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Interaction of Sulfophthaleine Anions with Cationic Dyes in Aqueous Solution

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Abstract—An interaction between the singly and doubly charged anions (HAn^- and An^{2-}) of sulfophthaleines (phenol red and its derivatives: bromophenol blue, bromocresol green, bromocresol purple, and bromothymol blue), and singly charged cations (Ct^+) of a polymethine (pinacyanol, quinaldine red), results in formation in an aqueous solution of heteroassociate with stoichiometric composition $(Ct^+)\cdot HAn^-$ and $(Ct^+)_2\cdot An^{2-}$. On the basis of spectrophotometric data the association constants were estimated. By quantum-chemical methods AM1 and PM3 the values of formation and reaction enthalpies of the species formed were calculated and the most probable structure of the heteroassociates was determined.

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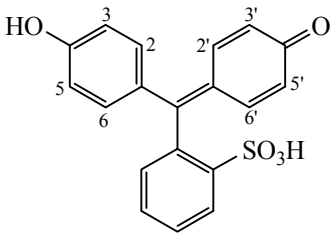
Sulfophthaleine dyes have long time been used not only as acid–base and metallochrome indicators, but also as analytical reagents for the photometric determination of many metal ions, surfactants, and other objects in solutions [1, 2]. Recently in addition to the unsubstituted phenol red, attention was drawn to the use of several sulfophthaleine bromo derivatives: bromophenol blue, bromocresol green, bromocresol purple, and bromothymol blue. They possess well resolved absorption bands of single- and double-charged ions, and, as a consequence, show high color contrast at the indicator transition [1, 3, 4]. Owing to these features the sulfophthaleines are used, in particular, for high-precision determination of pH of pure [5] and natural waters *in situ* (a mixture of sulfophthaleines is applied [6, 7]). Bromine-containing dyes form the basis of sensitive elements for the fiber optics biosensors and chips [8–10] (e.g., bromothymol blue and acetylcholinesterase doped in sol-gel film are sensitive to the content of organophosphorus pesticide chloropyrifos [9]). The dyes have been used effectively also for the study of serum albumin [11, 12]. Comparatively recently the sulfophthaleines found application as analytical reagents for the quantitative determination of some components in the biotechnology and pharmaceuticals: antiviral [13], antimicrobial [14], bactericidal [15], antihistaminic [16], hypotensive [17], antidepressant [18, 19], antiallergic [20], and others. It should be emphasized that the above methods are highly accurate, correct, and suitable to express application; they are based on the formation of heteroassociate (ion pair) between the test component and the anionic form of the dye. The heteroassociates often are extracted into the organic phase (chloroform [13, 14, 16], dichloromethane [20]). Sulfophthaleine solutions are fairly complex objects, since each dye is involved into many protolytic and tautomeric transformations. Even in thin-film state they may be an equilibrium mixture of the associated lactone, quinoid, and zwitter-ionic forms [21].

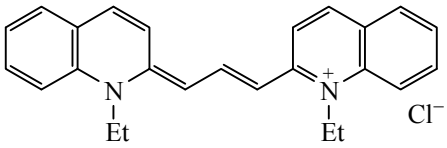
Analysis of published data shows the importance of study of the cation-anion interactions (both of Coulomb and non-Coulomb nature), leading to the formation of the heteroassociates composed of dyes anions (HAn^-, An^{2-}). Obviously without the knowledge of equilibrium thermodynamic characteristics of the processes of association it is impossible to find an effective application of the sulfophthaleines. Preiously [22, 23] we examined interactions of some sulfophthaleines with singly charged cationic polymethines (Ct^+). However, the structure of the associates and the energy characteristics of the association remain unclear.

In this report based on the results of spectrophotometric measurements and quantum-chemical calculations the cation–anion interaction is considered

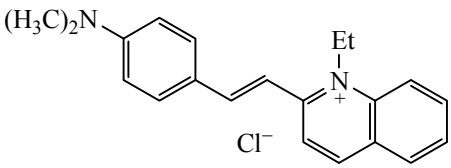
leading to the formation of stoichiometric heteroassociates between a singly or doubly charged sulfophthaleine anion (**A**) and a cations of pinacyanol (**B**) or quinaldine red (**C**) (see Table 1), and the properties and the probable structure of the heteroassociates Ct^++HAn^- and Ct^++An^{2-} are discussed. Due to the physical and chemical properties of these polymethine cations they were proved to be suitable counterions in studying the properties of heteroassociates of many dyes [23–26].



A



B



C

Structure of dyes in aqueous solution. Highly acidic or alkaline solutions containing univalent cations (Ct^+) of a polymethine are noticeably discolored due to the process $Ct^+ + H^+ \rightleftarrows HCt^{2+}$ and $Ct^+ + OH \rightleftarrows CtOH$, respectively, leading to the distortion of conjugation in the chromophore polymethine chain. Equilibrium of sulfophthaleines as tribasic acids in solutions can be represented by the

Table 1. Spectral-protolytic characteristics of dyes

Dye	Position of substituents	pK_{a1} [a]	pK_{a2} [b]	λ_{max}, nm ε_{max}, l mol^{-1} cm^{-1}	
	Sulfophthaleines				
				HAn^-	An^{2-}
Phenol red (**I**)	all substituents are H (phenolsulfophtalein)	1.03	8.00	430 (2.4×10^4)	558 (6.2×10^4)
Bromophenol blue (**II**)	3,3',5,5' – Br (3,3',5,5'-tetrabromphenolsulfophthalein)	–0.95	4.20	438 (2.5×10^4)	591 (8.0×10^4)
Bromocresol green (**III**)	2,2' – Me; 3,3',5,5' – Br (3,3',5,5'-tetrabromo-*m*-cresolsulfophthalein)	1.2	4.90	444 (1.8×10^4)	617 (4.0×10^4)
Bromocresol purple (**IV**)	3,3' – Me; 5,5' – Br (5,5'-dibromo-*o*-cresolsulfophthalein)	–0.75	6.40	430 (2.0×10^4)	588 (4.3×10^4)
Bromothymol blue (**V**)	2,2' – Me; 3,3' – Br; 5,5'– *i*-Pr (3,3'-dibromotimolsulfophthalein)	–1.17	7.30	436 (1.8×10^4)	616 (4.13×10^4)
	Polimetines				
	Ct^+				
Pinacyanol (**VI**)	{1-Ethyl-2-[3-(1-ethyl-1*H*-quinoline-2-ylidene-propenyl]quinolinium}	2.63	–	600, α-band (1.2×10^5) 550, β-band, 510, γ-band	
Quinaldine red (**VII**)	{2-[2-(4-Dimethylamino)phenyl]-1-etilquinolinium}	3.5	–	528 (3.1×10^4)	

[a] The error of pK_a values is ±(0.03–0.08), λ_{max} ±1 nm, ε_{max} ±500 l mol^{-1} cm^{-1}. [b] The pK_{a1} values for dyes **VI** and **VII** correspond to the process of dissociation of the cation HCt^{2+}.

