

## CHANGES IN THE EMISSION SPECTRA OF URANIN IN AQUEOUS SOLUTION WITHIN THE LOW-CONCENTRATION RANGE

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The present paper reports on a study of the time-evolution of emission spectra of uranin in the concentration range:  $3.5 \times 10^{-5}$  g/cm<sup>3</sup> to  $3.7 \times 10^{-7}$  g/cm<sup>3</sup>, and also on the effect of certain physical and chemical factors on such changes.

It was determined, on the basis of the research conducted, that during storage of the solutions the balance of ions present in solution is disturbed. This supports results obtained during the observation of the time-evolution of absorption spectra. It was concluded that the factor which could affect the time-development of the spectra is reaction with the basic constituents of air. Time changes in the emission spectra were not observed in solutions buffered over the whole pH range.

One of the objectives of the study, among others, was to relate specific ionic forms to the corresponding maxima of emission. The emission band of the single-valence anion of uranine cannot be resolved by experimental means. This band was determined by computation, and on the basis of the calculations its maximum was located at  $\lambda = 530$  nm.

### Introduction

Fluorescein is a xanthenic dye occurring with a wide range of pH values in various ionic forms [19]. Initial studies conducted by Pringsheim [16] and Levshin [14] for a concentration of  $5 \times 10^{-5}$  g/cm<sup>3</sup> suggested that fluorescein occurs as a bivalent anion in a basic environment, and as a cation in an acidic one. Zanker and Peter [19] studied fluorescein in a dioxane-water solution in a wide range of pH values. The authors described the stages of dissociation and gave a listing of seven distinct forms in which fluorescein can occur. According to the authors form VII is a transient state between a cation and a neutral particle. Also, no discernible contribution of the tautomeric form of the univalent anion to the spectra was observed. The spectral characteristics of the remaining forms of fluorescein were studied by many authors [5, 12, 15, 17] and others.

On the basis of the literature cited it can be said that the data pertaining to ionic

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forms of fluorescein are not in agreement. To determine the causes for the occurrence of discrepancy in the results, and to describe uniquely the position of emission and absorption maxima of individual ionic forms of fluorescein, the authors of Refs [5-8] performed a study of the absorption spectra of uranine in dilute aqueous solution as a function of dye concentration, pH value of solution, and storage method. In the course of observations of absorption spectra by the authors of Refs [5] and [17] it was noted that the absorption spectra of solutions of uranine and fluorescein which had been stored for a long time were different from the spectra of freshly prepared solutions.

The object of the present research was to see if the observed time evolution of absorption spectra also occurs in emission and to determine the causes for these changes as well as the conditions under which they occur.

This makes it possible to compare the results of various authors pertaining to tests of the theory of luminescence through elimination of error arising from the changeability of the solutions in time. It also allows one to avoid error in comparing series of measurements taken at fixed intervals of time, by determining the conditions in which the properties of the solutions do not change.

The research was also aimed at determining by computational methods the emission spectrum of the monovalent ion.

### *1. Description of experiment*

The sodium salt of fluorescein, uranin, produced by BDH L. Chem. Group, was used in the experiment. The essential solvent used was bidistilled water with a maximum air content, from a redistillator with a silvered tank.

Spectral measurements of uranine as a function of a variety of physical and chemical factors were carried out for the following solutions:

a) water solutions with a dye concentration of:  $3.5 \times 10^{-5}$ ,  $10^{-5}$ ,  $7 \times 10^{-6}$ ,  $3.5 \times 10^{-6}$ ,  $10^{-6}$ ,  $7 \times 10^{-7}$ ,  $3.5 \times 10^{-7}$  g/cm<sup>3</sup>. The corresponding masses of the substance were measured out to within  $10^{-6}$  g accuracy;

b) unbuffered acidic solutions with a pH value within the range 7 to 0, and buffered solutions with a pH value from 7 to 4, and also solutions of uranin in 5n HNO<sub>3</sub>.

