Interaction of chromophores in dissimilar associates of cationic and anionic polymethine dyes in water

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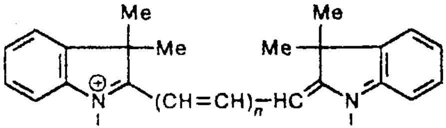
A strong interaction between chromophores of cationic and anionic components was found based on the analysis of electronic absorption spectra of aqueous solutions of mixtures of cationic indopolycarbocyanines with anionic cyanines. Strong dissimilar 1 : 1 associates are formed. Association constants were estimated spectrophotometrically. The main factors determining the degree of interaction of chromophores were revealed.

Key words: cationic and anionic polymethine dyes, interaction of chromophores; cation-anionic associates, association constants; electronic absorption spectra.

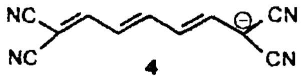
An interaction between chromophores is especially pronounced in electronic spectra of polymethine dyes, because the most narrow, intense, and resolved absorption bands are typical of them.[1] This phenomenon is well studied for covalently bound dimers, biscyanine dyes (biscyanines). The latter are very convenient objects because they have a certain number of chromophores, the distance and angle between which can be varied by chemical modification.[2] These interactions also can be observed in associates of the polymethine dyes in which the chromophores are not bound by covalent bonds. This phenomenon was studied in greatest detail in similar associates (consisting of molecules of the same compound).[3,4] The interaction of chromophores in dissimilar associates (predominantly of cationic dyes) has been studied to a lesser extent.[5] Such interaction of oppositely charged polymethine dyes in their ion pairs was observed only in low-polar organic solvents.[6–9] Dissimilar association of cationic and anionic dyes of this class in water was not studied.

In this work, the interaction of the chromophores upon the formation of mixed associates of the cations of indopolycarbocyanines **1—3**, Ph_4As^+, and Bu_4N^+ with anionic polymethine dyes **4—8** and Ph_4B^- was studied by electron spectroscopy.



1—3

n = 1 (**1**), 2 (**2**), 3 (**3**)



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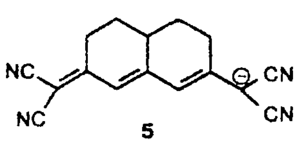

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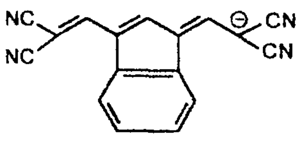

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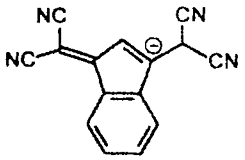

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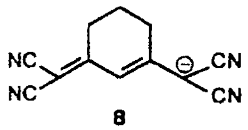

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The variation of the length of the polymethine chain of the cation makes it possible to control overlapping of bands of the cationic and anionic components up to their complete resolution. The use of dilute solutions allows one to rule out similar association (dimerization) almost completely and to assign all effects observed to dissimilar (cation-anionic) association.

Experimental

Polymethine dyes were synthesized as described previously.[10,11] Cationic dyes were used as chlorides, iodides, and

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tetrafluoroborates, as well as $Ph_4As^+Cl^-$; anionic dyes were used as tetramethylammonium salts and $Na^+Ph_4B^-$ (VEB Laborchemie Apolda). Tetrabutylammonium iodide (chemical purity grade) was used without additional purification. The concentration of aqueous solutions was refined by UV spectra.[12]

Absorption spectra were recorded on SF-46, Specord UV-VIS, and Hitachi-3010 spectrophotometers at ~20 °C. Fluorescence spectra were recorded on a Hitachi-4010 instrument.

Dyes **2** and **3** were dissolved in 96% ethanol. Experiments were performed in buffer-free aqueous solutions containing typically 4 vol.% ethanol. Oscillations of the pH value had no effect on the results, because not only cationic,[13] but also anionic polymethines are protonated only in very acidic media. The ionic strength of solutions did not exceed 10^{-3} mol L^{-1}.