Table 2. Linear regression equation of the form $A_\lambda = B + kC$

Ion, range of concentrations C, mol l^{-1}; n[a]	λ, nm	B	s_B[b]	$k\times10^{-4}$	s_k[b]	r	s_r[b]
$\mathbf{I}^{2-}$, 1×10^{-6}–9×10^{-5}, $n = 8$	558	0.00944	0.015	6.76	322	0.9999	0.0054
$\mathbf{II}^{2-}$, 1.0×10^{-6}–4.5×10^{-5}, $n = 6$	591	0.00438	0.0080	7.52	2569	0.99942	0.0036
$\mathbf{III}^{2-}$, 1.5×10^{-6}–2.5×10^{-5}, $n = 7$	617	0.000783	0.00387	0.773	45.3	0.99988	0.010
$\mathbf{IV}^{2-}$, 5×10^{-7}–4×10^{-5}, $n = 9$	588	–0.0020	0.0023	6.72	130	0.99999	0.0049
$\mathbf{V}^{2-}$, 5×10^{-7}–5×10^{-5}, $n = 9$	616	–0.00066	0.0030	3.92	120	0.99997	0.0061
$\mathbf{VII}^{+}$, 1×10^{-6}–1×10^{-4}, $n = 9$	528	–0.0038	0.015	3.37	324	0.9996	0.033

[a] The value of n corresponds to the initial molar concentration C of ions acquisition value. [b] The values of s_B, s_k, and s_r are the standard deviation of the free term in the regression B, the slope k and the correlation coefficient r, respectively.

scheme: $H_3An^+ \rightleftarrows H_2An^0 \rightleftarrows HAn^- \rightleftarrows An^{2-}$. Neutral structure forms a sultone-type tautomer which is practically colorless [26]. The substances recrystallized from concentrated ethanoic acid are flesh-colored. Anions, in particular An^{2-}, are rather strongly colored, which favors spectral study of ionic association at a very low (1×10^{-6} mol l^{-1}) concentration of species. The absorption bands of the structures HAn^- and An^{2-} are well resolvable spectrally. Due to significant difference in pK_{a1} and pK_{a2} values, solutions can be prepared with the acidity providing the occurrence of only the anionic form interacting with a cationic dye (see Table 1; characteristics of sulfophthaleines are given according to [26, 27] for pinacyanol and [26, 28–30]) for quinaldine red.

The interpretation of spectral changes in the framework of equilibrium approach (using the law of mass action to determine K_{as}) implies that behavior of the protolytic forms of interacting dyes is consistent with the basic law of light absorption. We found that at the studied concentrations of the dyes the linear regression equations of the law have the form shown in Table 2. The linear dependence $A_\lambda = B + kC$ of the optical density on the content of the dye (C, mol l^{-1}) in solution is obeyed satisfactorily within a fairly wide range of the dye concentrations. As shown in Table 2 the constant terms of regression B statistically equals to zero, so we have taken $A_\lambda = kC$. Note that practically the correlation coefficient equals unity. This suggests that sulfophthaleines and quinaldine red are practically nondimerized in the used concentration range.

In contrast, for pinacyanol the basic law of light absorption is observed at low concentrations (3×10^{-7} to 1×10^{-6} l^{-1}), since this polymethine is prone to self-association (the logarithm of dimerization constant of Ct^+ is 4.79±0.06; the pinacyanol properties in aqueous solution are considered in more details in [30]). The transformation of the monomer into the dimer is observed by a sharp weakening of the α-band absorption and increase in the β-band intensity (Table 1).

In order to determine the optimal conditions of association we calculated fractional content of the studied species in the light of the above protolytic processes. At the study of the interaction of HAn^- or An^{2-} with Ct^+ is necessary to provide the medium acidity that ensures coexistence of only the corresponding ionic forms. Otherwise the interpretation of spectral changes would be hampered by possible interactions with other species. Figure 1 shows an example of the fractional content of protolytic forms of dye **III** in dependence on the pH of the aqueous solution ($I \to 0$; for **III** besides the pK_1 and pK_2 the value of $pK_0 = -0.99$ [31]is taken into account). From the data in Fig. 1 follows that it is reasonable to study the interaction of Ct^+ with HAn^- at a pH about 4.2 (for **VI**) and 3.5 (for **VII**), and for polymethines with An^{2-} at pH ≥ 7.

Association of Ct^+ with HAn^- and An^{2-}, structure and energetics of the associates. Analysis of changes in electronic absorption spectra of the mixtures of Ct^+ with HAn^- and Ct^+ with An^{2-} reveals the nonadditivity of spectral bands. The absorption intensity of the mixture of interacting counterions is systematically lower than the total light absorption of the individual dye ions. A characteristic feature of the association also is a significant decrease in the intensity of the absorption that is clearly observed at the adding increasing amounts of sulfophthaleine at the unchanged content of polymethine (Figs. 2, 3). Moreover, this phenomenon is observed regardless of