The buffered solutions with the desired pH value were obtained by adding to the water, before dissolving the dye, a suitable amount of buffer composed of nitrous acid, ammonia, and sodium base;

c) basic solutions with a pH value in the range 7 to 12;

d) water solutions of  $c = 10^{-6}$  g/cm<sup>3</sup> concentration, saturated with such gases as nitrogen, oxygen, or carbon dioxide.

Saturation with the gases was carried out by running the gas through the solution with the aid of an inserted glass pipe.

It was endeavored to keep the rate of flow of the gas a constant for all the samples.

The solutions were stored at a constant temperature in dark containers.

Measurements of the emission spectra were carried out on a typical experimental set-up [9] at a constant room temperature.

To stimulate fluorescence in specified ranges of the spectrum, interference filters (IF Jena) of the following transmission maxima were used:

$\lambda = 435$  nm (filter no III)

$\lambda = 450$  nm (filter no I)

$\lambda = 500$  nm (filter no II).

These filters transmitted a band of a 15 nm. The pH value of the solutions was measured with a pH-meter of Polish production, type LBL A63, using a glass and calomel electrode.

## 2. Description of calculation of the emission spectra for a singly charged negative ion

The emission band of the singly charged negative ion is partly superimposed on the band of a different form of uranine with which it coexists in the solution. The object of the calculations is to resolve the emission spectrum of the singly charged ion on the basis of that spectrum which indicates its presence in the solution.

The intensity of light over the whole range of emission spectra of the solution analysed, which we obtain from measurement, can be expressed by the formula:

$$J(\lambda, \lambda', x) = \int_{x_1}^{x_2} \int_{\lambda'} J_0 e^{-\mu(\lambda)x} \eta(\lambda, \lambda') \mu(\lambda) d\lambda' dx \quad (2.1)$$

where  $J_0$  – intensity of exciting light,  $\mu(\lambda)$  – absorption coefficient for a given wavelength of the exciting light,  $\eta(\lambda, \lambda')$  – emission efficiency,  $x$  – distance from the beginning of the exciting pulse,  $\lambda$  – wavelength of the exciting light, constant for the spectrum analysed (monochromatic excitation),  $\lambda'$  – wavelength of light emitted.

Upon integration we obtain

$$J(\lambda, \lambda') = \int_{\lambda'} J_0 (e^{-\mu(\lambda)x_1} - e^{-\mu(\lambda)x_2}) \eta(\lambda, \lambda') d\lambda' \quad (2.2)$$

The light of fluorescence was recorded by means of a photomultiplier after spectral decomposition in a monochromatic analyser. The spectrum obtained is a superposition of emission intensities from both luminescent centres. We divide expression (2.2) by  $I_0$  to obtain an expression for relative intensity of emission. The intensity of exciting light  $I_0$  was constant in all the cases studied.

We then get:

$$\frac{J}{J_0} = \int_{\lambda'} (e^{-\mu(\lambda)x_1} - e^{-\mu(\lambda)x_2}) \eta(\lambda, \lambda') d\lambda' \quad (2.3)$$

The total intensity of emission for a given wavelength can be expressed as one term of the integral (2.3)

$$W(\lambda, \lambda') d\lambda' = (e^{-\mu(\lambda)x_1} - e^{-\mu(\lambda)x_2}) \eta(\lambda, \lambda') d\lambda' \quad (2.4)$$

where  $\eta(\lambda')$  – efficiency corresponding to a given wavelength of emitted light.

In order to compute  $\eta(\lambda)$  we take advantage of the definition for emission efficiency, which we can express by the formula:

$$\eta(\lambda) = \frac{\int W(\lambda, \lambda') d\lambda'}{E_a(\lambda)}. \quad (2.5)$$

The integral  $\int W(\lambda, \lambda') d\lambda'$  gives the total energy emitted upon absorption of energy  $E_a(\lambda)$ .