Results and Discussion

The parameters of long-wave absorption bands of compounds **1**—**8** are presented in Table 1. The typical changes in the absorption spectra occurring upon mixing of the cationic (**1**—**3**) and anionic (**4**—**8**) dyes in water are presented in Figs. 1 and 2. An increase in the concentration of the dye with a lower value of λ_{max} results in a considerable decrease in the intensity and broadening of the absorption band of the dye with a greater λ_{max}. For the band of anion **6**, the Bouger—Beer law is also fulfilled at equal concentrations of dyes **3** and **6**, although the band of indotricarbocyanine **3** changes substantially (see Fig. 2). The Kiprianov's effect[1,2] is most pronounced in mixtures of dyes **1** + **6** and **2** + **6**: not only a change in the intensity, but also a bathochromic shift of the long-wave band are observed.

The decrease in the intensity of the long-wave band is evidence for the interaction of the chromophores that converged due to the association. The introduction of rather bulky colorless ions in aqueous solutions of oppositely charged dyes (systems **3** + Ph_4B^-, **6** + Ph_4As^+, and **6** + Bu_4N^+) also results in a decrease in the intensity and broadening of bands of both cationic and anionic dyes (Figs. 3 and 4). However, these effects are somewhat less pronounced than those in the case of colored counterions. Due to binding in an ion associate, the intensity of the long-wave absorption band decreases, being 50—70% (see Figs. 3 and 4) and 26—33% (see Figs. 1 and 2) of the initial value in the first and second cases, respectively.

Table 1. Long-wave absorption bands of polymethines in water

Dye	λ_s[a]	λ_{max}	ε_{max}[b] $\cdot 10^{-3}$
	nm		/L mol^{-1} cm^{-1}
1[c]	510	540	144.00
2[c]	598	637	193.00
3[c]	682	737	201.00
4	528	563	33.73
5		540	19.67
6	542	580	60.77
7	618	581	14.10
8		441	119.00

[a] λ_s is a shoulder, inflection, or convexity in the spectrum.

[b] The values of ε_{max} were determined with an error of ±(3—5)% for 5—11 independent reflections.

[c] The spectra of cationic dyes **1**—**3** were recorded in the presence of 4 vol.% EtOH.

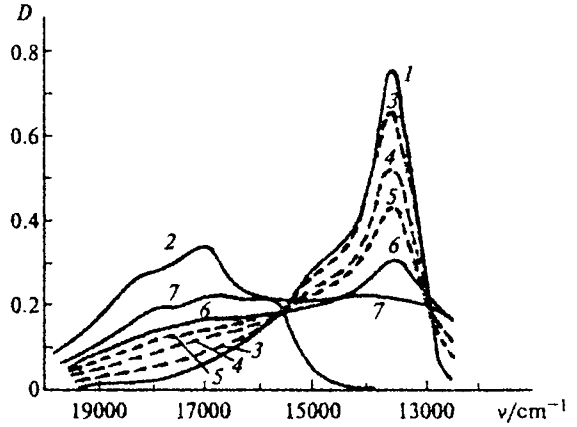

Fig. 1. Absorption spectra of individual dye **3**, [**3**] = $4.0 \cdot 10^{-6}$ mol L^{-1} (*1*); individual dye **7**, [**7**] = $1.6 \cdot 10^{-5}$ mol L^{-1} (*2*); mixture **3** + **7** (*3*—*7*): [**3**] = $4.0 \cdot 10^{-6}$ mol L^{-1} = const, [**7**]/mol L^{-1} = $7.9 \cdot 10^{-7}$ (*3*), $1.6 \cdot 10^{-6}$ (*4*), $2.4 \cdot 10^{-6}$ (*5*), $3.2 \cdot 10^{-6}$ (*6*), and $4.7 \cdot 10^{-6}$ (*7*).

