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Cation–Anionic Interactions of Dyes in Aqueous Solutions: Bromocresol Purple in the Processes of Dissimilar Association

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Abstract: The interaction between single- or double-charged anions of bromocresol purple (BP) and cyanine cations (quinidine blue, QB, or quinidine red, QR) at concentrations of dyes 5.0 × 10⁻⁷–4.0 × 10⁻⁵ mol/L has been investigated by vis-spectroscopy. The thermodynamic constants of dissimilar associations (K_{as}) have been studied. Comparison of the values of lg K_{as} shows that QB⁻ associates of BP⁺ are more stable (6.61 ± 0.07) than QR associates (4.84 ± 0.06); a similar phenomenon is observed for associates of the BP²⁻ anion. Semi-empirical calculations (PM3 method) are in agreement with the vis-spectroscopy data and indicate that the association of dye into an associate is possible. The standard enthalpies of formation of associates (ΔfH°) and energy diagrams have been determined. The ΔfH° data indicate that the formation of an associate between dye ions is an energetically favourable process. The gain in energy significantly exceeds the systematic error of semi-empirical calculations and increases from 157 kJ/mol (associate “BP⁺ + QB⁻”) to 729 kJ/mol (associate “BP²⁻ + QR⁺”). The most probable structures of dissimilar associates are presented. The study of the dissimilar association develops the concept of intermolecular interactions in solutions.

Keywords: bromocresol purple; dissimilar association; vis-spectroscopy; enthalpy of formation; semi-empirical method

1. Introduction

Sulfonephthalein dyes have a wide range of applications, from acid–base or metallochromic indicators to analytical reagents for spectral determination of a number of organic substances [1–3]. The bromine derivatives attract attention due to favorable specific features, such as the stability of protolytic forms, weak dimerization, good diversity of absorption bands of single- and double-charged anions, and high contrast of color reactions [3,4]. In particular, they are used in technologies for determining the acidity of pure and natural waters [5–7] and are also the basis of sensitive elements of optical pH sensors, fiber optic biosensors, and chips [8–11]. Quantitative determination of components in bio- and pharmaceuticals is one of the most promising areas of their application as analytical reagents: Antimicrobial, antihistamines, bactericidal, antidepressants, and others [12–26]. The effective use of 3,3’-dimethyl-5,5’-dibromophenolsulfonephthalein (BP) in technologies is expanding [27–49]. It includes sensitive gas sensors [27,28], electrochemical DNA biosensors to the antitumor drug [39], highly efficient extraction of heavy metals from industrial effluents by adsorption on a modified zeolite surface [40], lysine decarboxylase analysis [41], the adsorption of hydropic molecules on the membrane of erythrohematoxemia cells [42], and evaluation of the properties of serum albumin [38,43–48] and extracellular lactase [49]. It is noteworthy that many applications are based on the formation of dissimilar associates between the anionic form of sulfonephthalein and the anlyte. In some cases, associates are able to be extracted into the organic phase (chloroform, dichloromethane [12,13,15–19,21,24,26]). Studies of the dissimilar association of sulfonephthaleines and other dyes are becoming practical. They provide information on the nature of physicochemical interactions and
the role of both chromophore fragments and functional groups. For example, it was found that the "dye + counterion" associates and the binding of each of them with biochemical receptors (with DNA [50,51] or proteins [52–54]) affect the action of medicinal agents; this problem has also been studied in the interaction of antibiotics with aromatic molecules (polyphenols, methylxanthines such as caffeine, etc.) [55]. Therefore, the dissimilar association is directly related to improving the effectiveness of pharmaceuticals. The analysis of publications indicates the need for in-depth study of cation–anionic interactions that cause the formation of associates, which include anions (HAn−, An2−) of BP or other sulfonephthalein dyes.

Various instrumental methods are used to study the association. At concentrations of interacting particles of 1 \( \times \) 10⁻⁵ mol/L or more, it is known to use conductometry; however, this method is suitable for media with low dielectric constants. The most "sensitive" method is vis-spectroscopy (fluorimetry), which makes it possible to study the interactions of colored particles at concentrations 1 \( \times \) 10⁻⁷–1 \( \times \) 10⁻⁴ mol/L.