The emission spectra used were normalised with respect to any given wavelength, so it can be stated that:

$$W(\lambda, \lambda') = bK(\lambda, \lambda')$$

where  $b$  is the normalisation factor, and  $K(\lambda, \lambda')$  is the relative intensity of emitted light. Expression (2.5) can be written in the form:

$$\eta(\lambda) = \frac{\int bK(\lambda, \lambda') d\lambda'}{E_a(\lambda)} = \frac{b}{E_a(\lambda)} \int K(\lambda, \lambda') d\lambda' \quad (2.5')$$

$\eta(\lambda) = \int \eta(\lambda, \lambda') d\lambda'$ , so we can write

$$\eta(\lambda, \lambda') = \frac{b}{E_a(\lambda)} \cdot K(\lambda, \lambda') = B \cdot K(\lambda, \lambda') \quad (2.6)$$

$B = \frac{b}{E_a(\lambda)}$  is a constant which can be determined from relation (2.5').

$$B = \frac{\eta(\lambda)}{\int K(\lambda, \lambda') d\lambda'}$$

Substituting expression (2.6) into (2.4) we obtain

$$W(\lambda, \lambda') = (e^{-\mu(\lambda)x_1} - e^{-\mu(\lambda)x_2}) \cdot B \cdot K(\lambda, \lambda'). \quad (2.7)$$

From experiment, we know the emission spectrum of the doubly charged ion, and also the spectrum which is a superposition of the bands of singly and doubly charged ions  $W_c(\lambda, \lambda')$ . Assuming that

$$W_c(\lambda, \lambda') = W_I(\lambda, \lambda')c + (1-c)W_{II}(\lambda, \lambda') \quad (2.8)$$

where  $W_c(\lambda, \lambda')$  — total intensity of emission which is a superposition of emission from both ionic forms, corresponding to a given wavelength of emitted light,  $W_I(\lambda, \lambda')$  — emission intensity of the singly charged anion,  $W_{II}(\lambda, \lambda')$  — emission intensity of the doubly charged ion,  $c$  — relative concentration of the monovalent ion, the relative concentration of the monovalent ion is expressed by the ratio of the concentration of the monovalent negative ion to the concentration of uranine in the solution, *i.e.* by

$$c = \frac{C_{HR^-}}{C}$$

$c$  was computed by the method described by Drabent [4] in the calculation of the absorption spectrum of a singly-charged negative ion.

The intensity of emission in a given wavelength of a monovalent anion  $W_I(\lambda, \lambda')$  can be expressed as:

$$W_I(\lambda, \lambda') = \frac{W_c(\lambda, \lambda') - (1-c)W_{II}(\lambda, \lambda')}{c}. \quad (2.9)$$

The unknowns  $W_c(\lambda, \lambda')$  and  $W_{II}(\lambda, \lambda')$  in formula (2.9) were calculated from (2.7) using the appropriate absorption and emission spectra. For the sake of calculation formula (2.7) can be written in the following form:

$$W_{II}(\lambda, \lambda') = (e^{-\mu_{II}(\lambda)x_1} - e^{-\mu_{II}(\lambda)x_2}) \cdot B_{II} \cdot K_{II}(\lambda, \lambda'). \quad (2.10)$$

The absorption coefficient for a bivalent ion corresponding to a given wavelength of exciting light —  $\mu_{II}(\lambda)$ , was read off from the absorption spectrum of uranin solution with a pH of 11. The intensity of emission  $K_{II}(\lambda, \lambda')$  corresponding to a given wavelength of emitted light was read off from the emission spectrum of that solution. The emission spectrum was also used in computing the constant  $B_{II}$ . To this end the area contained by the emission curve was computed. Next the constant  $B_{II}$  was obtained by dividing the absolute efficiency of emission of a basic uranin solution [9] by the computed area.

Using formula (2.7),  $W_c(\lambda, \lambda')$  can be written in the following form:

$$W_c(\lambda, \lambda') = J_0(e^{-\mu_c(\lambda)x_1} - e^{-\mu_c(\lambda)x_2}) \cdot B_c \cdot K_c(\lambda, \lambda'). \quad (2.11)$$

Using this expression we can, by means of relation (2.9), determine the value of emission intensity for a monovalent negative ion.