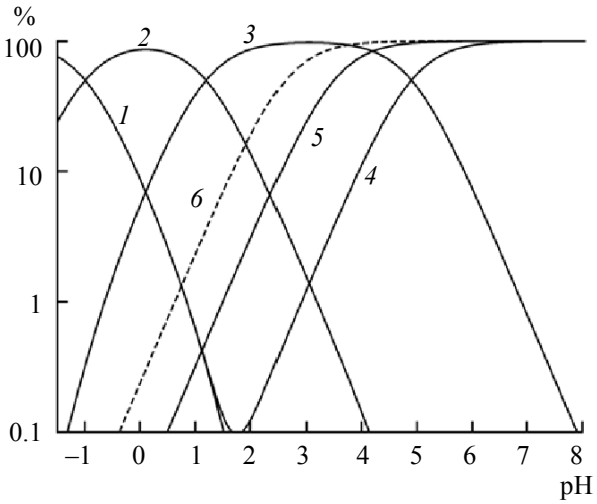


Fig. 1. Fraction of the protolytic forms of bromocresol green [(*1*) H_3An^+, (*2*) H_2An, (*3*) Han^-, (*4*) An^{2-}], cations Ct^+ of (*5*) pinacyanol and (*6*) quinaldine red vs. pH of the aqueous solution.

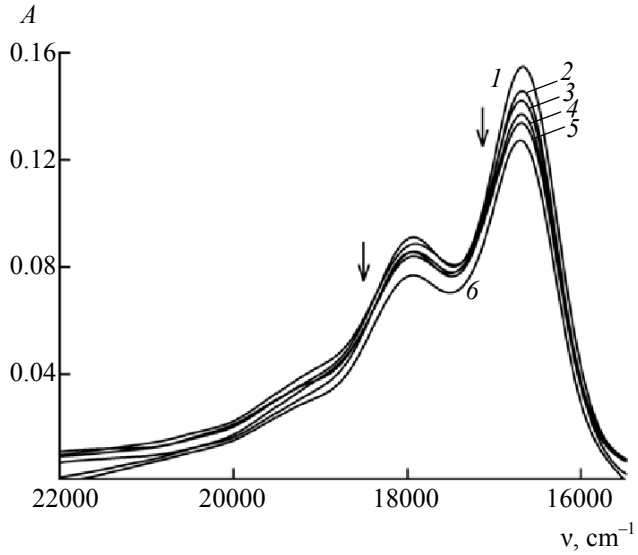


Fig. 2. Change in the light absorption by pinacyanol (4.9×10^{-7} mol l^{-1}) at adding bromocresol purple: (*1*) 0, (*2*) 1.5×10^{-6}, (*3*) 2.0×10^{-6}, (*4*) 2.5×10^{-6}, (*5*) 3.5×10^{-6}, and (*6*) 5.0×10^{-6} mol l^{-1}. The thickness of the absorbing layer 5.00 cm, pH 9.2, solutions of comparison: (*1*) water and (*2–6*) a solution of sulfophthalein of the appropriate concentration.

the initial concentrations of anions and cations. For example, the initial concentrations of **VI** in Figs. 2 and 3 differ about 100 times: in Fig. 2 the intensity of α-band of compound **VI** is higher than the β-band; in Fig. 3 the opposite situation occurs for the systems $Ct^+ + HAn^-$ and $Ct^+ + An^{2-}$, respectively (arrows indicate the directions of the spectral shifts).

Electrostatic attraction contributes to the convergence of the counterions. However, chromophore systems of polymethine cations and sulfophthaleine anions, as well as the energy of electron transitions, are different. In addition, the counter ions in the heteroassociates are more distant than the species in the conventional dimers (interplanar distance in the dimer Ct_2^{2+} **VI** does not exceed 3.9 Å [31], while the distance between the counter ions, for example, in the associate $\mathbf{VI}^+\cdot\mathbf{V}^-$ is ~5 Å, see below). Therefore, the observed spectral changes at the formation of associates with Ct^+, the decrease in the intensity of the absorption band without a significant change in λ_{max}, is explainable by the dispersion interactions that are not very sensitive to the difference in the absorption regions of free counter ions [24]. The hypochromism of the Ct^+ absorption bands and the absence of new bands, being in line with the interpretation of the relevant spectral shifts [24], suggests solvent-separated structure of the heteroassociates. More so, in the more concentrated solutions of mixtures of dyes the appearance of turbidity is noticeable and a change in the color of the solution. This fact indicates the formation of associates of a more complex stoichiometry and

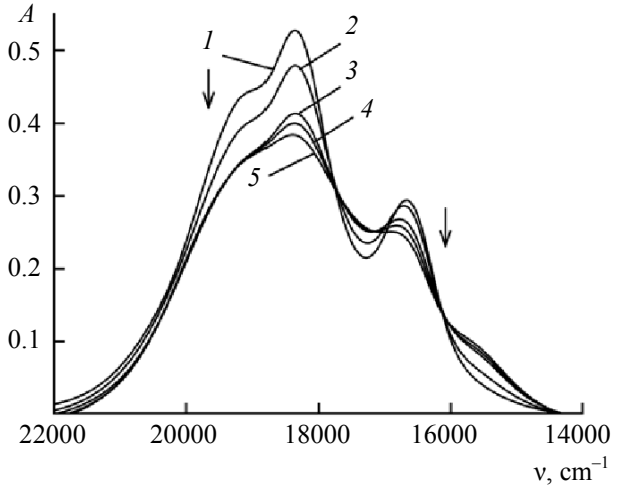


Fig. 3. Change in the light absorption of pinacyanol (4.9×10^{-5} mol l^{-1}) at adding bromocresol purple: (*1*) 0, (*2*) 1.5×10^{-5}, (*3*) 2.5×10^{-5}, (*4*) 3.0×10^{-5}, (*5*) 3.5×10^{-5} mol l^{-1}. The thickness of the absorbing layer 0.20 cm, pH 4.2, solutions of comparison: (*1*) water and (*2–5*) a solution of sulfophthalein of the appropriate concentration.

probably of insoluble aggregates of various composition.