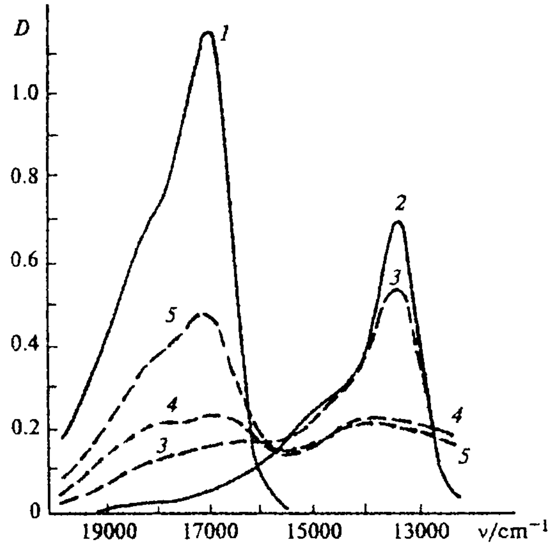

Fig. 2. Absorption spectra of individual dye **6**, [**6**] = $2.0 \cdot 10^{-5}$ mol L^{-1} (*1*); and mixture **3** + **6** (*2*—*5*): [**3**] = $4.0 \cdot 10^{-6}$ mol L^{-1} = const, [**6**]/mol L^{-1} = 0 (*2*), $2.0 \cdot 10^{-6}$ (*3*), $4.0 \cdot 10^{-6}$ (*4*), and $8.0 \cdot 10^{-6}$ (*5*).

In aqueous solutions, the anionic dye (or Ph_4As^+ and Bu_4N^+) usually attains a concentration whose excess does not result in further changes in the absorption

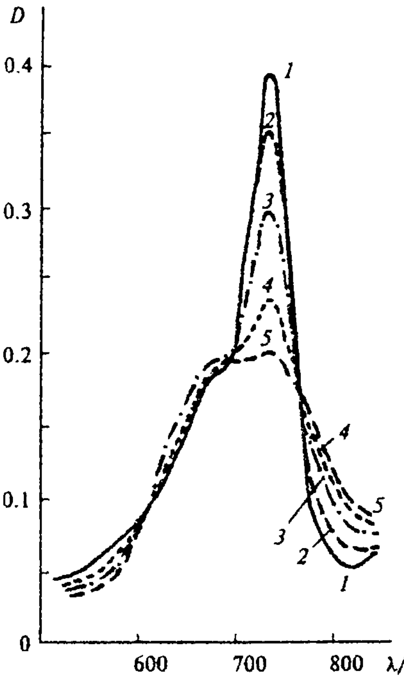

Fig. 3. Absorption spectra of the mixture **3** + Ph_4B^-; [**3**] = $2.0 \cdot 10^{-6}$ mol L^{-1} = const, [Ph_4B^-]/mol L^{-1} = 0 (*1*), $0.8 \cdot 10^{-6}$ (*2*), $1.6 \cdot 10^{-6}$ (*3*), $2.4 \cdot 10^{-6}$ (*4*), and $2.8 \cdot 10^{-6}$ (*5*).

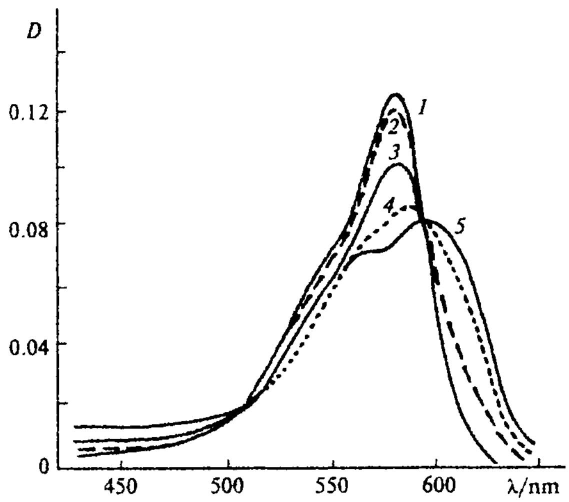

Fig. 4. Absorption spectra of the mixture **6** + Ph_4As^+; [**6**] = $2.0 \cdot 10^{-6}$ mol L^{-1} = const, [Ph_4As^+]/mol L^{-1} = 0 (*1*), $2.0 \cdot 10^{-6}$ (*2*), $3.95 \cdot 10^{-6}$ (*3*), $1.2 \cdot 10^{-5}$ (*4*), and $2.4 \cdot 10^{-5}$ (*5*).

spectra of the cationic dye (or compound **6**) taken in a small concentration. When such "saturation" is achieved, the spectrum of the mixture in the long-wave region almost coincides with that of the specially synthesized corresponding cation-anionic dye. This suggests that a 1 : 1 associate is formed in water.

