

## Association of Indopolymethine Cyanine Cations with Anions of Sulfonephthalein and Xanthene Dyes in Water

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A associação do corante catiônico indoheptametinocianina com vários corantes aniônicos (quatro sulfonaftaleínas e cinco xantinas) em solução aquosa foi investigada usando espectroscopia de absorção no visível. Os valores das constantes de associação estão na faixa de  $10^4$  a  $7 \times 10^7$  mol<sup>-1</sup> L. Em todos os casos, um efeito hipocrômico significativo foi observado para a banda de absorção do cátion ( $\lambda_{\text{max}} = 737$  nm). O mesmo foi observado para a interação do cátion indotrimetínio ( $\lambda_{\text{max}} = 540$  nm) com espécies aniônicas. Interações eletrostáticas, de Van der Waals e hidrofóbicas são identificadas como as forças que dirigem esta associação. A adição de surfatantes iônicos destrói os compostos de associação do corante, primeiramente devido à interação com os íons de corante com carga oposta. Este processo é acompanhado pela restauração dos espectros de absorção visível dos corantes aniônico e catiônico.

The association of the cationic dye indoheptamethine cyanine with various anionic dyes (four sulfonephthaleins and five xanthenes) in aqueous solutions was detected using the Vis-spectroscopic method. The values of the association constants are within the range ( $10^4$  to  $7 \times 10^7$  mol<sup>-1</sup> L). In all the cases a substantial hypochromic effect is observed for the Vis absorption band of the cation ( $\lambda_{\text{max}} = 737$  nm). The interaction of indotrimethinium cation ( $\lambda_{\text{max}} = 540$  nm) with anionic species manifests itself in analogous manner. Electrostatic, Van der Waals, and hydrophobic interactions are regarded as driving forces of the association. Addition of ionic surfactants destroys the dye associates, primarily due to interactions with the oppositely charged dye ions. This process is accompanied by the restoration of the initial Vis absorption bands of both the cationic and the anionic dye.

**Keywords:** polymethine cyanine dyes with indoline end groups, sulfonephthaleins, xanthenes, Vis absorption spectra, ion association in water, ionic surfactants

### Introduction

The purpose of this paper is to elucidate some features of the ionic association phenomenon in aqueous solutions. Ion association processes in water, with respect to the unique role of this solvent, are of great interest for physical organic chemistry<sup>1</sup> and organic chemistry of electrolytes<sup>1,2</sup> as well as for biochemistry and related sciences.<sup>1,3</sup> In analytical chemistry, namely in extraction-photometric (fluorimetric) determinations, ion pairs formed in water are transferred to organic solvents;<sup>4</sup> association of oppositely charged ions in water are of importance for chromatography as well.<sup>5</sup> In the case of organic ions association in water, not only electrostatic interactions are

of significance, but also hydrophobic ones, as well as Van der Waals attraction (including interactions between  $\pi$ -electronic systems) and hydrogen bond formation.<sup>1,2,6</sup> Hence, much higher stability of associates in water can be expected for bulky organic ions as compared with those formed by small inorganic ones.

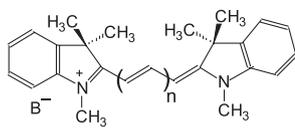
Even organic ions of the same charge are able to associate in water. For example, the tetraphenylborate ion,  $\text{B}(\text{C}_6\text{H}_5)_4^-$ , forms associates in 0.01 mol L<sup>-1</sup> aqueous solutions,<sup>7</sup> which demonstrates the increasing role of non-coulombic interactions. For the tetraphenylarsonium ion,  $\text{As}(\text{C}_6\text{H}_5)_4^+$ , this property is even more expressed;<sup>7</sup> interestingly, the nature of the inorganic counter-ion ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) does not noticeably influence this process. The well-known dimerization phenomenon of dye ions with similar charge in aqueous media<sup>6,8,9</sup> is a typical example of

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expressed hydrophobic + Van der Waals interactions, which are present despite of electrostatic repulsion. Stepwise aggregation of some ionic dyes in water, *e.g.* Congo red and Benzopurpurin, results even in formation of lyophobic hydrosols.<sup>10</sup>

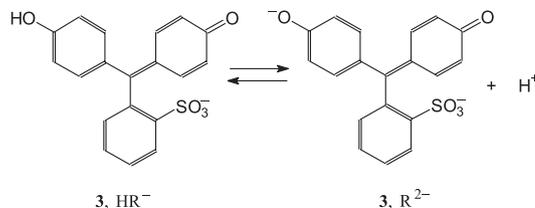
The effects of association of organic ions with opposite charges are rather versatile. The association of aryl and alkylsulfonates, alkylsulfates, alkylborates, and other anions with cations such as alkyl and arylammonium, tetraphenylarsonium, and tetraphenylphosphonium has been reported.<sup>2,6,11</sup> Other phenomenon, typical for aqueous dye solutions, is the association of dye ions with surfactant ions of opposite charge within the concentration range below the critical micelle concentration (cmc) of surfactant homomicelles, leading to step-by-step formation of poorly soluble salts and mixed dye-surfactant micelles.<sup>12,13</sup> The interactions of such a kind are often accompanied by prominent changes in the Vis spectra as, for instance, in the case of the association of hydroxyxanthene anions with quaternary ammonium drugs,<sup>14</sup> or of the cationic dye neutral red with *n*-dodecylsulfate.<sup>15</sup> The limited stability of such systems sometimes requires the application of stabilizers, *e.g.* polyvinyl alcohol, which allows to minimize the formation of deposits.