By the methods of evaluation of the stoichiometric composition [24, 25, 32] we found that under certain conditions (the initial concentration of counterions, their molar ratio) in solution the heteroassociates $Ct^+ \cdot HAn^-$ and $(Ct^+)_2 \cdot An^{2-}$ can be formed according to the schemes: $Ct^+ + HAn^- \rightleftarrows Ct^+ \cdot HAn^-$ and $2Ct^+ + An^{2-} \rightleftarrows (Ct^+)_2 \cdot An^{2-}$. A measure of the stability of these compounds is the equilibrium association constant K^T_{as}, defined by the law of mass action: $K^T_{as} = [Ct^+ \cdot HAn^-] \cdot [Ct^+]^{-1} \cdot [HAn^-]^{-1}$ and $K^T_{as} = [(Ct^+)_2 \cdot An^{2-}] \cdot [Ct^+]^{-2} \cdot [An^{2-}]^{-1}$ (in brackets are given the equilibrium molar concentration of the respective species determined spectrophotometrically. Since $I \leq 0.004$, the concentration association constant is numerically the same as thermodynamic one). The values of K^T_{as} obtained are listed in Table 3 (some data on the associates **VII** are taken from [33, 34]). From the data in Table 3 follows that associates **VI** are markedly more stable than the associates **VII**. One reason for this is the increased fraction of hydrophobic interactions in pinacyanol associates. The hydrophobic contribution of quinoline fragment in the molecule **VI** apparently is higher than that of *N*,*N*-dimethylaniline fragment in molecule **VII**. In addition, the dispersion interaction manifested largely by extended π-electron systems [24] also contribute to the increased association. In view of the structural features, they are more inherent to cation $\mathbf{VI}^+$, than to $\mathbf{VII}^+$.

The obtained K^T_{as} values show that alkyl substituents favor a decrease, and that halogen atoms contribute to the increase in K^T_{as}. This is connected with a known fact [26] that the alkyl groups favor a decrease in the molecule planarity (leading to increase in the distance between the counterions in associate) and reduce the component of the dispersion interactions. In contrast, the bromine atoms are practically not affecting the sulfophthaleine geometry, but significantly increase the hydrophobic component of the intermolecular interactions. Increase in the number of bromine atoms and a decrease in the number of alkyl substituents leads to an increase in K^T_{as} both of the single- and double-charged anions. Stability of the pinacyanol associates is changed in the series: $\mathbf{VI}^+ \cdot \mathbf{V}^- < \mathbf{VI}^+ \cdot \mathbf{IV}^- \approx \mathbf{VI}^+ \cdot \mathbf{III}^- < \mathbf{VI}^+ \cdot \mathbf{II}^-$ and $(\mathbf{VI}^+)_2 \cdot \mathbf{V}^{2-} \approx (\mathbf{VI}^+)_2 \cdot \mathbf{IV}^{2-} < (\mathbf{VI}^+)_2 \cdot \mathbf{III}^{2-} < (\mathbf{VI}^+)_2 \cdot \mathbf{II}^{2-}$, and associates of quinaldine red in the series: $\mathbf{VII}^+ \cdot \mathbf{V}^- < \mathbf{VII}^+ \cdot \mathbf{IV}^- < \mathbf{VII}^+ \cdot \mathbf{III}^- < \mathbf{VII}^+ \cdot \mathbf{II}^-$ and $(\mathbf{VII}^+)_2 \cdot \mathbf{V}^{2-} < (\mathbf{VII}^+)_2 \cdot \mathbf{IV}^{2-} < (\mathbf{VII}^+)_2 \cdot \mathbf{III}^{2-} < (\mathbf{VII}^+)_2 \cdot \mathbf{II}^{2-}$.

Table 3. The values of log K^T_{as} of the sulfophthaleines heteroassociates

Comp. no.	log K^T_{as}			
	VI		**VII**	
	$Ct^+ \cdot An^-$	$(Ct^+)_2 \cdot An^{2-}$	$Ct^+ \cdot An^-$	$(Ct^+)_2 \cdot An^{2-}$
I	5.83±0.10	11.81±0.10	5.13±0.09	8.64±0.09
II	6.88±0.05	13.73±0.10	5.27±0.05	8.86±0.08
III	6.74±0.04	12.09±0.09	5.04±0.07	8.64±0.07
IV	6.67±0.05	11.07±0.10	4.78±0.06	8.23±0.04
V	5.95±0.1	10.89±0.09	4.45±0.08	7.85±0.09

It is natural that K^T_{as} is maximal for associates of **II** containing the largest number of bromine atoms but no alkyl substituents. Remarkable is also the fact that the associates of the unsubstituted **I** by stability occupy an intermediate position between the associates of **V** and **II**. The values of log K^T_{as} for the $\mathbf{VI}^+ \cdot \mathbf{I}^-$ and $(\mathbf{VI}^+)_2 \cdot \mathbf{I}^{2-}$ are higher than for $\mathbf{VII}^+ \cdot \mathbf{I}^-$ and $(\mathbf{VII}^+)_2 \cdot \mathbf{I}^{2-}$, respectively.

Formation of associates in solutions is typical of dyes with planar shape of the molecule, high hydrophobicity, with π-conjugated electronic systems, that enhance the contribution of dispersion interactions. The group of such dyes includes squaranines [35], spiropyrans [36], some diazines, such as piridazine and pyrazine [37] , mero- and thiacyanines [38, 39], which find application in the study of peptides, formation of J-and H-aggregates and Langmuir–Blodgett films [36, 38]. Unlike these structures, sulfophthaleine anions cannot be considered as flat π-electronic systems. Nevertheless, as follows from the spectral data, a noticeable interaction occurs between the Ct^+ and anions. Based on the data on composition, it can be assumed that the planar polymethine cation is coordinated at a single-charged anion (or two cations at a doubly-charged anion). Therefore, it seems appropriate to elucidate the most probable structure of the stoichiometric heteroassociates and to compare their energies (the values of enthalpy of formation, ΔH^0_{form}) using quantum-chemical calculations.