The study of the association in aqueous solutions of the systems containing an anion that almost does not absorb in the region of λ_{max} of the cation shows that the composition of the associates established by the saturation method[14] is equal to 1 : 1 for different concentrations of the cationic dye:

$$Ct^+ + An^- \rightleftharpoons Ct^+ \cdot An^-, \qquad (1)$$

where Ct^+ is the cation and An^- is the anion.

It is known[15] that similar methods give only a ratio of stoichiometric coefficients. However, in this case, the formation of 2 : 2 associates are improbable. In the chromophores of both cationic[16] and anionic[17] dyes, the positive and negative charges alternate at constant overall charges: +1 for the former and −1 for the latter. The greater the distortion of the uniformity in the charge distribution in the chromophore, the stronger the intermolecular interactions in the dye—dye and dye—solvent systems.[1] The nonuniformity in the charge distribution increases as the polymethine chain elongates.[18] This explains probably the fact that the tendency for the association with an anion is enhanced in the series of cationic dyes **1**—**3**. This is also favored by an enhancement of dispersion interactions due to the elongation of the π-system. A similar effect is achieved when the system is branched due to the introduction of aromatic cycles.[4]

The decrease in the long-wave absorption band when dissimilar associates are formed indicates their "sandwich" structure. This is also confirmed by the decrease in the fluorescence of dye **2** when anion **6** is added to its aqueous solutions (Fig. 5). It has been shown previ-

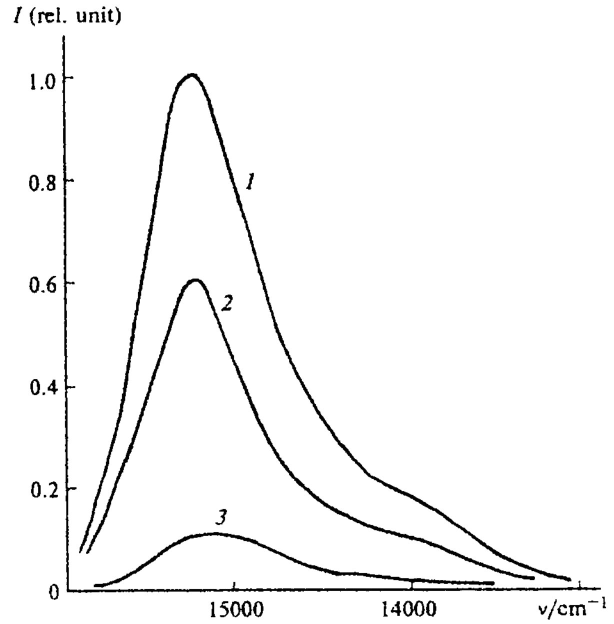

Fig. 5. Quenching of the fluorescence of the cationic polymethine in the system **2** + **6**: [**2**] = $2.0 \cdot 10^{-6}$ mol L^{-1} = const, [**6**]/mol L^{-1} = 0 (*1*), $1.0 \cdot 10^{-6}$ (*2*), and $2.0 \cdot 10^{-6}$ (*3*) (l = 1 cm).

ously[6] that the interaction of anion **5** with the oxazine dye (λ_{max} = 658 nm) in benzene results in an approximately twofold decrease in the intensity of the absorption band of the latter in the associate, while the intensity of the band of dye **5** remains almost unchanged.

Due to the difference in energies of the electronic transition of the chromophores of the cation and anion in the dissimilar associates, the resonance interactions resulting in decoupling of the energy levels of the excited state[5] are reduced to the minimum. This first of all results in a small change in the λ_{max} values of the cations and anions upon association. The greater the difference between the absorption regions of the ions, the weaker the shifts of their absorption bands in the associate, which is observed experimentally. However, the intensities and widths of the bands change substantially upon the formation of the associates, and their change, unlike that in λ_{max}, depends slightly on the differences in the absorption regions of the cation and anion.