Earlier we reported,<sup>16</sup> that cationic polymethine cyanine dyes with indoline end groups, or indopolycarbocyanines – vinylene analogues of astraphloxine, form rather stable 1:1 associates with anionic polymethines of various structure. The present study is devoted to the interactions of cations (Ct<sup>+</sup>) of trimethine and heptamethine dyes with indoline end groups, **1** (astraphloxine) and **2** (indotricarbocyanine), respectively:

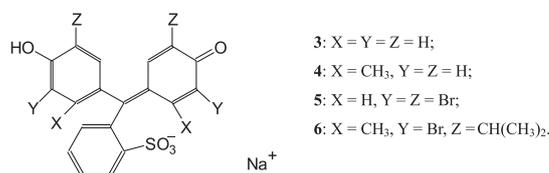


(1: n = 1; 2: n = 3; B<sup>-</sup> = Cl<sup>-</sup> or BF<sub>4</sub><sup>-</sup>)

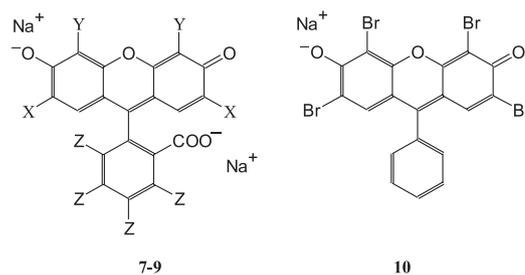
with anions of sulfonephthaleins and hydroxyxanthenes. Apart from other reasons, the knowledge of regularities of polymethine dyes association with various species is significant for rationalization of their use in optical memory systems. Our previous study<sup>16</sup> demonstrated that small inorganic counter-ions, such as Na<sup>+</sup>, K<sup>+</sup>, Cl<sup>-</sup>, BF<sub>4</sub><sup>-</sup> *etc.*, cannot compete with bulky organic ones in their association with dye ions in aqueous media. In aqueous solutions, at medium and high pH, the sulfonephthaleins exist as mono- and dianions, HR<sup>-</sup> and R<sup>2-</sup>, respectively; the equilibrium of the unsubstituted phenol red **3** is as follows:



The following sulfonephthaleins were studied: phenol red, **3**; 2,2'-dimethylphenolsulfonephthalein, or *m*-cresol purple, **4**; 3,3',5,5'-tetrabromophenolsulfonephthalein, or bromophenol blue, **5**; 2,2'-dimethyl-5,5'-di-*iso*-propyl-3,3'-dibromophenolsulfonephthalein, or bromothymol blue, **6**. Their general structure in form of sodium salt is given below:

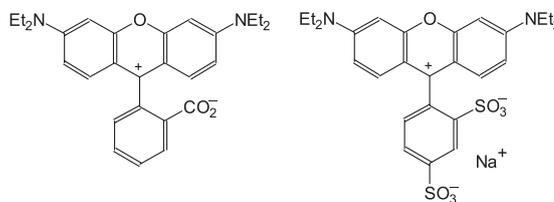


The general structure of R<sup>2-</sup> anions of 2,7-dichlorofluorescein, **7**; 2,4,5,7-tetrabromofluorescein, or eosin, **8**; 2,4,5,7-tetraiodo-3',4',5',6'-tetrachlorofluorescein, or rose Bengal, **9**, in the form of disodium salts, as well as the structure of R<sup>-</sup> anion of 2,4,5,7-tetrabromophenylfluorone, **10**, in the form of sodium salt are given below:



7: X = Cl, Y = Z = H; 8: X = Y = Br, Z = H; 9: X = Y = I, Z = Cl.

Within the aforementioned pH region, the aminoxanthene dyes rhodamine B, **11**, and rhodamine 200 B, **12**, exist as zwitter-ion and anion (depicted as a sodium salt), respectively:



11

12

The choice of the dyes in this study is caused by their Vis-spectral and protolytic properties. So, the absorption bands of the anions and that of **2** are well-resolved (Table 1). The spectra of HR<sup>-</sup> and R<sup>2-</sup> ions differ strongly in the case of sulfonephthaleins, while their bands are much closer in the case of hydroxyxanthenes. The protonation of dianions of eosin and rose Bengal B results in very modest ( $\Delta\lambda_{\max} = 2$  to 5 nm) bathochromic shifts ( $\text{CO}_2^- \rightarrow \text{CO}_2\text{H}$ ).<sup>22-24</sup> Moreover, the successive protonation of dianions (up to H<sub>2</sub>R) occurs in the case of hydroxyxanthenes within a narrow pH region. Hence, the association of Ct<sup>+</sup> was studied only with double-charged anions R<sup>2-</sup> of dyes **7**, **8**, and **9**. Dyes **10** and **12** exist in form of single-charged anions R<sup>-</sup> within a wide pH range.<sup>4,20</sup> The knowledge of stepwise protonation constants of R<sup>2-</sup> or R<sup>-</sup> ions,  $K_{\text{H},1}$  and  $K_{\text{H},2}$ , given in Table 1, allows to create proper conditions for the predominance of required dye species in solutions. The dyes **1** and **2** exist in solutions as single-charged cations, Ct<sup>+</sup>, at  $2.5 \geq \text{pH} > 10$ . Protonation of Ct<sup>+</sup> occurs in more acidic media, while in alkaline solutions the formation of carbinols, CtOH, takes place.

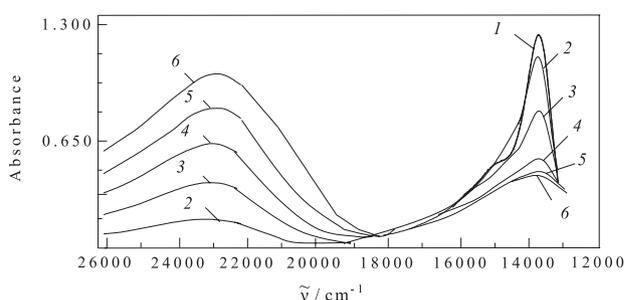
## Experimental

UV-Vis absorption spectra were obtained by using SP-46, Specord UV-VIS, and Hitachi U-3210 apparatus and emission spectra with Hitachi F-4010. The pH values were checked by means of a glass electrode, in cells with liquid junction. Polymethine dyes with indoline end groups, **1** and **2**, were synthesized as described previously<sup>25</sup> and used in the form of chlorides and tetrafluoroborates. Rhodamine 200 B, **12**, was purchased from Shostka factory of chemicals, Shostka, Ukraine, while other dyes were of Minkhimprom (USSR) origin, except for the disodium salt of 2,7-dichlorofluorescein, **7**, (VEB Apolda, DDR). Dyes **8** and **9** were purified by column chromatography. Dye **10** was prepared in HR form as described earlier.<sup>20</sup> The purity of all the dyes used was checked by TLC. Sodium *n*-dodecylsulfate (Sigma, 98-99%) was used as such; *N*-cetylpyridinium chloride was purified through re-crystallization. The weighted amounts of dyes **1**, **11**, and **12** were dissolved in pure water, those of sulfonephthaleins and hydroxyxanthenes – in water with addition of equivalent quantities of NaOH, while in the case of dye **2** 96% aqueous ethanol was used for preparation of stock solutions. As a rule, the working solutions contained 4 vol. % ethanol. The UV/Vis spectra were run at 20 °C in acetate, phosphate, and borate buffer solutions, as well as in diluted aqueous HCl and NaOH solutions. Ionic strength of the working solutions did not exceed 0.01 mol L<sup>-1</sup> (except for some of the experiments with surfactants).