It is known [41, 42] that even for small molecules, ab initio calculations lead to errors in the values of ΔH^0_{form} exceeding 100 kJ mol^{-1}. This is due to the incompleteness of the basis used and neglecting the electron correlation energy. With an increase in the size of a molecule the error in the ab initio calculations

Table 4. The scale of variation of ΔH^0_{form} values for the dye ions

Ion	Method	
	AM1	PM3
$\mathbf{I}^-$	–556…–576	–575…–586
$\mathbf{I}^{2-}$	–479…–492	–534…–536
$\mathbf{II}^-$	–465…–479	–435…–460
$\mathbf{II}^{2-}$	–473…–474	–450…–451
$\mathbf{III}^-$	–471…–481	–469…–478
$\mathbf{III}^{2-}$	–476…–478	–469…–472
$\mathbf{IV}^-$	–583…–602	–584…–609
$\mathbf{IV}^{2-}$	–554…–556	–566…–570
$\mathbf{V}^-$	–662…–681	–685…–691
$\mathbf{V}^{2-}$	–634…–639	–658…–666
$\mathbf{VI}^+$	1076…1073	980…968
$\mathbf{VII}^+$	989…984	918…912

of ΔH^0_{form} rises to a large extent having a systematic character. Therefore, to evaluate ΔH^0_{form} of the heteroassociates ions we used semiempirical AM1 method as one of the more advanced versions of the method MNDO (Modified Neglect of Diatomic Overlap), and the PM3 method (see Table 4; programs MOPAC-2002, HyperChem 7.0 [43, 44]). The parameters of these methods are chosen to reproduce best the experimental values of ΔH^0_{form} of organic compounds. Application of two methods of calculation allows not only to achieve greater accuracy in the absolute values of ΔH^0_{form}, but also to minimize a systematic error at

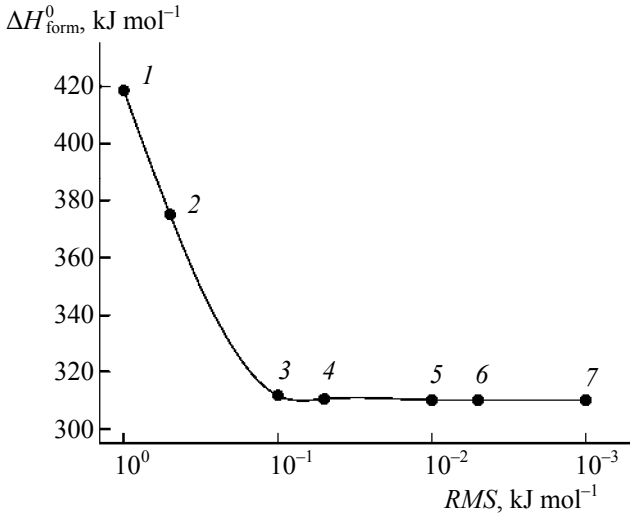


Fig. 4. Change in the ΔH^0_{form} value of heteroassociates of pinacyanol with a doubly charged anion of bromothymol blue vs. the given values of *RMS*-gradient [method AM1; the figures above the curve indicate the corresponding structure in the Table 5, (*1*) is the starting position of the geometry optimization, (*7*) is final position].

elucidating the changes in the formation enthalpy for a series of the heteroassociates of different composition.

The convergence gradient [the RMS-gradient, the rate of change of energy (1st derivative) at the change of the location of an atom in three mutually perpendicular directions, the local minimum energy of a structure is achieved when it equals to zero] in successive iterations decreased from 4.2 to 0.04 kJ mol^{-1}. The scale of variations of the ΔH^0_{form} values did not exceed 13 kJ mol^{-1} ($\mathbf{I}^-$, Table 4) in the AM1 calculation and 25 kJ mol^{-1} (anions $\mathbf{II}^-$ or $\mathbf{IV}^-$) at the use of PM3 method. Comparing the absolute values of ΔH^0_{form} in two semiempirical methods, we suggest that the difference is not principal in the context of this study. Moreover, the average error in the calculation of ΔH^0_{form} is 25 kJ mol^{-1} [43]. If as the final value of ΔH^0_{form} is taken the most negative one, it is easy to see that the maximal difference between the results obtained by AM1 and PM3 is 44 kJ mol^{-1}, for $\mathbf{I}^{2-}$ (Table 4).

To obtain correct values of ΔH^0_{form} of heteroassociates it is important to find the global energy minimum. Therefore we tested six to seven initial mutual positions of the counterions in heteroassociates (geometry of each counterion was previously optimized as described above). From the calculated set of the local energy minima was chosen the lowest one, and the energy of this structure was taken as the corresponding to the global minimum. Then an additional geometry optimization was carried out of the heteroassociate structure with a series of decreasing values of *RMS*-gradient (as a rule, *RMS* decreased from 0.1 to 5×10^{-3} ... 1×10^{-4} kJ mol^{-1}). The optimization process completed at the absence of changes in ΔH^0_{form} at the change in the RMS value (for polymethine cations commonly at 5.0×10^{-2}…5.0×10^{-3} kJ mol^{-1}, for sulfophthaleines at lower values). Fig. 4 shows as an example the dependence of ΔH^0_{form} values on the values of *RMS*-gradient for the heteroassociates **V**, and Table 5 shows the course of successive geometric optimization of the heteroassociates $[(\mathbf{VI}^+)_2\cdot\mathbf{V}^{2-}]$ (the anion in the center; for better visibility are given the stereo images; the position of the anion $\mathbf{V}^{2-}$ relative to the observer is arbitrarily fixed; hydrogen atoms are not shown). As can be seen from Fig. 4 and Table 5, optimization of the geometry of the structure depends strongly on the values of *RMS*, but it is almost finalized even at *RMS* = 0.01 kJ mol^{-1}; the minimization leads to a decrease in the distance between the counterions.