These effects can be explained as follows. In the molecules of cationic cyanine dyes **1—3**, the positive charge is predominantly localized on the heterocycle.[13] Therefore, the anion in the "sandwich" is displaced toward the heterocycle due to the Coulomb attraction of the unlike charges. This disturbs the electron symmetry in both ions due to the shift of the charges to the ends of their chromophores. As a result, as in nonsymmetric cyanines, the alternation of ordinary and double bonds occurs in the cation and anion of the dissimilar associates.[19] The result of this alternation is an enhancement of the vibronic interactions,[20] which depend on the degree of interaction of the charges. Therefore, the intensity and width of the bands upon the association of the cationic and anionic dyes are less sensitive to the difference in the absorption regions of the free ions. In fact, the spectra of dye **6** change almost similarly for the interaction with the ions Ph_4As^+ and Bu_4N^+.

The alternative positive and negative charges, as well as easily polarized conjugated bonds both in the cations and anions of the dyes, result in the fact that the changes in the electron asymmetry and, hence, vibronic interactions in their associates are greater than those in the associates based on colorless counterions. Therefore, in the latter case, the interaction of the chromophores is less pronounced (see Figs. 3 and 4).

For the calculation of the association constants, the equilibrium concentrations of the associate $Ct^+ \cdot An^-$ were determined from the spectral data in the region of λ_{max} of cation **1** (**2**, **3**) by the equation

$$[Ct^+ \cdot An^-] = x = \frac{\varepsilon_{Ct}C_{Ct}l - D}{(\varepsilon_{Ct} - \varepsilon_{as})l}, \qquad (2)$$

where C_{Ct} is the analytical concentration of cationic dye **1**, **2**, or **3** (which does not vary in a single series of experiments); l is the cell length; D is the optical density for the current value of the analytical concentration of the anion (C_{An}); and ε_{Ct} and ε_{as} are the molar absorption coefficients of the cation and associate, respectively. The search for x values is substantially facilitated by the fact that the association is pronounced. Therefore, it is not necessary to create such an excess of the ions An^- for which the absorption of the latter in the region of the wavelengths under analysis would be taken into account even if the difference in λ_{max} of the cation and anion has been already taken into account (in particular cases these corrections were introduced, but their contribution was not substantial). In the case of dyes **5—8**, a 5—15-fold excess of An^- resulted in the almost complete binding of Ct^+ into the associate at $C_{Ct} = (2—4) \cdot 10^{-6}$ mol L^{-1}, which made it possible to estimate ε_{as} (at $C_{as} \to C_{Ct}$). Moreover, due to the high values of the association constants (K_{as}) calculated by the equation

$$K_{as} = \frac{[Ct^+ \cdot An^-]}{[Ct^+][An^-]} = \frac{x}{(C_{An} - x)(C_{Ct} - x)}, \qquad (3)$$

great dilution was required to attain statistically significant differences between x and C_{Ct}.

In particular cases (association of dyes **2** and **3** with **8** and Ph_4B^-), a certain scatter in the values of the constants was observed, which has been previously mentioned[21] for the systems "cationic dye + anionic dye." This can be related to the stepwise character of the association as the concentration of the dye increases. The resulting data for K_{as} were obtained for $C_{Ct} = 2 \cdot 10^{-6}$ mol L^{-1}, 10—15 values of C_{An}, and 3—4 working wavelengths; the fiducial intervals of $\log K_{as}$ were calculated for a fiducial probability of 0.95 (Table 2).

The same approach was used for the systems **6** + Ph_4As^+ and **6** + Bu_4N^+ (see Table 2), but the corresponding parameters of the anion were used instead of ε_{Ct} and C_{Ct} in Eq. (2). The measurements performed in the concentration range of $1 \cdot 10^{-6}—5 \cdot 10^{-5}$ mol L^{-1} for 20 solutions of dye **6** containing only the cations Me_4N^+ (l = 0.2—5.0 cm) show that under these conditions, the Bouger—Beer law is fulfilled.