### 3. Presentation of results

#### 3.1. Emission spectra of aqueous solutions of uranine as a function of dye concentration

The experiments were conducted for water solutions with concentrations from  $3.5 \times 10^{-5}$  g/cm<sup>3</sup> to  $3.7 \times 10^{-7}$  g/cm<sup>3</sup>.

The measurements were repeated several times, with fresh solutions being prepared each time. The spectra were measured upon excitation through filters I and II. The most typical sequence of changes in the spectrum is depicted in Fig. 1.

For the lowest concentration, a spreading of the band in the direction of long wavelengths is apparent. As the concentration increases, the emission band gets narrower and possesses just one maximum.

#### 3.2. Effect of concentration on the time evolution of emission spectra

Changes in emission spectra with solution storage time are observable at all concentrations. By way of example, the time evolution of emission spectra for aqueous solutions, with  $3.5 \times 10^{-5}$  g/cm<sup>3</sup> and  $10^{-6}$  g/cm<sup>3</sup> concentration is shown in figures 2 and 3.

The increase in emission intensity with solution storage time is greater for small concentrations. The relative increase of emission intensity with storage time is higher during exci-

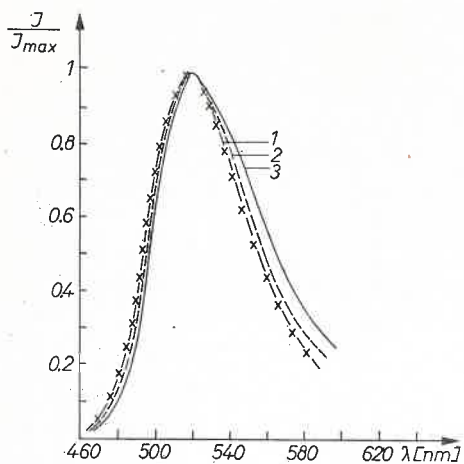


Fig. 1

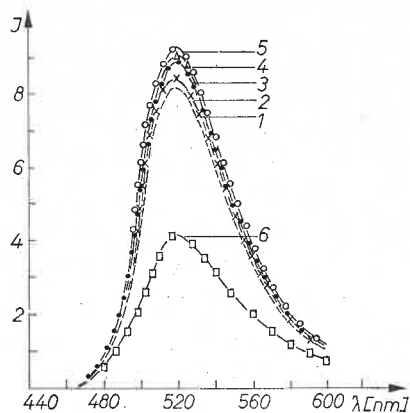


Fig. 2

Fig. 1. Emission spectra of uranin in aqueous solution for varying dye concentrations. Curves: 1 —  $3.5 \times 10^{-5}$ , 2 —  $1 \times 10^{-5}$ , 3 —  $3.5 \times 10^{-5}$  g/cm<sup>3</sup>

Fig. 2. Emission spectra of an aqueous solution of uranin of concentration  $c = 3.5 \times 10^{-5}$  g/cm<sup>3</sup> and pH = 7.05, after varying times ( $t$ ) of storage (during excitation through filter II). Curves: 1.  $t_1 = 0$ ; 2.  $t_2 = 24$  hours; 3.  $t_3 = 48$  hours; 4.  $t_4 = 5$  days; 5.  $t_5 = 9$  days; 6. spectrum obtained during excitation with filter I (after a time  $t = 0$  and  $t = 5$  days)

