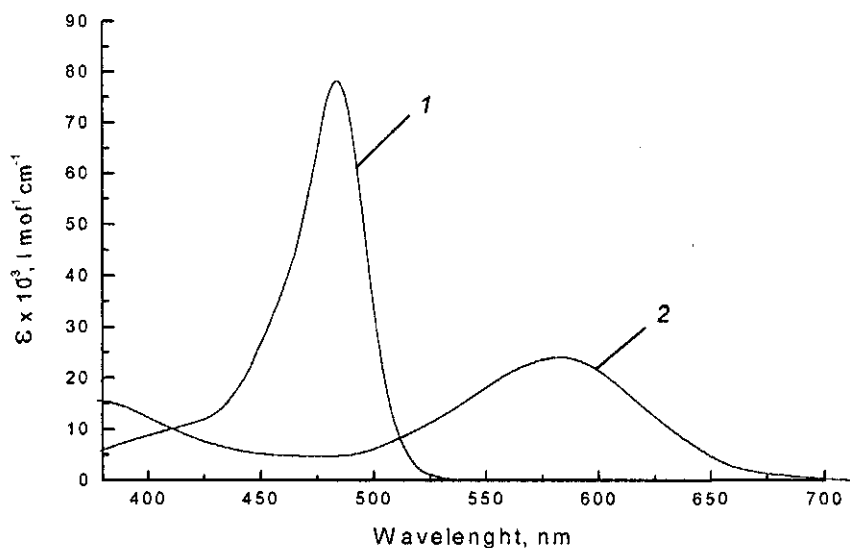
(VI)
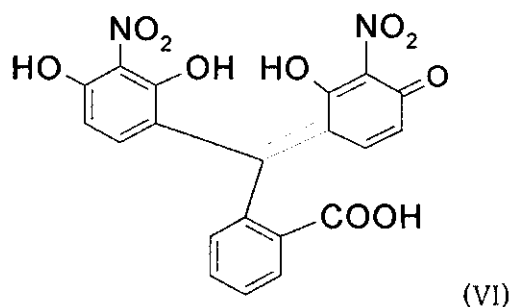
though its structure is unequally proved.

Fig. 9. Absorption spectra of dye (I) in 0.1 M $NaHCO_3$ solution (pH 8.5) and dye (VI) in 0.1 M NaOH solution (pH 13).

Deep blue colour (λ_{max} 580 nm, $\lg\varepsilon$ 4.37, Fig. 9) of this substance in aqueous solution at pH > 11 may be referred to completely ionized form (tetraanion), and at pH 3-4 substance (VI) has almost the same spectrum as a parent compound (I) (λ_{max} 482 nm, lg ε 4.81). At intermediate pH region colour of dye (VI) is greenish-brown and so may be attributed to the mixture of acid-base forms. Owing to these properties it might be reasonable

to have used this substance as acid—base indicator with wide pH range (2—10) of colour variation.

Dye (VI) under action of phosphoric acid or being heated at 90°C during 2 hours forms initial compound (I). 2,7—dibromo—4,5—dinitrofluorescein (II) under action of alkali gives the similar dye of Phenolphtalein group, which slightly differs from dye (VI) in properties, with exeption that it begins transformation into parent compound (II) just at 100°C.

References

1. Colour Index International, 3rd Edition. The Society of Dyers and Colourists (1971).

2. Hewitt J.T., Woodforde J. W. C. J. Chem. Soc. 1902. V.81. P. 893-900.

3. Samoylov D.V., El'tsov A. V., Martynova V. P., Zh. Obsh. Khim. (Russ. J. Gen. Chem). 1999. V. 69. 9. P. 1509-1519.

4. Gandin E., Piette J., Lion Y. F. J. Chromatogr. 1982. V.249. 1. P. 393-401.

5. Freidlaender Fortschritte der Thierfarbenfabrikation und verwandter Industriezweige. Berlin, Springer Verlag. 1908. Bd.8. S. 18.

6. Levillain P., Fompeydie D. Anal. Chem. 1985. V.57. 13. P. 2561-2563.

7. G. Oster, G.H. Oster, G. Karg. J. Phys. Chem. 1962. V.66. 12. P. 2514-2516.

8. Issa I.M., Issa R.M., Ghoneim M.M. Z. phys. Chem. (Leipzig). 1972. Bd.250. H.3,4. S. 161-173.

9. Amat—Guerri F., Lopez—Gonzalez M. M. C., Sastre R., Martinez—Utrilla R. Dyes and Pigments 1990. V.13. P. 219—232.

10. Mchedlov—Petrossyan N.O., Adamovich L.P., Nikishina L.E. Zh. Anal. Khim. (Russ. J. Anal. Chem.). 1980. V.35. 8. P. 1495-502.

11. Mchedlov—Petrossyan N.O., Romanenko A.V., Nikishina L.E. Zh. Anal. Khim. (Russ. J. Anal.Chem.). 1984. V.39. 8. P. 1395—1403.

12. Mchedlov—Petrossyan N.O. Zh. Anal. Khim. (Russ. J. Anal.Chem.). 1986. V.41. 10. P.1771—1779.

13. Mchedlov—Petrossyan N.O., Salinas Mayorga R., Surov Yu.N. Zh. Obsch. Khim. (Russ. J. Gen. Chem.) 1991. V.61. 1. P. 225—233.

14. Kozakova E., Čsefalvayova B., Zajacova J. Chem. Zvesti.1982. V.36. 1. P.345-351.

15. Mchedlov—Petrossyan N.O., Salinas Mayorga R. J. Chem. Soc., Faraday Trans., 1992. V.88. 20. P. 3025-3032.

16. Mchedlov—Petrossyan N.O., Kleshchevnikova V.N. J. Chem. Soc., Faraday Trans. 1994. V.90. 4. P. 629—640.

17.Reed W., Politi M. J., Fendler J. H. J. Am. Chem. Soc. 1981. V.103. 15. P. 4591-4593.

Поступила в редакцию 13 марта 2000 г.

Положение кислотно-основных и таутомерных равновесий нитропроизводных Флуоресцеина весьма чувствительны к числу нитрогрупп и положению их в молекуле красителя. Ксантеновые красители с нитрогруппами в положениях 2 и 7 образуют анионные лактоны, ответственные за снижение интенсивности поглощения света. Такие соединения демонстрируют высокую подвижность таутомерного равновесия (хиноидный анион) $\rightleftarrows$ (лактонный анион) при переходе от воды к мицеллярным растворам коллоидных ПАВ. 4,5–Динитропроизводные проявляют сходство с галогенпроизводными и не образуют анионов-лактонов. Процессы, протекающие при изменении pH в широких пределах, не ограничиваются обратимыми протолитическими превращениями: 4,5–динитропроизводные при действии холодной щелочи образуют глубокоокрашенные интермедиаты с частично разомкнутым пирановым циклом. Реакция легко обратима при действии кислоты или при нагревании.