Table 5. Geometry optimization of the associate $(\mathbf{VI}^{+})_2\mathbf{V}^{2-}$ by AM1 method

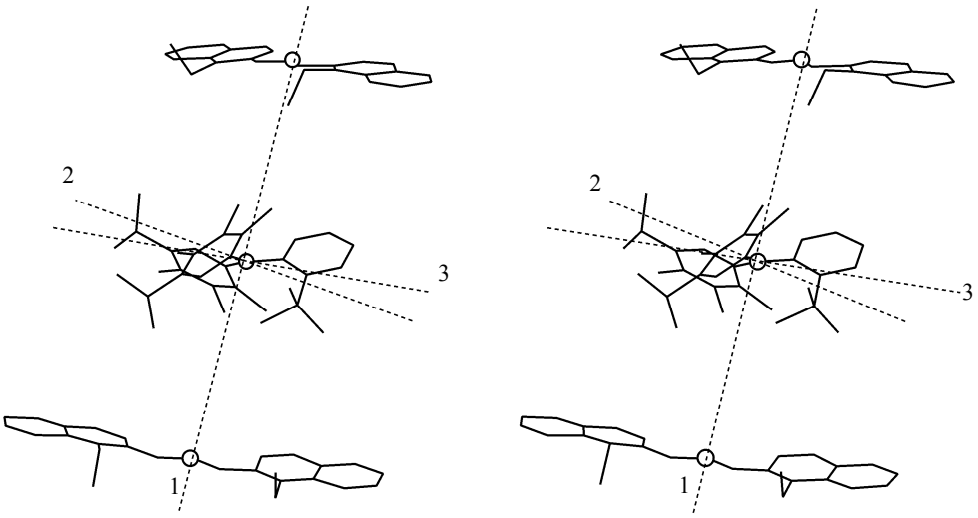
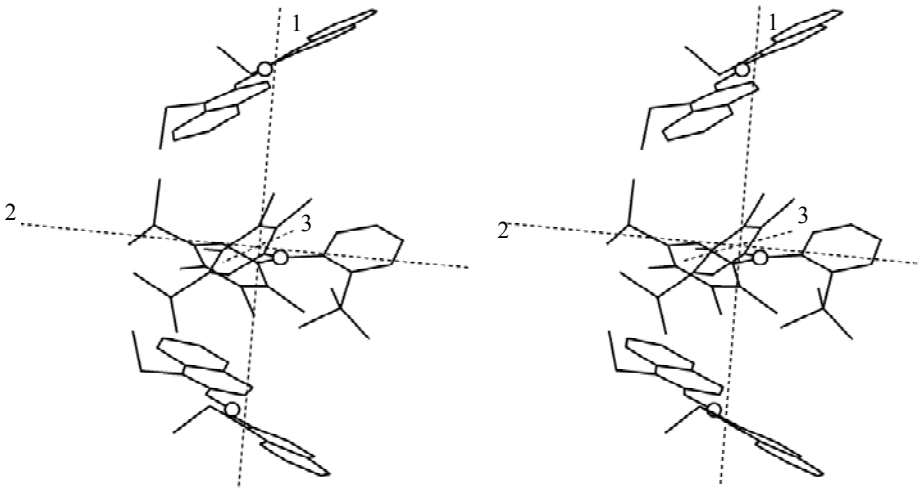
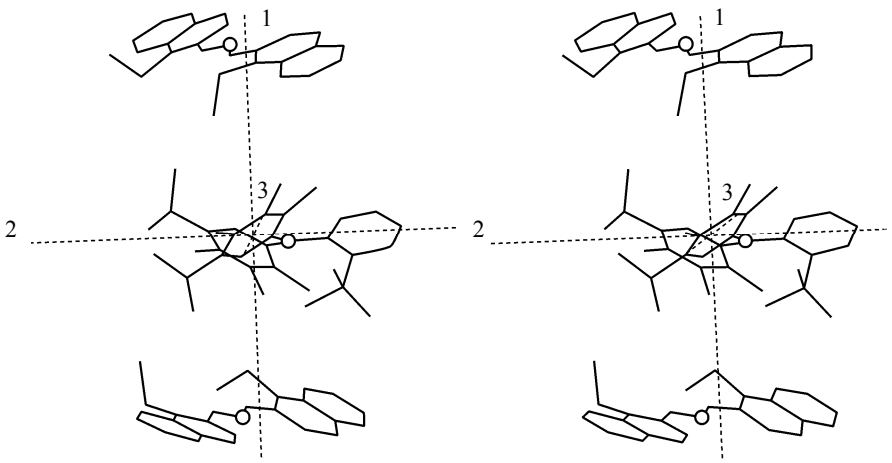
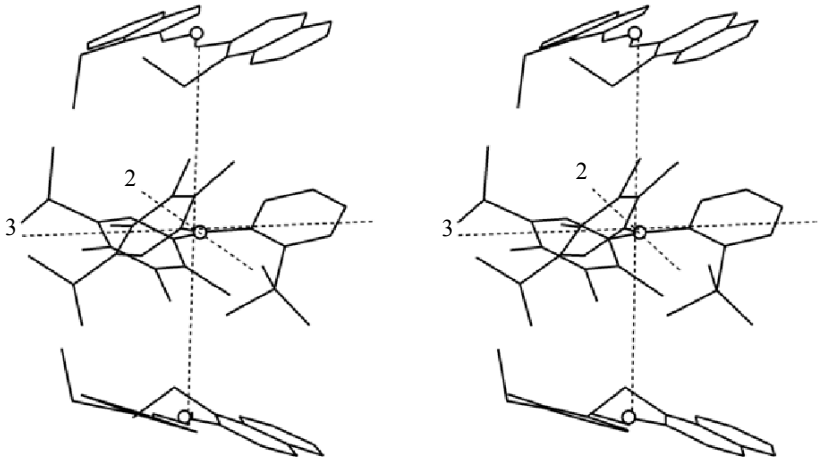
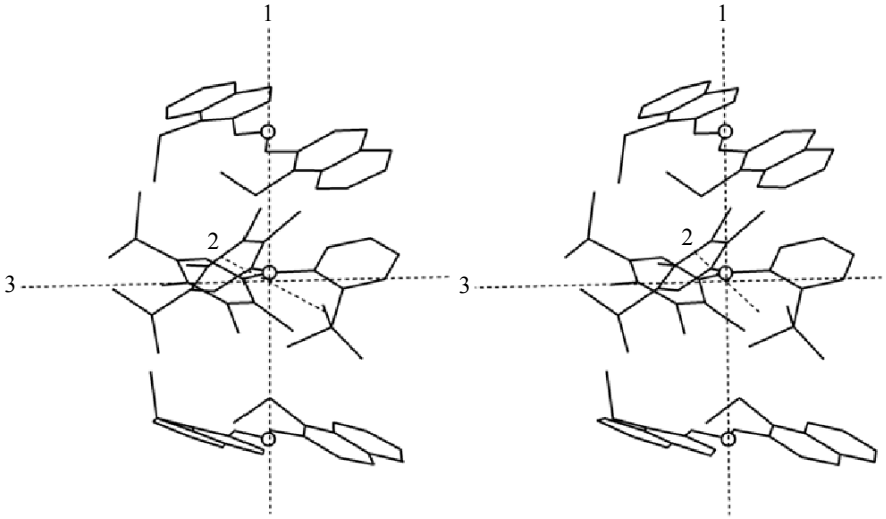
RMS-gradient (see Fig. 4)	Stereoimage of structure and the distance between two atoms (upper and middle, middle and bottom)
1	 8.0, 8.0 Å
2	 6.7, 5.8 Å
3	 6.2, 5.6 Å

Table 5. (Contd.)