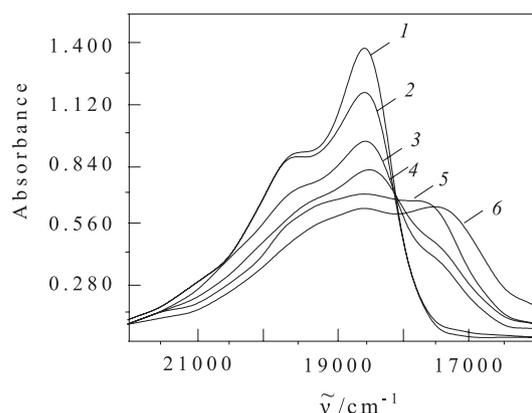
## Results

### Vis-Spectroscopic estimation of ion association constants

The ion association was studied by using the spectrophotometric method in aqueous solutions of **1** and in 4 vol. % C<sub>2</sub>H<sub>5</sub>OH of **2**, at dye concentrations of  $1 \times 10^{-6}$  -  $5 \times 10^{-6}$  mol L<sup>-1</sup>. At the concentrations used, only the 'cation + anion' association is observed. The solutions containing only one kind of dye (cationic or anionic ones) obey Beer's law. The interaction of Ct<sup>+</sup> with anions An<sup>-</sup> manifests itself primarily in a hypochromic effect of the long-wavelength absorption band of the cation. The intensity decreases by 53%-60%, and the width of the initial band of Ct<sup>+</sup> becomes markedly larger (Figure 1); sometimes a splitting of the band occurs (Figure 2).

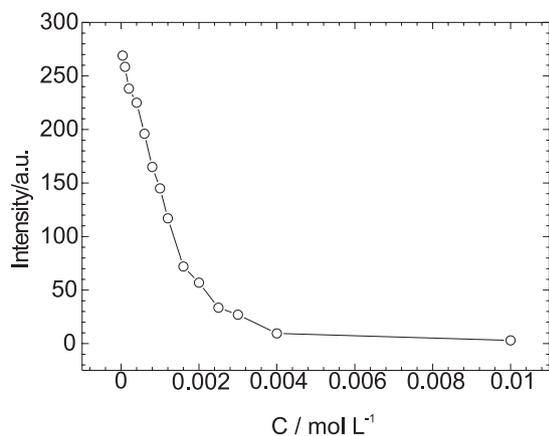


**Figure 1.** UV/Vis absorption spectra of **2** ( $2.0 \times 10^{-6}$  mol L<sup>-1</sup>) at various concentrations of **6**: 0 mol L<sup>-1</sup> (1),  $2.3 \times 10^{-6}$  (2),  $4.6 \times 10^{-6}$  (3),  $9.0 \times 10^{-6}$  (4),  $1.1 \times 10^{-5}$  mol L<sup>-1</sup> (5);  $1.4 \times 10^{-5}$  mol L<sup>-1</sup> (6); pH = 2.9, optical path length 3.0 cm; solvent blank: water.



**Figure 2.** Vis absorption spectra of **1** ( $1 \times 10^{-5}$  mol L<sup>-1</sup>) at various concentrations of **6**: 0 mol L<sup>-1</sup> (1),  $4.0 \times 10^{-5}$  (2);  $6.0 \times 10^{-5}$  (3);  $8.0 \times 10^{-5}$  (4);  $1.6 \times 10^{-4}$  (5)  $2.0 \times 10^{-4}$  mol L<sup>-1</sup> (6); pH 2.9, optical path length 3.0 cm; solvent blank: the corresponding aqueous solution of **6**.

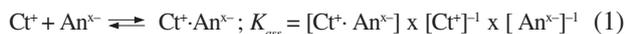
Figure 2 shows a representative set of spectra from a much larger body of data. Besides, the association of sulfonephthalein anions with indoheptamethinium cation is accompanied by fluorescence quenching of the cationic



**Figure 3.** The intensity of fluorescence at 767 nm of aqueous  $2.1 \times 10^{-6}$  mol L $^{-1}$  solution of the dye **2** at various concentrations of the quencher **3**, pH = 4.0, optical path length 1.0 cm.

dye (Figure 3), analogously with the case of interaction of the latter with anionic polymethines.<sup>16</sup>

The analysis of the absorption spectra by applying the isomolar series and saturation methods revealed, that within the mentioned concentration range, at 3–10-fold excess of anion, the associates with stoichiometry 1:1 predominate in aqueous solutions:



Though sometimes the isosbestic points were somewhat vague, it appeared to be impossible to describe the experimental data using more complicated equilibrium models. The determination of equilibrium concentrations  $[\text{Ct}^+ \cdot \text{An}^{x-}]$ ,  $[\text{Ct}^+]$ , and  $[\text{An}^{x-}]$ , of the equilibrium constant  $K_{\text{ass}}$  (mol $^{-1}$  L), and the re-calculation of  $K_{\text{ass}}$  to the thermodynamic values were done as described in detail earlier.<sup>16</sup> The  $[\text{Ct}^+ \cdot \text{An}^{x-}]$  values were determined from the

spectral data in the region of  $\lambda_{\text{max}}$  of the cation by the equation:

$$[\text{Ct}^+ \cdot \text{An}^{x-}] = y = [\varepsilon_{\text{Ct}} c_{\text{Ct}} l - A] [\varepsilon_{\text{Ct}} - \varepsilon_{\text{ass}}]^{-1} l^{-1}, \quad (2)$$

where  $c_{\text{Ct}}$  is the analytical (total) concentration of cationic dye **1** or **2**,  $l$  is optical path length;  $A$  is absorbance for the current value of the analytical concentration of anion,  $c_{\text{Ct}}$ ,  $\varepsilon_{\text{An}}$  and  $\varepsilon_{\text{ass}}$  are the molar absorptivities of the cation and associate, respectively. The  $\varepsilon_{\text{ass}}$  value was obtained within appropriate concentration range, when the Vis spectra became unaffected by creating further excess of  $\text{An}^{x-}$ . The association constants were calculated by the following equation:

$$K_{\text{ass}} = y [c_{\text{An}} - y]^{-1} [c_{\text{Ct}} - y]^{-1} \quad (3)$$