The facts of the interaction of sulfonephthalein anions with cations (Ct⁺) of some dyes (rhodamines, cyanines) have been discussed previously [56–58]. However, the most probable structure of BP associates and their energy characteristics, in particular, the standard enthalpy of formation \( (\Delta fH^\circ) \), have not been studied. In this report, using the results of spectrophotometric measurements and quantum chemical calculations, we analyzed the cation–anion interactions that lead to the formation of stoichiometric associations between single or double-charged anions of BP and single-charged cations of polymethine dyes.

A systematic study of association in aqueous solution implies the use of such dyes that have satisfactory solubility and the ability to change light absorption upon association. Among the "standard" dyes that meet these requirements, attention is drawn to quinidine blue (QB) and quinidine red (QR). QB has a developed vibrational structure and a three-band absorption spectrum in water or organic solvents. Even a slight effect on the chromophore system, which has a counterion, changes its spectrum. A redistribution of the intensities of the absorption bands occurs, and frequency shifts appear. Such unique spectral properties have found application in methods for the qualitative and quantitative determination of a number of metals, in the study of the properties of polyelectrolytes, DNA, surfactants, and metal complex systems [3]. The observed spectral changes can also be linked to a certain type of formed particles in the process of heterogeneous association. However, the disadvantage of QB is the instability of its aqueous solutions. On the contrary, QR is more stable, although it does not have a developed vibrational structure. The advantage of QR is also the possibility to study the association in a wide range of concentrations since it is not as prone to self-association as QB.

Note that these cations have been used previously under the study of the processes of anionic dye association [57–59].

2. Materials and Methods

Disodium salts of sulfonephthaleins were used: QB was in the form of chloride salt, and QR was in the form of iodide salt (trademark "Merck KGaA", Darmstadt, Germany; the content of the basic component was not less than 95%). The proper qualification of the chemical purity of the preparations of each of the dyes was verified spectrophotometrically, taking into account the known values of the molar absorption coefficient (\( \varepsilon_{\text{max}}, \text{L}/(\text{mol}\cdot\text{cm}) \)) and the maximum absorption band (\( \lambda_{\text{max}} \)) for the most intensely colored of protolytic form. The acidity of the medium was created with phosphate, borate, acetate buffer solutions, and in some cases, hydrochloric acid or sodium hydroxide. Additional observations have shown that the addition of buffer solutions does not significantly affect the light absorption of dyes and association processes. The pH was monitored with a glass electrode. The ionic strength (I) of the solutions did not exceed 0.004 mol/L. Distilled water was used to prepare the solutions with an electrical conductivity of no more 4 \( \times \) 10⁻⁶ S. The values of the optical density, which are the basis for the calculations of the equilibrium constants of the association \( (K_{\text{ass}}) \), were checked for compliance with the basic law of light absorption. The
absorption spectra were measured on the upgraded spectrophotometer “Hitachi U3210”, Hitachi, Inc., Tokio, Japan (at room temperature) with an error value in determining the absorption wavelength of no more than ± 0.5 nm. It is experimentally verified that temperature fluctuations within 2–3 degrees practically do not affect the spectral properties of the studied dyes.

The methods of preparation of mixtures of dyes and the calculation of spectral and equilibrium characteristics of associates are covered in [56–58]. To calculate the standard enthalpies of the formation of dye ions and their associates, as well as to establish their structure, the semi-empirical quantum chemical method PM3 was used. The method is integrated into the software packages “HyperChem 8.0”, Hupercube, Inc., New York, NY, USA (evaluation version) and “MOPAC 2009”, Stewart Computational Chemistry, Colorado Springs, CO, USA. The principles of calculations for the structures of dyes and their ionic associates have been described in more detail previously [3,56,59,60].

3. Results

3.1. Dyes in the Aqueous Solution

Under the study of the interaction of HAn− (or An2−) with Ct+, we adhered to the acidity of the solution, which would ensure the coexistence of the corresponding ionic forms (Figure 1). Otherwise, the interpretation of spectral changes is difficult due to possible interactions involving mixtures of proprietary dye forms.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The relative content of protolytic forms of dyes depending on the pH of the aqueous solution.