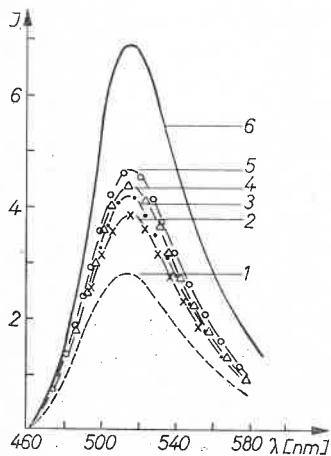


Fig. 3a

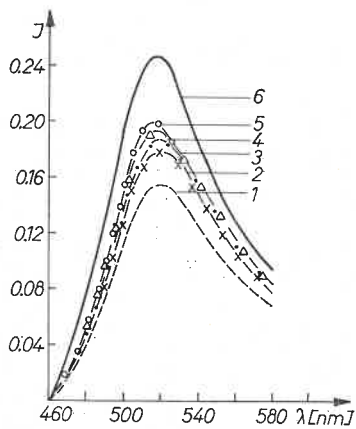


Fig. 3b

Fig. 3a. Emission spectra of aqueous uranin solutions of concentration  $c = 10^{-6}$  g/cm<sup>3</sup> and pH = 6.45 after various times ( $t$ ) of storage (during excitation through filter II). Curves: 1.  $t_1 = 0$ ; 2.  $t_2 = 24$  hours; 3.  $t_3 = 48$  hours; 4.  $t_4 = 7$  days; 5.  $t_5 = 9$  days. 6. solution with pH value around 10

Fig. 3b. Emission spectra of water solution of uranin with concentration  $c = 10^{-6}$  g/cm<sup>3</sup> and pH = 6.45, after varying storage times ( $t$ ) (during excitation through filter I). The curves are designated as in Fig. 3a

tation with filter II than with filter I. The emission maximum obtained during excitation through filter I is shifted somewhat toward long wavelengths relative to the emission maximum obtained in the course of excitation through filter II. A characteristic property is the change in the pH value of the solutions during the time of storage (Table I).

The time evolutions of the spectra cease to appear after a period of about 9 days, while changes in pH — value become unobservable after only around three days.

TABLE I  
pH — values of aqueous solutions of uranine in the course of storage (redistilled water, with pH = 5.85)

Solution concentration $c = \text{g/cm}^3$	Solution storage time		
	$t = 0$	$t = 24 \text{ hrs}$	$t = 48 \text{ hrs}$
$3.5 \cdot 10^{-5}$	7.05	7.10	7.15
$1.0 \cdot 10^{-5}$	6.65	6.85	6.90
$7.0 \cdot 10^{-6}$	6.52	6.75	6.80
$3.5 \cdot 10^{-6}$	6.47	6.66	6.70
$1.0 \cdot 10^{-6}$	6.45	6.65	6.70
$7.0 \cdot 10^{-7}$	6.40	6.65	6.72
$3.5 \cdot 10^{-7}$	6.12	6.28	6.55

### 3.3. Effect of varying pH — value upon the time evolution of emission spectra in uranine solutions of $10^{-6} \text{ g/cm}^3$ concentration

The observation of emission spectra during storage was carried out in a wide range of pH — values. Fig. 4 shows the time changes in emission spectra of a water solution of uranine with pH = 5.05. The emission spectrum shown has two maxima. The long-wave maximum, most clearly discernible on curves 1 and 2, disappears in the course of solution storage. Fig. 5 shows the relative changes in long-wave and short-wave maxima in absorption and emission spectra. From the experiments conducted on changes in emission

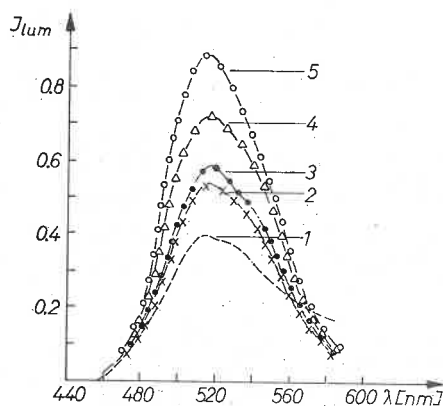


Fig. 4. Emission spectra of uranine solution with pH = 5.05 (excited through filter II), after varying times ( $t$ ) of storage. Curves designated as in Fig. 3a

spectra as a function of solution storage time for different pH — values, it appears that these changes occur in a pH range from 7 to 4.55. These data confirm the results obtained by the authors in reference [6], on the basis of analogous tests conducted on absorption spectra. For solutions with  $2.7 \leq \text{pH} < 4.55$  the emission intensity is weak, and the changes in intensity as a function of storage time are small. It was to be expected that in emission