The concentration of cationic dye **1** or **2** does not vary in a single series of experiments; as a rule, 10–15 values of concentrations of anionic dyes **3–8**, **10**, **12** and 3–4 working wavelengths were used to obtain the resulting data. For the estimation of the thermodynamic association constants, the activity coefficients of the ionic species  $\text{Ct}^+$  and  $\text{An}^{x-}$  were calculated by using the Debye–Hückel second approach, taking the ionic parameter value as equal to 5. Counter-ions  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{BF}_4^-$ , introduced in the system together with the dyes, make negligible contribution to the total ionic strength of buffer mixtures used for  $y$  calculations.

In the case of **1**, the bands of cationic and anionic dyes are overlapping, and the effects become evident only if the spectra are obtained against the corresponding solution of anionic dye as ‘solvent blank’. The principal characteristics of the free ions in aqueous solutions as well as the associates are compiled in Tables 1 and 2.

**Table 1** Principal characteristics of the dyes studied

Anionic dye	$\lambda_{\text{max}} / \text{nm}$ ( $\varepsilon_{\text{max}} / 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ )	$\log K_{\text{H},2}$	$\log K_{\text{H},1}$	$\lambda_{\text{max}} / \text{nm}$ ( $\varepsilon_{\text{max}} / 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) of cations $\text{Ct}^+$ and their associates with anions	
				<b>1, Ct<sup>+</sup></b>	<b>2, Ct<sup>+</sup></b>
No organic anion added				540 (144)	737 (201±8)
<b>3</b> , HR <sup>-</sup>	430 (24)	1.03	8.00	—	735–740 (82)
<b>4</b> , HR <sup>-</sup>	436 (18)	1.7	8.70	—	735–740 (87)
<b>5</b> , R <sup>-</sup>	438 (25)	-0.95	4.20	—	735–740 (90)
<b>6</b> , HR <sup>-</sup>	436 (18)	1.5	7.30	538–540 (65), 574 (65)	735–740 (93)
<b>7</b> , R <sup>2-</sup>	503 (100)	4.11	5.32	—	735–740 (75)
<b>8</b> , R <sup>2-</sup>	515 (91)	2.81	3.75	—	735–740 (72)
<b>9</b> , R <sup>2-</sup>	547 (93)	—	4.05–5.7	—	plateau 730–740 (67)
<b>10</b> , R <sup>-</sup>	515–516 (86)	—	≈3.0	540–545 (94)	plateau 730–740 (70)
<b>11</b> , R <sup>±</sup>	553 (110)	—	3.22	—	—
<b>12</b> , R <sup>-</sup>	565 (110)	—	0.08	540–545 (98)	735–740 (78)

The values  $\lambda_{\text{max}}$ ,  $\varepsilon_{\text{max}}$ , and  $\log K_{\text{H}}$  for anions are taken from literature.<sup>4,16–24</sup> The  $\varepsilon_{\text{max}} / 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$  of ion associates are determined with confidence interval  $\pm (1.5\text{--}3)$ .

**Table 2** Logarithms of association constants,  $\log K_{ass}$ , of organic cations with anionic species in water (in the case of dye **2**: 4 vol. %  $C_2H_5OH$ ); composition of the associate 1:1

Cation (Ct <sup>+</sup> ) of cyanine	Anion, An <sup>-</sup>	$\log K_{ass}$
<b>1</b>	<b>6</b> , HR <sup>-</sup>	4.2 <sup>a</sup>
<b>1</b>	<b>12</b> , R <sup>-</sup>	5.45±0.10
<b>1</b>	<b>10</b> , R <sup>-</sup>	6.52±0.11
<b>1</b>	B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	5.4±0.2 <sup>b</sup>
<b>2</b>	<b>3</b> , HR <sup>-</sup>	3.91±0.18 <sup>b</sup>
<b>2</b>	<b>4</b> , HR <sup>-</sup>	4.40±0.16
<b>2</b>	<b>5</b> , HR <sup>-</sup>	6.13±0.10
<b>2</b>	<b>6</b> , HR <sup>-</sup>	5.97±0.12 <sup>a</sup>
<b>2</b>	<b>10</b> , R <sup>-</sup>	7.85±0.15
<b>2</b>	<b>12</b> , R <sup>-</sup>	6.51±0.10
<b>2</b>	<b>7</b> , R <sup>2-</sup>	5.33±0.16
<b>2</b>	<b>8</b> , R <sup>2-</sup>	5.9±0.2
<b>2</b>	B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> <sup>-</sup>	6.2±0.3 <sup>b</sup>

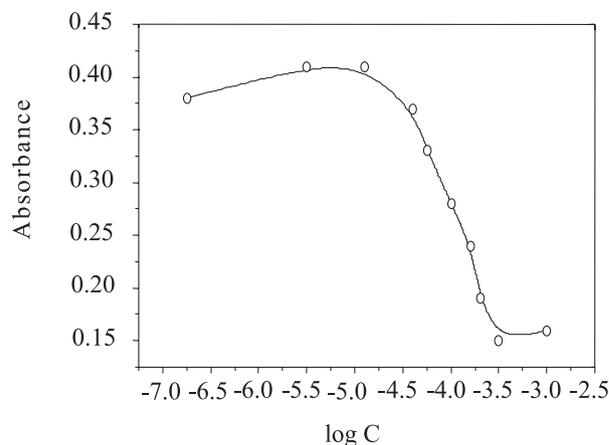
<sup>a</sup> From ref. <sup>26</sup>; <sup>b</sup> from ref. <sup>16</sup>.