Upon creating the optimal acidity of the solution, the values of pK_{a1} and pK_{a2} were taken into account (see Table 1; the characteristics of BP and cyanine dyes are given for I → 0 according to [61,62]; the error of pK values is ±(0.03–0.08); the values of pK_{a1} for QB and QR refer to the process of dissociation of the HCl^{2+} cation).
Table 1. Spectral and protolytic characteristics of dyes.

| Dye | \(pK_{a1} \) (\(\lambda_{\text{max}}, \text{nm} \)) | \(pK_{a2} \) (\(\lambda_{\text{max}}, \text{nm} \)) |
|-----|-----------------------------------|-------------------------------|
| 3,3-bis(3-bromo-4-hydroxy-5-methylphenyl)-3H-2,1,3-benzoxathiole-1,1-dione (BP) | -0.75 | 6.40 |
| 1-ethyl-2-[3-(1-ethyl-1,2-dihydroquinolin-2-ylidene)prop-1-en-1-yl]quinolin-1-ium chloride (QB+) | 3.5 | - |
| 2-(-(4-dimethylamino)styryl)-1-ethylquinolinium iodide (QR+) | 2.63 | - |

3.2. Spectral Properties of the Dyes

Features of BP and the cyanines are the following: (1) Dyes form stable protolytic forms in aqueous solutions; (2) dyes are able to associate at concentrations not exceeding their solubility in water; (3) ionic forms have a sufficient color intensity and the ability to significantly change the light absorption during association, which allows the study of quite small concentrations of interacting particles.

Interpretation of spectral changes from the standpoint of the equilibrium approach (using the law of active masses) implies compliance with the basic law of light absorption by protolytic forms of interacting dyes. The absorption spectra of aqueous BP solutions were investigated in the concentration range of 4.96·10^{-6} to 4.96·10^{-5} mol/L using a buffer solution and without the addition of salt additives or an organic solvent. The Savitsky–Goley procedure was used to smooth the electronic spectra [63,64]. The dependence of \(A_{\lambda} \) on the BP concentration for \(\lambda_{\text{max}} = 431 \) nm is a line passing through the origin. The linear regression equation has the form:

\[
A_{431} = 0.00047(0.0043) + 24798.1(139.8) \times C_{\text{BP}}.
\]

The correlation coefficient is equal to 0.99, and its standard deviation is 0.0038. The free term of the regression equation (in parentheses) is statistical zero. This nature of the dependence obeys the basic law of light absorption and gives one reason to believe that in the studied range of concentrations, the single-charge BP anion is not prone to dimerization. It is experimentally set that this also applies to the double-charged ion BP.

Sulfonephthalein dyes are characterized by a number of protolytic transformations: \(H_{3}An^{+} \rightleftharpoons H_{2}An^{0} \rightleftharpoons HAn^{-} \rightleftharpoons An^{2-} \). Cationic and neutral protolytic forms exist only in a strongly acidic environment. Anions, especially \(An^{2-} \), have the most intense color; the light
absorption bands of HAn\(^-\) and An\(^{2-}\) forms are well spectrally spaced (\(\lambda_{\text{max}} (\text{HAn}\(^-\)) = 430\text{ nm,}\)
\(\lambda_{\text{max}} (\text{An}\(^{2-}\)) = 588\text{ nm with molar absorption coefficients } \epsilon_{\text{max}} (\text{HAn}\(^-\)) = 24,900 \text{ L/(mol} \cdot \text{cm}),
\epsilon_{\text{max}} (\text{An}\(^{2-}\)) = 67,200 \text{ L/(mol} \cdot \text{cm}))\). This contributes to the experimental study of the ionic association of dyes at particle concentrations at the level of \(5 \cdot 10^{-6} \text{ mol/L}\). It is noteworthy that the coefficient of the linear regression equation practically coincides in value with the given \(\epsilon_{\text{max}} (\text{HAn}\(^-\))\). This indicates that only one protolytic form of BP exists at a certain acidity of the solution in the aqueous solution. In turn, significant differences in the values of \(pK_a1\) and \(pK_a2\) (see Table 1) allow for regulating the acidity of the solution to create conditions under which the existence of only a single- or double-charged anion is possible.

The linear regression equation has the form in the concentration range of \(1.0 \cdot 10^{-6} - 1.0 \cdot 10^{-4} \text{ mol/L for QR [59]}\):

\[
A_{528} = -0.0038_{(0.015)} + 3.37 \cdot 10^4_{(324)} \times C_{\text{QR}}.
\]

The correlation coefficient is equal to 0.99\(_{(0.03)}\). The value of the free regression term is statistical zero as in the case of BP anions.