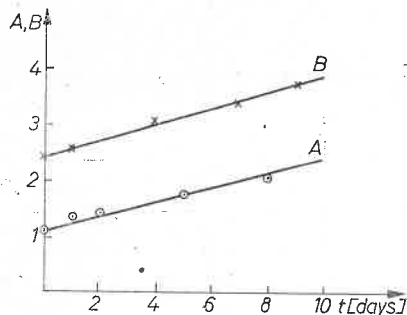


Fig. 5. Successive changes in maxima of absorption (A) and emission (B) of uranin solutions with  $\text{pH} = 5.05$

as in absorption, time — evolution of spectra for solutions with  $\text{pH} > 7$  is not observed. This was confirmed by experiment. Changes in pH with time for solutions of  $\text{pH} = 1.95$  were not observed.

### 3.4. Effect of basic constituents of air on time evolution of emission spectra of uranine in aqueous solution at a concentration of $10^{-6} \text{ g/cm}^3$

The effect of nitrogen, oxygen and carbon dioxide on the time evolution of emission spectra was studied. During infusion of nitrogen and oxygen into the solution its pH rose slightly. The rise caused an increase in intensity of emission (Fig. 6). On repetition of observations after differing periods of storage, further characteristic changes in the spectrum are observed.

### 3.5. Emission spectra of individual ionic forms of uranin

In order to compute the total emission intensity from formula 2.11, emission spectra of solutions with a pH range of 5.1 to 4.7, (measured immediately after preparation) were used. Absorption coefficients for a given wavelength,  $\mu_c(\lambda)$ , and the relative intensity of emitted light  $K_c(\lambda)$  were read off from the emission and absorption spectra of the above solutions. The method of calculating the constant  $B_c$  was the same as that for  $B_{II}$ , using the appropriate emission spectra. The absolute efficiency of emission was calculated on the basis of data obtained by Rozwadowski [17] who tested the solutions efficiency as a function of pH. The values of emission intensity for a monovalent negative ion were calculated using relation (2.9) and normalised relative to the maximum value. Fig. 7 depicts the emission spectrum of uranin solution of  $10^{-6} \text{ g/cm}^3$  concentration with  $\text{pH} = 10$  (curve no 2), and the emission spectrum calculated by the method discussed previously.



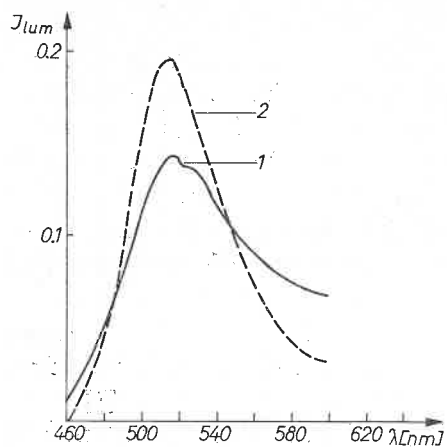


Fig. 6

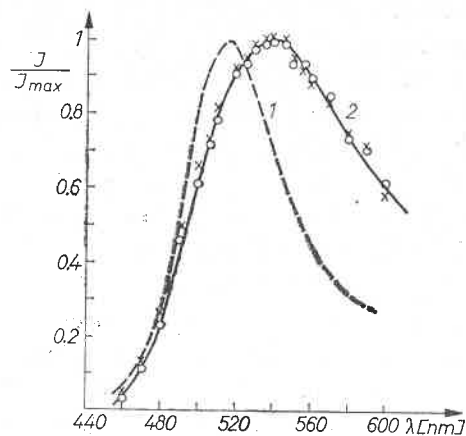


Fig. 7

Fig. 6. Emission spectra of water solutions of uranin. Curve 1 unsaturated solution, 2 the same solution after infusion of nitrogen

Fig. 7. Emission spectra of uranine solution with  $\text{pH} = 10$  (curve 1), and the emission spectrum of the singly charged negative ion (curve 2)