#### Association of indopolymethinium cyanine cations with sulfonephthalein anions

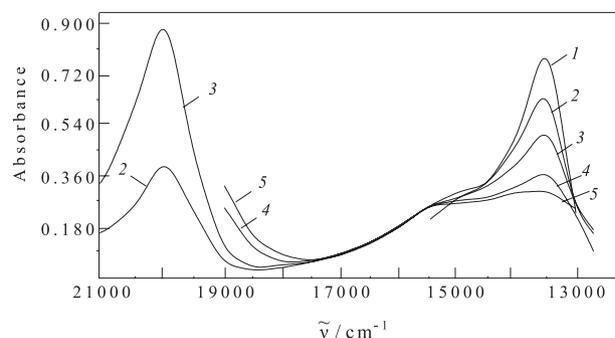
The shape and position of the Vis absorption band of HR<sup>-</sup> species of sulfonephthaleins stay practically unaffected during the association process and obey Beer's law. The measurements at low concentrations of sulfonephthalein and relatively high concentrations of **1** and **2** are hindered by the limited solubility of indopolymethine cyanine dyes in 4 vol. % ethanol, while the increase in the content of  $C_2H_5OH$  or other organic solvents leads not only to the rise of cyanine dyes solubility, but also to the decay of associates (decrease in  $K_{ass}$ ). Interestingly, the double-charged sulfonephthalein anions R<sup>2-</sup> interact with Ct<sup>+</sup> of the dye **2** weaker than single-charged anions HR<sup>-</sup> do: the decrease in the Ct<sup>+</sup> band intensity does not exceed 25-30 %. The introduction of substituents into the sulfonephthalein chromophore, making the species more hydrophobic, facilitates the association of both mono- and di-anions with Ct<sup>+</sup>. So, at sulfonephthalein concentration of  $7.0 \times 10^{-6}$  mol L<sup>-1</sup>, the interaction with  $2.0 \times 10^{-6}$  mol L<sup>-1</sup> **2** is less expressed for **4**, as compared with that in the case of **5** and **6**. For phenol red **3**, the most hydrophilic among the sulfonephthaleins studied, the  $K_{ass}$  values can be determined only at very high concentrations of the anion (Figure 4). For 100-fold and an even higher excess of the dye **3**, its own absorption at  $\lambda_{max}$  of **2** must be taken into account, despite the high resolution of the bands of An<sup>-</sup> and Ct<sup>+</sup>.

#### Association of indopolymethinium cyanine cations with hydroxyxanthene anions

Contrary to double-charged anions of sulfonephthaleins,



**Figure 4.** Dependence of absorbance of an aqueous **2** solution ( $2.1 \times 10^{-6}$  mol L<sup>-1</sup>) vs. logarithm of **3** total concentration;  $\lambda = 737$  nm, pH = 4.0, optical path length 1.0 cm; solvent blank: the corresponding aqueous solution of **3**.



**Figure 5.** Vis absorption spectra of an aqueous **2** solution ( $4.0 \times 10^{-6}$  mol L<sup>-1</sup>) at various concentrations of **7**: 0 mol L<sup>-1</sup> (1),  $4.6 \times 10^{-6}$  (2),  $9.1 \times 10^{-6}$  (3),  $3.4 \times 10^{-5}$  (4),  $4.6 \times 10^{-5}$  mol L<sup>-1</sup> (5); pH = 9.2, optical path length 1.0 cm; solvent blank: water.

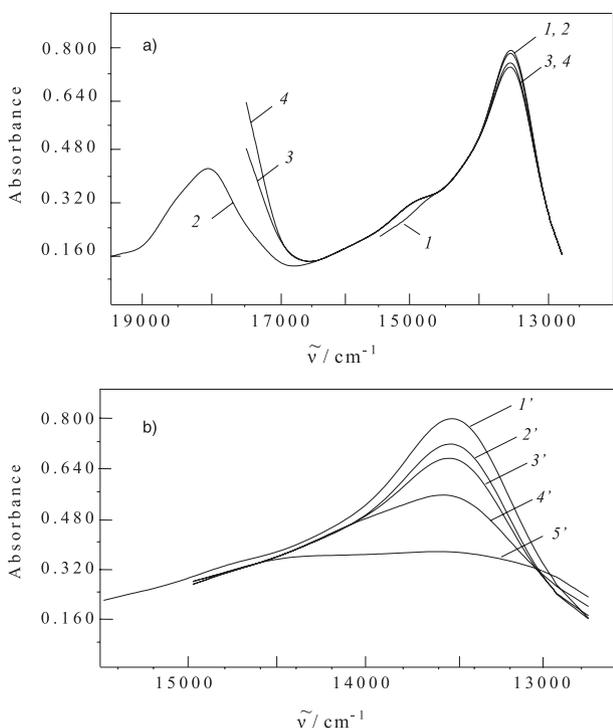
the completely deprotonated forms of xanthenes, R<sup>-</sup> or R<sup>2-</sup>, associate strongly with the Ct<sup>+</sup> of **2** (Figure 5).

In the case of the R<sup>2-</sup> ion of **9**, which is extremely hydrophobic due to eight halogen atoms, an associate (Ct<sup>+</sup>)<sub>2</sub>·R<sup>2-</sup> with indoheptamethinium cation appears, whose  $\log K_{ass}$  is  $12.43 \pm 0.05$ .<sup>27</sup> However, even such a stable associate dissociates in aqueous media, if relatively small amounts of 1,4-dioxane are introduced; the initial band of **2** is restored. The  $\log K_{ass}$  values for 1:1 associates of R<sup>2-</sup> ions are collected in Table 2.

#### Interaction of indoheptamethinium cyanine cation with aminoxanthene dyes

Two rhodamine dyes examined in the present study possess the same aminoxanthene moiety (see the above structural formulae). In aqueous solutions, at pH  $\geq 5$ , the Vis absorption bands of the zwitter-ion of **11** and that of **12** anion are very similar. While addition of **11** to **2** solution

leads to negligible changes of the long-wavelength absorption band of the polymethine dye (Figure 6a), the introduction of the same concentrations of **12** causes a much more expressed hypochromic effect (Figure 6b).