RMS-gradient (see Fig. 4)	Stereoimage of structure and the distance between two atoms (upper and middle, middle and bottom)
4	 5.6, 5.5 Å
5—7	 4.6, 5.4 Å

Figures 5 and 6 give examples of the energy characteristics of dye ions and heteroassociates of bromthymol blue (AM1 calculation method, the figures at the arrows indicate the range of variation in the value of ΔH^0_{form}, kJ mol^{-1}, of the corresponding species). In Fig. 5 to the ions **VII**$^+$ and **V**$^-$ correspond the values of ΔH^0_{form} 989...984 and –681… –662 kJ mol^{-1}, respectively (Table 4). Their algebraic sum 327... 303 kJ mol^{-1} (energy level *1*) exceeds ΔH^0_{form} = 149...147 kJ mol^{-1} of the associate **VII**$^+$·**V**$^-$ (level *2*) by 180...154 kJ mol^{-1}.

Similarly, in Fig. 6 to the ions **VI**$^+$ and **V**$^{2-}$ correspond the values of ΔH^0_{form} 1076...1073 kJ mol^{-1} and –634...–639 kJ mol^{-1}, respectively, therewith two cations **VI**$^+$ have energy of 2152...2146 kJ mol^{-1}. The algebraic sum for the counterions is 1518...1507 kJ mol^{-1} (level *1*). Since ΔH^0_{form} of the heteroassociates (**VI**$^+$)$_2$·**V**$^{2-}$ was found equal to 887...858 kJ mol^{-1} (level *2*), the algebraic sum of the excess energy of the counterions over ΔH^0_{form} of the heteroassociate is 660... 620 kJ mol^{-1}.

We calculated ΔH^0_{form} values for all investigated heteroassociates (Table 6, the minimum value was accepted as final one). Table 6 also contains the values of Σ and relative errors of ΔH^0_{form}, %. The Σ is the algebraic sum of the ΔH^0_{form} values of the

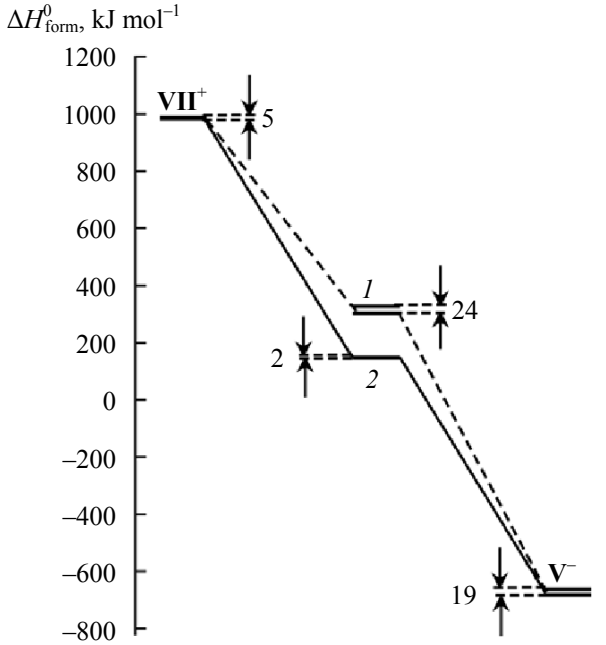


Fig. 5. The values of ΔH^0_{form} of quinaldine red (**VII**$^+$) and bromothymol blue (**V**$^-$) ions; algebraic sum of (*1*) ΔH^0_{form} of these ions; (*2*) ΔH^0_{form} of associate (**VII**$^+$ + **V**$^-$).

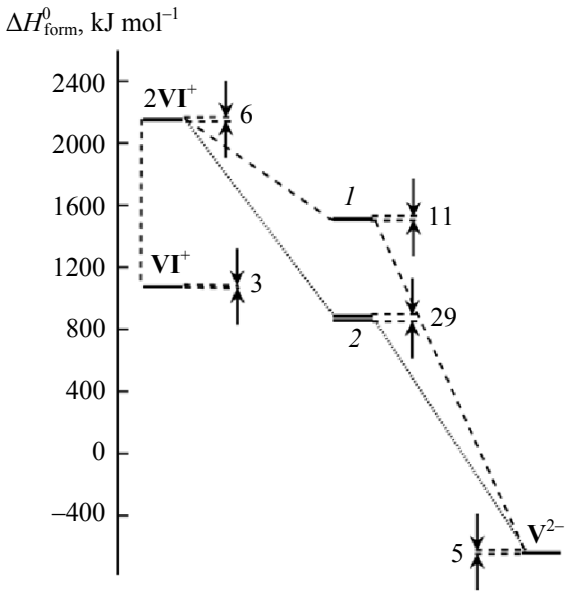


Fig. 6. The values of ΔH^0_{form} of pinacyanol (**VI**$^+$) and bromothymol blue (**V**$^{2-}$); algebraic sum of (*1*) ΔH^0_{form} of these ions; (*2*) ΔH^0_{form} of associate [(**VI**$^+$)$_2$**V**$^{2-}$].

corresponding ions in the associates, defined as $i\Delta H^0_{form}$(Ct) + ΔH^0_{form}(An), where i is the number of cations in associates (Table 4).