Table 2. Values of the logarithms of the association constants of indopolycarbocyanines **1—3**, Ph_4As^+, and Bu_4N^+ with anionic dyes in water (4 vol.% EtOH, 20 °C)

Anion	Rh6G[a]	log K_{as}				
		1	**2**	**3**	Ph_4As^+	Bu_4N^+
4	—	—	—	2.9±0.2	—	—
5	—	—	—	6.1±0.2	—	—
6	—	—	—	6.46±0.07	5.14±0.06	4.1±0.3
7	—	—	—	6.65±0.15	—	—
8	—	—	5.98±0.19	6.63±0.15	—	—
Ph_4B^-	5.01	5.4±0.2	5.6±0.2	6.2±0.3	—	—
$(PR)^-$ [b]		—	—	—3.91±0.18	—	—

[a] Rhodamine 6G (Ref. 22).

[b] Phenolic Red.

Dyes **2** and **3** and their associates with the anionic dyes are poorly soluble in pure water. The addition of small amounts of ethanol enhances their solubility.

Electronic absorption spectra give information on the existence of the association and mutual arrangement of the chromophores in the associate,[1—3,6,23] but they do not allow one to establish unambiguously the character of the associates: contact or solvate-separated ion pairs, with or without participation of colorless counterions (for example, Ct_2^{2+} or $Ct_2^{2+}An_2^{2-}$).[23]

The reasons for the association can be different. In organic solvents, especially in low-polar solvents, the association of the cation-anionic dyes is mainly caused by the Coulomb interactions. It is shown[24] that in chloroform, the triphenylpyrilium and triphenylthiopyrilium cations form associates (charge-transfer complexes) with tetracyanomethanide and tetracyanopropenide (K_{as} = 10^4—10^5 L mol^{-1} and higher). In chloroform and ethyl acetate, the cation-anionic polymethine dyes are characterized by the values of K_{as} from $6 \cdot 10^4$ to $5 \cdot 10^6$ L mol^{-1} (according to the conductometric data),[7] and in benzene with additions of methanol,[6] K_{as} = (3—5) $\cdot 10^5$ L mol^{-1}; the association is also observed in dichloroethane and acetonitrile.[1]

In aqueous solutions, for the cation-anionic dyes, the Coulomb interaction is weakened, but the hydrophobic interactions leading to the association begin to play a substantial role.[25] Dipolar and dispersion, as well as π-electronic interactions, enhance the association. This is favored by the planar structure of the dyes.[25] Even the association of likely charged ions in water was theoretically substantiated[25] and observed for dyes several times.[5,25] For example, for the series of the cationic dyes in water,[26] values of the dimerization constants in the range from 10^2 to $5 \cdot 10^3$ L mol^{-1} were obtained. It is shown that in concentrated aqueous solutions, both the tetraphenylarsonium and tetraphenylborate ions are inherent in self-association.[27] In the considered case of the dissimilar association of the cationic and anionic dyes, Coulomb attraction (instead of repulsion upon the dimerization) is an additional factor of the stabilization of the associates, which is predominant over electrophilic (accompanied by the formation of H-bonds) and nucleophilic solvation. For example, the value of the association of the rhodamine 6G cation with the Ph_4B^- ion in water is more than 40 times greater than the value of the dimerization constant of this dye.[22,26]

The similar structure of the polymethine systems of the cationic and anionic cyanine dyes provide optimum conditions for the intermolecular electrodynamic (oscillating instantaneous dipoles along the long axis of the chromophore of the cation and anion are oriented oppositely to one another) and electrostatic (unlike charges are arranged oppositely) interactions of the chromophores in their dissimilar associates. Therefore, these associates are stronger than those based on their cationic or anionic components not only with a colorless counterion, but also with a colored counterion of an organic dye of another class.

For the series of the other cation-anionic pairs in water,[21] the K_{as} values range from 10^4 to 10^5 L mol^{-1}, and only in particular cases do they approach a value of 10^6 L mol^{-1}. For cations **2** and **3** with anionic polymethines **5**—**8**, $K_{as} \geq 10^6$ L mol^{-1} (see Table 2). The exception is dye **4**, whose size is likely too small to result in sufficiently strong destruction of the normal structure of water and thus provide a strong hydrophobic interaction.