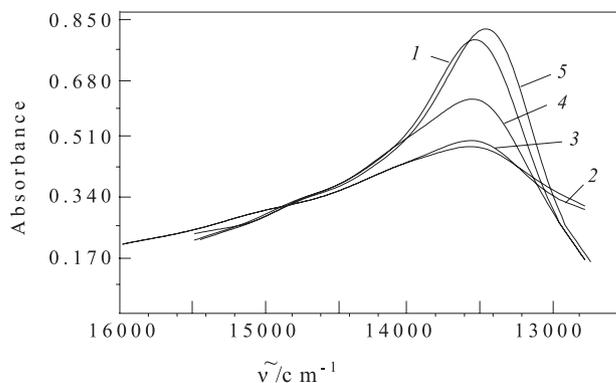
**Figure 6.** Vis absorption spectra of an aqueous **2** solution ( $4.0 \times 10^{-6}$  mol L $^{-1}$ ) at various concentrations of rhodamine dyes; (a) dye **11**: 0 mol L $^{-1}$  (1),  $4.0 \times 10^{-6}$  (2),  $8.0 \times 10^{-6}$  (3),  $2.0 \times 10^{-5}$  mol L $^{-1}$  (4); (b) dye **12**: 0 mol L $^{-1}$  (1'),  $3.8 \times 10^{-6}$  (2'),  $7.6 \times 10^{-6}$  (3'),  $1.9 \times 10^{-5}$  (4'),  $3.8 \times 10^{-5}$  mol L $^{-1}$  (5'); pH 6.8, optical path length 1.0 cm; solvent blank: water.

Hence, these experiments demonstrate that the degree of interaction strongly depends on the charge of the species: in the case of neutral species **11** the interactions with the cation Ct $^{+}$  of the dye **2** are minor.

#### Effect of surfactant additives

Our study revealed that ionic surfactants are able to destroy the dye associates of Ct $^{+}$ ·An $^{-}$  type. Figure 6 demonstrates this effect taking the **2** (Ct $^{+}$ ) + **6** (HR $^{-}$ ) system. The addition of the anionic surfactant sodium *n*-dodecylsulfate (Figure 7) at concentrations exceeding cmc (in pure water, cmc =  $8 \times 10^{-3}$  mol L $^{-1}$ )<sup>28</sup> certainly leads to the decomposition of the dye ion pair, due to binding of the Ct $^{+}$  species by the negatively charged micellar surface.

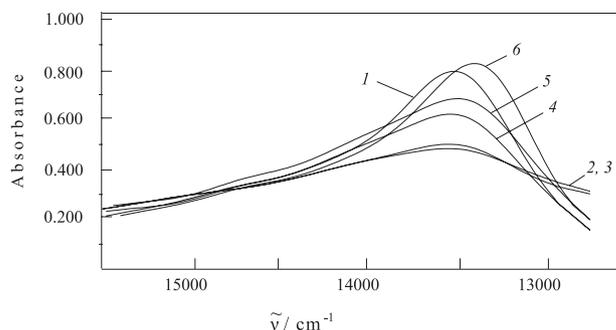
As a result, the absorption band of **2** (curve 5) corresponds to the associate of cation Ct $^{+}$  rather with the anionic surfactant than with HR $^{-}$  ion of dye **6**, and the red shift ( $\Delta\lambda_{\max}$  ca. 10 nm) as compared to the spectrum in water gives evidence for the change of the environment



**Figure 7.** The influence of sodium *n*-dodecylsulfate additions on the Vis spectra of a mixed aqueous solution of **2** ( $2.0 \times 10^{-6}$  mol L $^{-1}$ ) and **6** (0 (1);  $6.0 \times 10^{-6}$  mol L $^{-1}$  (2-5)); surfactant concentrations: 0 mol L $^{-1}$  (1),  $2.0 \times 10^{-6}$  (2),  $2.0 \times 10^{-5}$  (3),  $6.0 \times 10^{-5}$  (4),  $1.0 \times 10^{-2}$  mol L $^{-1}$  (5); pH 3.8, optical path length 1.0 cm; solvent blank: water.

from aqueous to micellar one. Probably, the HR $^{-}$  ion of **6** is also fixed at micellar surface, as the binding constant of this relatively hydrophobic dye anion in sodium *n*-dodecylsulfate micelles at ionic strength 0.2 mol L $^{-1}$  (NaCl) equals  $1 \times 10^4$  L mol $^{-1}$ .<sup>29</sup>

A similar picture is observed in the case of a cationic surfactant (Figure 8). The addition of pre-micellar concentrations of *N*-cetylpyridinium chloride (in pure water, cmc =  $1 \times 10^{-3}$  mol L $^{-1}$ ,<sup>28</sup> while in the presence of acetate buffer this value somewhat decreases) destroys the Ct $^{+}$ ·An $^{-}$  dye associate. In this case, the *n*-C $_{16}$ H $_{33}$ NC $_5$ H $_5$  $^{+}$  interacts first of all with the HR $^{-}$  anion of **6**;<sup>22</sup> however, at *N*-cetylpyridinium micellar concentrations (curve 6), a small red shift ( $\Delta\lambda_{\max}$  ca. 5 nm) is registered for the hydrophobic cation of **2** as well.



**Figure 8.** The influence of *N*-cetylpyridinium chloride additions on the Vis spectra of a mixed aqueous solution of **2** ( $2.0 \times 10^{-6}$  mol L $^{-1}$ ) with **6** (0 (1);  $6.0 \times 10^{-6}$  mol L $^{-1}$  (2-6)); surfactant concentrations: 0 mol L $^{-1}$  (1),  $2.0 \times 10^{-6}$  (2),  $2.0 \times 10^{-5}$  (3),  $6.0 \times 10^{-5}$  (4),  $2.0 \times 10^{-4}$  (5),  $6.0 \times 10^{-4}$  mol L $^{-1}$  (6); pH 3.8, optical path length 1.0 cm; solvent blank: water.