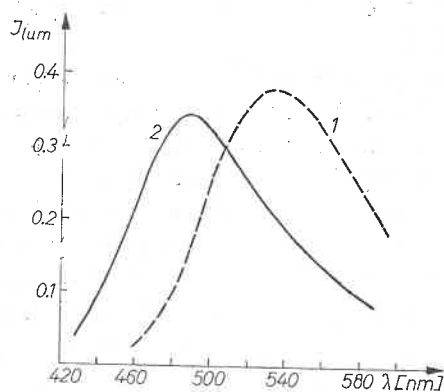


Fig. 8. Emission spectra of uranine solution with  $\text{pH} = 1.9$  (curve 1) and in  $5\text{nHNO}_3$  (curve 2)

The calculations were checked for several sets of observations. The plotted points on curve 2 exemplify two sets of observations. Normalized values of emission intensity were plotted along the ordinate, and wavelength was plotted along the abscissa.

The emission spectrum of uranin solutions with  $\text{pH} \leq 2.4$  is shown on Fig. 8. The emission band shifts from long to short wavelengths on addition of acid to the solution.

#### 4. Discussion of results

The observed changes in the spectra with variation of concentration in water solutions of uranin within the range  $3.5 \times 10^{-5} \text{ g/cm}^3$  to  $3.7 \times 10^{-7} \text{ g/cm}^3$ , seem to indicate the existence of two centres of absorption and emission. In comparing the results obtained with data

taken from literature ([1, 4, 11, 12, 15, 19] and others) one can infer that the short-wave maximum of emission corresponds to the bivalent anion, and that the long-wave maximum of emission should be associated with the monovalent anion. The expectation that the hydrolysis reaction of uranin, [15], is responsible for concentration changes in the spectra for dilute solutions, is borne out by changes observed in the emission spectra. In solutions of highest concentration the bivalent anion predominates, as indicated by a clear-cut maximum of emission at  $\lambda = 515$  nm (Fig. 1, curve 1). In contrast to the spectrum for the solution with lowest concentration, in which there is a comparable amount of both ions, the long-wave maximum of the monovalent negative ion is clearly apparent.

It follows from observation of the time evolution of emission spectra, that during the time of storage the balance of ions coexisting in solution is disturbed. This confirms the results obtained in observing the time evolutions in absorption spectra [7].

It can be seen from Fig. 3, that during stimulation of fluorescence through filter II, whose transmittance maximum is approximately equal to the absorption maximum for a negative-two ion, the emission intensity of the observed spectrum increases with the solutions storage time. There is then some analogy with the rising maximum of absorption of the bivalent anion. During stimulation of fluorescence through filter I, whose transmittance maximum corresponds approximately to the maximum of absorption for monovalent negative ions, one also notes a gradual (but smaller) rise of emission intensity with time (Fig. 3b).

It is known that the absorption band for a singly-charged negative ion is partly superimposed on the absorption band of a doubly-charged ion, admitting the supposition that both centres of emission are excited simultaneously. Since the fluorescence efficiency of the bivalent ion is higher (0.82 [14]) than that of the monovalent ion (0.62 — Grzywacz, unpublished), it seems reasonable to think that the emission intensity of the singly-charged negative ion, which decreases in time, is superimposed on the rising emission intensity of the doubly charged negative ion. So in consequence of the superposition of the emissions we observe not a decrease but a slight increase of intensity of fluorescence. Assuming such an interpretation for the obtained emission spectra we can maintain that an analogy exists between changes in the emission and absorption spectra during the time of storage.

During storage of the solutions, a rise in their pH-values was noted (Table I). It was decided to see if the pH of the solution affects the time-evolution of the spectra. It was found, similarly as in the case of absorption spectra [6], that the greatest changes in emission spectra during storage time are observed at that pH value which allows for the coexistence of both ions, (*i.e.* singly and doubly charged) in the solution.