In monomeric carbanions, charges are delocalized. This favors solvation due to the dispersion interactions in many organic solvents, but hydration is not favored. In fact, in some organic solvents, the anionic polymethines (carbanions) with the cationic polymethines form less stable associates than other anions do.[7]

In low-polar solvents, the specific solvation of the polymethine dyes preventing the association is reduced to the minimum;[28] however, additions of methanol destroy the associates.[6] At the same time, the destruction of the associates was also observed in aqueous solutions when organic solvents were added. After 8—10 vol.% of methanol, acetone, or dioxane were added to a mixture of dyes **3** ($2 \cdot 10^{-6}$ mol L^{-1}) and **5** ($6 \cdot 10^{-6}$ mol L^{-1}), the intensity of the absorption band of the cation was recovered, which testified that the associate was destroyed. This is caused by the solvation of the comparatively hydrophobic dyes by the organic co-solvent (the decrease in the dielectric permeability is less substantial). The data presented in Table 2 allow one to monitor the effect of the structural factor on the values of the free energy of the association ($\Delta G_{as} = -RT \cdot \ln K_{as}$). The high degree of the charge delocalization in carbanions **5**—**8** causes their tendency for the dispersion interactions and a weak ability to form H-bonds. Therefore, for the association with the same cation, the ΔG_{as} values for these anions are ~12 kJ mol^{-1} lower than those in the case of the strongly hydrated yellow monoanion of phenolsulfophthalein (see Table 2). Tetraphenylborate, a spherical ($r \approx 4.2$ Å) anion with a well-screened charge, is closest to the anionic polymethines in its ΔG_{as} value and can be considered a reference hydrophobic anion.

The comparison of the constants and free energies of the association of the rhodamine 6G cation and cations **1**—**3** with those of the Ph_4B^- anion (see Table 2) shows that the elongation of the polymethine chain and the increase in the cation charge favor the enhancement of the association, and the log K_{as} values for the formation of the associates of ions **2** and **3** with the Ph_4B^- anion differ by 0.6 (as for the association with anion **8**).

It should be elucidated how constant are the contributions of different ions to the resulting value of ΔG_{as} in aqueous solutions. It is evident that the better the description of the real picture by the additive scheme, the smaller the specific interactions. If the contributions of tetraphenylborate and tetraphenylarsonium are considered to be equal, it can be calculated from the data for the pairs of ions **3**—**6**, **3**—Ph_4B^-, Ph_4As^+—**6**, and

Bu_4N^+—**6** that the contribution of the dyes to ΔG_{as} are the following: for **3**, −21.2; **6**, −15.0; Ph_4B^- and Ph_4As^+, −13.6; and Bu_4N^+, −8.0 kJ mol^{-1}. If the hypothesis on additivity is valid, these data allow one to estimate the K_{as} value for tetraphenylarsonium tetraphenylborate in water, which should be somewhat lower than $1 \cdot 10^5$ L mol^{-1} (direct measurements are impossible because the solubility of this compound in water is very low). A similar approach can be used for the description of extraction equilibria[29]

$$Ct_w^+ + An_w^- \rightleftharpoons (Ct^+An^-)_o \qquad (4)$$

(indices "w" and "o" designate the aqueous and organic phases, respectively).

The individual contribution of the extraction of the Ph_4As^+ ion to the log$K$ value (equilibrium (4))[29] is 1.1 units greater than that of the Bu_4N^+ ion and 6.4 units greater than that of the Me_4N^+ ion. The contribution of the Ph_4B^- ion is 4.9 units greater than that of the F_4B^- ion and 6 units greater than that of I^-. These data confirm indirectly that the counterions in the initial dyes (see Experimental) should not compete with the larger hydrophobic counterions during the ion association in water. This agrees with the fulfillment of the Bouger—Beer law in dilute solutions of both cationic and anionic individual dyes.

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