## Discussion

#### Composition of associates

The isomolar series method and other methods used

by us for determination of the associates composition does not allow to distinguish between the stoichiometries 1:1, 2:2, etc. Basing on the results of spectrophotometric titrations, Armitage, Retterer and O'Brien suppose that the spectral effects are caused only by Ct<sup>+</sup> dimerization, which occurs within the associates – dimers of ionic pairs.<sup>30</sup> In the event that more complicated species than 1:1 are formed in solution, the stepwise association is rather probable. However, attempts to attribute the spectral changes to (Ct<sup>+</sup>)<sub>2</sub>An<sup>-</sup> lead as a rule to extremely inconstant values of the corresponding 'equilibrium constant'.

If the 1:1 associates form a kind of 'pseudophase', or 'sub-colloidal' aggregates, or dispersed solid phase of hydrosols, then the solubility product [Ct<sup>+</sup>]<sup>x</sup>[An<sup>x-</sup>] would be constant, and not  $K_{ass}$ . However, this was not the case.

#### *The nature of the Vis-spectral changes*

Due to the difference in energies of the electronic transitions of the cationic and anionic chromophores, the resonance interactions resulting in decoupling of the energy levels of the excited state<sup>16</sup> are reduced to the minimum. The intensities and widths of the absorption bands change substantially upon the formation of the associates, and their change, unlike that in  $\lambda_{max}$ , depends slightly on the difference in the absorption regions of Ct<sup>+</sup> and An<sup>x-</sup>.

The spectral effects can be explained as follows. In the cations Ct<sup>+</sup> of **1** and **2**, the positive charge is predominantly localized on the heterocyclic moiety.<sup>16</sup> Therefore, the An<sup>x-</sup> ion in the associate is displaced towards the heterocycle due to electrostatic attraction of opposite charges. This results in disturbs of the electron symmetry in both ions due to the shift of the charges. As a result, an alternation of single and double bonds occurs in the Ct<sup>+</sup> chromophore. This, in turn, results in enhancement of the vibronic interactions, which depend on the degree of interaction of charges.

It must be pointed out that while studying the interaction between cationic cyanines (including trimethinium cyanine dye with indoline end group) and hydrophobic borate anions [including B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup>], some authors (see preceding section) suggested that the corresponding spectral changes, very similar to those shown in Figures 1, 2, and 5, appear not due to cation-anion interaction itself, but are caused by the 'dimerization of cyanine dyes in water driven by association with hydrophobic borate anions', *e.g.* (Ct<sup>+</sup>·An<sup>-</sup>)<sub>2</sub>.<sup>30</sup> Hence, they attribute the observed effects to Ct<sup>+</sup> dimerization.<sup>30</sup>

However, our experiments with another cationic polymethine dye, pinacyanol<sup>26</sup>, does not confirm such an

explanation. This substance, due to the flat structure of its chromophore, easily forms in water the so-called H-aggregates, *i.e.* species with a band shifted towards the blue against the initial 'monomeric' band. But also in this case, the addition of HR<sup>-</sup> ion of bromothymol blue, as well as of B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup>, results in a hypochromic effect accompanied by a distinct red shift ( $\Delta\lambda_{max}$  up to *ca.* 25 nm).

Moreover, we registered the red shifts of the absorption bands and fluorescence quenching of diluted solutions of indopolymethine cations in the presence of C<sub>60</sub> hydrosol,<sup>31</sup> an ultramicroheterogeneous system with negatively charged colloidal particles. The spectral effects were very similar to those observed with various anionic dyes and tetraphenylborate ion in water.<sup>18</sup> This can be regarded as a strong argument for the interaction between the cationic chromophores and negative charge.

It must be also noted that the interaction of B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup> ion in water with some other cationic dyes, rhodamine 6 G,<sup>32</sup> rhodamine B and rhodamine 3 B,<sup>33</sup> manifests itself in a hypochromic effect and a red shift of the absorption bands of the dyes, but the spectral changes strongly differ from those observed for cationic dyes dimerization. An analogous picture was observed for the 1:1 complex formation of methylene blue, rhodamine 6 G, pyronine G, safranin T, and crystal violet with naphthalenesulfonates and similar anions;<sup>34</sup> the red shifts in the absorption and fluorescence spectra of these dyes are explained in terms of charge-transfer complex formation.<sup>34</sup> In the system methylene blue – eosin<sup>35</sup> the alterations of the absorption band of the cationic thiazine dye are also the same (red shift). Hence, the explanation of the spectral changes reported in the present communication (Figures 1,2,5,6b) by interaction between Ct<sup>+</sup> chromophores within their associate with An<sup>x-</sup><sup>30</sup> seems less probable.

However, such interactions between identical Ct<sup>+</sup> ions can really take place within the region of pre-micellar 'dye + surfactant' associates (see below), especially in the case of dye-reach sub-colloidal particles (Figures 7 and 8). At the same time, the spectra of the dye **2** in micellar media of both cationic and anionic surfactants, as well as in 96 % aqueous ethanol are closer to that in pure water (Figure 1, curve 1) but shifted towards the red. Such 'positive' solvatochromism is typical for the heptamethinium cationic dye.<sup>1</sup>

#### *Driving forces of association*

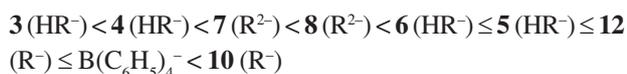
The  $K_{ass}$  values are at least 2 or 3 orders of magnitude higher than the dimerization constants of the corresponding dyes. The contribution of electrostatic cation – anion attraction is demonstrated in Figure 6.

However, semi-quantitative estimations, based on Bjerrum's electrostatic theory, show, that in water the association of such large ions must be negligible. Hence, there are some other reasons for such high  $K_{ass}$  values ( $10^4$  to  $7 \times 10^7$  mol<sup>-1</sup> L).

Such reasons can be the Van der Waals interactions<sup>1,2,6</sup> and hydrophobic effect (hydrophobic bond).<sup>1,6</sup> The latter seems to be of more significance so that while adding acetone, ethanol, 1,4-dioxane, etc., the associates dissociate: the water-miscible organic solvents solvate the relatively hydrophobic organic anions, and they became stable enough even in isolated form in the solvent.