It was not possible to observe the emission of these solutions in the pH-range of 4.55 to 2.7 because they exhibit a weak intensity of fluorescence. It is to be expected that neutral particles can occur in this pH range. It should be mentioned that changes in emission spectra with time are not observed in solutions buffered over the whole pH range. This is obvious, since in buffered solutions the pH is constant, making hydrolysis impossible.

The reactions with the basic elements of air were recognised as factors which could influence the course of spectrum change with time. From the results obtained for absorp-

tion spectra [8] and emission spectra (Fig. 6) it can be inferred that the constituents of air are not the only factors responsible for time evolution of the spectra.

One of the objectives of the experiment was to ascribe to individual ionic forms the appropriate maxima of emission. On the basis of results obtained the emission maximum at  $\lambda = 515$  nm was ascribed to the bivalent anion (Fig. 7). This result agrees with data reported by most authors.

Emission and absorption bands of the monovalent anion of uranine cannot be obtained by experiment, because the ion always appears in solution with another ionic form. The emission and absorption bands of this ion were resolved by calculation. The absorption spectrum was calculated by Drabent [4]. The method for calculating the emission band was described above. On the basis of the calculations, the band obtained possesses a maximum at  $\lambda = 530$  nm. This result is in agreement with the result reported by Alensev [2].

From measurements of the absorption spectra [7] it appears that in a solution with sufficiently low pH, in which only the cationic form occurs, the position of the maximum is a constant. It was, however impossible to determine the position of the cation's emission spectrum (Fig. 8). The emission band shifts toward short wavelengths with the increase of acid concentration in the solution, starting at  $\text{pH} < 2.7$ . The difference in effect of the solvent reagent of the emission and absorption spectra can be explained by the differing strengths of particle interaction between solvent and dye molecules in the ground and excited states. The solvent's effect can be observed only in those cases when the lifetime of the particle's excited state is longer than the relaxation time [3, 18].

The effect of the solvent on the emission spectrum of tripofflavin in glycerine was first noted by Szalay and Tombacz [18]. They also report the lifetime of fluorescein and tripofflavin ( $\tau \approx 4$  ns), and the relaxation time ( $\tau' \approx 0.01 - 1$  ns). Since  $\tau > \tau'$ , one can expect that the solvent effect will occur also in uranin solutions. The cation as a positive molecule probably interacts with water dipoles in its excited state, causing the emission spectra to be shifted relative to the monovalent anion band ( $\lambda_{\text{max}} = 530$  nm) in the direction of long wavelengths. Upon addition of acid the relative amount of water is decreased, causing a reduction of the particle interaction strength between the solvent molecules and the cationic form in its excited state (the spectrum of emission shifts to short wavelengths).

On the basis of the obtained results it seems highly probable that changes in the position of the emission spectrum are caused by various interactions between the solvent molecules and dye particles in their ground and excited states; however the information collected does not allow one to exclude the effect of the protolytic reaction upon this phenomenon.

## 5. Conclusions

1. Changes in the emission spectra of dilute water solutions of uranin as a function of dye concentration have confirmed the supposition that the hydrolysis reaction is responsible for these changes.
2. Time evolutions of emission spectra occur under the same conditions as the observed changes in absorption spectra [5].

3. The supposition that in a strongly acid medium the solvent molecules react in differing ways with dye molecules in their ground and excited states can serve to explain the variable position of the emission band maximum while the position of the absorption band is fixed.

4. The calculation method applied allowed us to determine the emission band of the monovalent ion, fixing its maximum at  $\lambda_{\max} = 530$  nm.

In the present work it was found that the time evolutions of emission spectra occur for the same parameters as do the changes observed in absorption spectra [5]. The conditions under which time evolutions occur, as well as those which could eliminate certain factors influencing such changes were determined.

The conditions in which individual ionic forms of uranin occur are also reported, making possible a comparison of experimental results of various authors with theoretical predictions.

Taking advantage of a wide variety of experimental material dealing with studies of this problem, we determined the emission spectrum of the monovalent anion by calculation.

We were not successful in explaining the change in pH-value of water solutions of uranin with time, or the resulting time evolutions of emission and absorption spectra.

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