Analysis of the data in Table 6 and the obtained results leads as a whole to a number of significant conclusions. Since the error of ΔH^0_{form} value is not higher than the above mentioned average error of the method for calculating ΔH^0_{form} (except heteroassociates **VII**$^+$·**II**$^-$), then it could be stated that the formation of every heteroassociate is energetically favorable, especially in the case of the heteroassociation of sulfophthaleines with the structures containing developed π-electron systems (**VI**$^+$); the gain reaches about 150–160 kJ mol^{-1} (the heteroassociates of singly charged sulfophthaleines, see also Fig. 5) and 605–700 kJ mol^{-1} (the doubly charged, Fig. 6).

Changes in the values of ΔH^0_{form} (vacuum), and K^T_{as} (aqueous solution) are not necessarily consistent with each other. In addition, semiempirical calculations are unable to account for the some specific interactions (e.g., hydrophobic, that are typical of bulky polyatomic counterions of dyes). Nevertheless, the calculations reveal approximately the same sequence of changes in ΔH^0_{form} as that of the experimental values of K^T_{as}, despite the systematically lower values of ΔH^0_{form} obtained by PM3 method. For the pinacyanol heteroassociates (in parentheses the values of ΔH^0_{form}, kJ mol^{-1}, PM3 method) is revealed the following sequence: **VI**$^+$·**V**$^-$ (105) < **VI**$^+$**IV**$^-$ (202) < **VI**$^+$**III**$^-$ (328) < **VI**$^+$**II**$^-$ (347), (**VI**$^+$)$_2$**V**$^{2-}$ (527) < (**VI**$^+$)$_2$**IV**$^{2-}$ (703) < (**VI**$^+$)$_2$**III**$^{2-}$ (817) ≤ (**VI**$^+$)$_2$**II**$^{2-}$ (824). For quinaldine red: **VII**$^+$**V**$^-$ (81) < **VII**$^+$**IV**$^-$ (107) < **VII**$^+$**III**$^-$ (241) < **VII**$^+$**II**$^-$ (267), (**VII**$^+$)$_2$·**V**$^{2-}$ (406) < (**VII**$^+$)$_2$·**IV**$^{2-}$ (525) < (**VII**$^+$)$_2$·**II**$^{2-}$ (547) < (**VII**$^+$)$_2$·**III**$^{2-}$ (628).

As in the case of K^T_{as}, the ΔH^0_{form} of the phenol red heteroassociates are of intermediate value regardless of the composition: **V** < **I** < **II**. The latter is in favor of the assumption that the presence of bromine atoms in the structure of sulfophthaleine, in contrast to the alkyl substituents, favors the interaction with counterions.

Thus, the differences found in the values of K^T_{as} or ΔH^0_{form} even among the heteroassociates with the same type of structure are of regular character. By an example of systematic study of the interactions between the single and doubly charged sulfophthaleine anions with the polymethine cations it becomes clear that the process of heteroassociation of polyatomic species is accompanied by a rather complicated combination of Coulomb forces and of hydrophobic, dispersion, and, as a special case, of π-electron

Table 6. Energy characteristics of heteroassociates

Heteroassociate	AM1			PM3		
	Σ, kJ mol^{-1}	ΔH^0_{form}, kJ mol^{-1}	relative error of ΔH^0_{form}, %	Σ, kJ mol^{-1}	ΔH^0_{form}, kJ mol^{-1}	relative error of ΔH^0_{form}, %
Pinacyanol heteroassociates						
VI$^+$I$^-$	497	344	19	382	134	9
VI$^+$II$^-$	593	423	19	507	347	21
VI$^+$III$^-$	592	432	19	490	328	14
VI$^+$IV$^-$	471	312	29	359	202	28
VI$^+$V$^-$	391	240	21	277	105	12
(VI$^+$)$_2$I^{2-}	1654	979	6	1400	788	7
(VI$^+$)$_2$II^{2-}	1672	1011	3	1485	824	8
(VI$^+$)$_2$III^{2-}	1668	1060	3	1464	817	6
(VI$^+$)$_2$IV^{2-}	1590	928	4	1367	703	6
(VI$^+$)$_2$V^{2-}	1507	858	6	1270	527	8
Quinaldine red heteroassociates						
VII$^+$I$^-$	407	258	16	326	122	8
VII$^+$II$^-$	504	339	14	451	267	34
VII$^+$III$^-$	502	331	13	434	241	9
VII$^+$IV$^-$	382	219	13	303	107	14
VII$^+$V$^-$	303	147	14	221	81	7
(VII$^+$)$_2$I^{2-}	1475	757	5	1288	518	4
(VII$^+$)$_2$II^{2-}	1494	839	9	1373	547	3
(VII$^+$)$_2$III^{2-}	1489	853	13	1352	628	7
(VII$^+$)$_2$IV^{2-}	1411	737	7	1254	525	7
(VII$^+$)$_2$V^{2-}	1328	703	8	1158	406	12

interactions. Their further study imply comparing the results of spectral measurements with the data of computer simulation.

EXPERIMENTAL

We used pinacyanol chloride and quinaldine red (Sigma) and sulfophthaleine disodium salts of "chemically pure" grade. Purity of each dye was verified spectrophotometrically by comparing with the known values of molar absorption coefficient (ε_{max}, l mol^{-1} cm^{-1}) at the maximum of absorption band (λ_{max}) of the most intensely colored protolytic form. The medium acidity was created using phosphate, borate, and acetate buffers, and by adding hydrochloric acid or sodium hydroxide. It was revealed by special experiments that the components used in buffer solutions did not affect noticeably the studied processes of heteroassociation. Ionic strength (I) of the solutions for the photometry did not exceed 0.004 mol l^{-1}. The values of pH were measured with a glass electrode. The numerical values of the optical density used as a basis in the calculations of the equilibrium association constants (K^T_{as}) were tested on the correspondence to the Bouguer–Lambert–Beer law. Absorption spectra were measured at room temperature immediately after preparation of the photometric solutions, on a Hitachi-U3210 or a SF-46 spectrophotometer. The error in the values of λ_{max} was ±0.5 nm. The general principles of quantum-chemical calculations applied to the structures of dyes and their ion associates have been described previously [44].

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