Destroying dye associates of Ct<sup>+</sup>An<sup>x-</sup> type in the presence of surfactants also demonstrates the significance of the hydrophobic effect, because the nature of both homomicelles and mixed dye-surfactant micelles formation is known to be to high extent hydrophobic.<sup>12,13</sup> In the region of pre-micellar surfactant concentration ( $6 \times 10^{-6}$  -  $6 \times 10^{-5}$  mol L<sup>-1</sup>), formation of 'dye + surfactant' associates and mixed micelles manifest itself in a hypochromic effect, in agreement with earlier reports.<sup>13</sup> Thus, the role of the anionic surfactant (Figure 7) consists in competition with the HR<sup>-</sup> dye ion in its interaction with the **2** chromophore (Ct<sup>+</sup> + HR<sup>-</sup>  $\rightleftharpoons$  Ct<sup>+</sup>·HR<sup>-</sup> and Ct<sup>+</sup> +  $n$ -C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub><sup>-</sup>  $\rightleftharpoons$  Ct<sup>+</sup>· $n$ -C<sub>12</sub>H<sub>25</sub>OSO<sub>3</sub><sup>-</sup>). The cationic surfactant (Figure 8) competes with the ion Ct<sup>+</sup> (HR<sup>-</sup> +  $n$ -C<sub>16</sub>H<sub>33</sub>NC<sub>5</sub>H<sub>5</sub><sup>+</sup>  $\rightleftharpoons$  HR<sup>-</sup>· $n$ -C<sub>16</sub>H<sub>33</sub>NC<sub>5</sub>H<sub>5</sub><sup>+</sup>). The dissociation of the initial dye associate in the presence of surfactant micelles can be regarded as a result of 'dilution' by the micellar pseudophase, analogous to solvation with organic solvents (see above).

For the Ct<sup>+</sup> cation of **2** the anions An<sup>x-</sup> can be arranged in the following row, in accord with the corresponding  $K_{ass}$  values, or Gibbs energies of association,  $\Delta G_{ass} = -2.303 RT \log K_{ass}$ :



Hence, the introduction of bromine and *iso*-propyl groups leads to an essential strengthening of the ion association: compare the data for HR<sup>-</sup> ions of **3** (-9.5 kJ mol<sup>-1</sup>) and **4** (-10.7 kJ mol<sup>-1</sup>), on one hand, and **6** (-14.6 kJ mol<sup>-1</sup>) and **5** (-14.9 kJ mol<sup>-1</sup>), on the other. Comparison of the data for the R<sup>-</sup> ion of **10** (-19.1 kJ mol<sup>-1</sup>) with that of R<sup>2-</sup> ion of **8** (-14.4 kJ mol<sup>-1</sup>) demonstrates that an additional negative charge weakens the association with the counterion – the dianion R<sup>2-</sup> is hydrated stronger than the R<sup>-</sup> ion. This proves the significance of hydrophobic interactions in organic ion association in aqueous media.

Though the contributions of the given cation or anion

to the  $\Delta G_{ass}$  values are not exactly constant, the increase in the number and total volume of the hydrophobic substituents always results in stabilization of the associates.

In the case of the Ct<sup>+</sup> cation of **1**, the sequence of  $K_{ass}$  values for the anions An<sup>-</sup> studied, namely HR<sup>-</sup> of **6**, R<sup>-</sup> **10**, **12**, and B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup>, is just the same. On the other hand, the log  $K_{ass}$  values for the given anion An<sup>-</sup> are markedly larger in the case of **1**, as compared with those for **2**, the difference ranges from 0.8 (tetraphenyl borate) to 1.8 (bromothymol blue **6**). The length of the polymethine chain facilitates the disturbance of the electron symmetry, increasing the association with ions with opposite charge. The enlargement of the  $\pi$ -system also leads to an increase in the values of association constants.

Several  $K_{ass}$  values for other cationic dyes are available in literature. So, for rhodamine 6G cation the association in water with B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup>, rhodamine 200 B (R<sup>-</sup>), and eosin the following log  $K_{ass}$  are reported: 5.01,<sup>32</sup> 5.0,<sup>3</sup> and 5.84-5.91,<sup>3</sup> respectively. For association of B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub><sup>-</sup> with cations with a higher number of carbon atoms, rhodamine B and rhodamine 3B, the log  $K_{ass}$  are higher than that for rhodamine 6 G, *i.e.* 5.4 and 6.6<sup>33</sup>. This again demonstrates the significance of hydrophobic and Van der Waals interactions. For association of eosin anions with cations of malachite green, crystal violet, and methylene blue the log  $K_{ass}$  values equal 5.28,<sup>3</sup> 5.30-5.5,<sup>3</sup> and 5.0-5.5,<sup>35</sup> respectively. However, it must be noted that if in the case of eosin the proper (high enough) pH value is not maintained constant, a mixture of HR<sup>-</sup> and R<sup>2-</sup> ions can actually exist in solution. For instance, a  $\lambda_{max}$  value of 520 nm was registered for eosin while studying its association with methylene blue cation;<sup>35</sup> such a value indicates the presence of HR<sup>-</sup> anion rather than R<sup>2-</sup> one.<sup>22</sup>

## Conclusions

Cations of polymethine dyes with indoline end groups associate with anions of sulfonephthaleins and xanthenes in water. The association constants determined using the Vis-spectroscopy are within the range ( $10^4$  to  $7 \times 10^7$ ) mol<sup>-1</sup> L. The principal spectral effect accompanying the formation of 1:1 ionic associates is a (1.5-2.5)-fold decrease in intensity of the absorption bands of indoheptamethinium ( $\lambda_{max} = 737$  nm) and indotrimethinium ( $\lambda_{max} = 540$  nm). The most probable driving forces of association are hydrophobic and Van der Waals interactions; the electrostatic attraction of the oppositely charged ions also makes its contribution to the association process. Addition of ionic surfactants leads to the decomposition of the dye ion pairs primarily due to interactions with the oppositely charged dye ions; the

process manifests itself in the restoration of the initial Vis absorption bands of both cationic and anionic dye.

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Received: June 2, 2004

Published on the web: February 23, 2005