For QB, in contrast to other dyes, the basic law of light absorption is fulfilled only at relatively low (not more than \(3 \cdot 10^{-6} \text{ mol/L}\)) concentrations because QB is very prone to self-association [65]. It is spectrally manifested by a weakening of the absorption of the \(\alpha\)-band and an increase in the intensity of the \(\beta\)-band (see Table 1).

Aqueous solutions of single-charged cyanines are markedly discolored due to the processes of protonation (the formation of \(\text{HCt}^{2+}\) particles in acidic conditions) and hydrolysis (the occurrence of \(\text{CtOH}\) and the appearance of turbidity in an alkaline solution).

4. Discussion

4.1. Spectral and Equilibrium Properties of Dissimilar Associates

A significant decrease in the intensity of the light absorption bands is a characteristic feature of the formation of cation-anionic associates. It is most clearly observed if increasing amounts of BP are added to the constant content of cyanine dye and the light absorption is measured against a solution containing the same concentration of BP as in the dye mixture. An analysis of changes in the electronic absorption spectra of mixtures of Ct\(^+\) with HAn\(^-\) and Ct\(^+\) with An\(^{2-}\) leads to the conclusion that the principle of additivity of light absorption is violated. The absorption intensity \((A)\) of the mixture of interacting counterions becomes less than the total light absorption of individual dye ions. This phenomenon occurs regardless of the initial concentrations of anions or cations (in the above ranges), as shown in Figures 2 and 3. The intensity of the \(\alpha\)-band is greater than the \(\beta\)-band for QB in Figure 2. However, the situation is the opposite (see Figure 3), where the concentration of QB is much more (“Ct\(^+\) + An\(^{2-}\)” system). Such spectral shifts of the absorption bands in the absence of new or the splitting of existing bands suggest a solvate-separated type of dissimilar associate structure (in accordance with the general features of spectral shifts for dye associate systems [3,66]).
Using methods for estimating the stoichiometric composition (similar to studies [12,13,56,60]), it was found that under certain conditions (such as initial concentrations of counterions and their molar ratios), anions of BP can form $\text{Ct}^+ \cdot \text{HAn}^-$ associates of the composition $\text{Ct}^+ \cdot \text{HAn}^-$. From the experimental data, it can be concluded that for dissimilar associates of BP, the stoichiometric ratio of $\text{QB}: \text{counterion}$ is $1:1$ for the case of the anion $\text{HAn}^-$, and it is $2:1$ for the case of $\text{An}^2-$. For equilibria of type $\text{jCt}^+ + \text{An}^2- \rightleftharpoons (\text{Ct}^+)_{\text{j}} \cdot \text{An}^2-$, the association constants ($K_{\text{as}}$) were calculated taking into account the ratios of the stoichiometric coefficients. The concentration constant of the association $K_{\text{as conc.}}$ practically does not differ from the thermodynamic one $K_{\text{as thermod.}}$ because $l \leq 0.004$ in all experiments:

$$K_{\text{as thermod.}} = K_{\text{as conc.}} = \frac{[(\text{Ct}^+)_{\text{j}} \cdot \text{An}^2-]}{(\text{C}_{\text{Ct}^+} - j \times [(\text{Ct}^+)_{\text{j}} \cdot \text{An}^2-]) \times (\text{C}_{\text{An}^2-} - [(\text{Ct}^+)_{\text{j}} \cdot \text{An}^2-])}$$
where \( C_{Ct}^+ \) is the initial molar concentration of the cationic dye (which does not change within the series); \( C_{An}^- \) is the initial molar concentration of the anion; \([Ct^+]_j \cdot An^-\) is the equilibrium molar concentration of the associate (as):

\[
[Ct^+]_j \cdot An^- = \frac{[Ct]_j \times \varepsilon_{Ct} \times l + [An] \times \varepsilon_{An} \times l - A}{l \times \varepsilon_{Ct} + \varepsilon_{An} - \varepsilon_{as}}.
\]

The last value was calculated on the principle of additivity of optical density \( A \) of a mixture of colored particles in the solution by the equation:

\[
A = A_{Ct} + A_{An} + A_{as} \text{ at a fixed wavelength } \lambda.
\]

\[
A_{Ct} = [Ct]_j \times \varepsilon_{Ct} \times l = (C_{Ct} - j \times [(Ct^+]_j \cdot An^-]) \times \varepsilon_{Ct} \times l,
\]

\[
A_{An} = [An] \times \varepsilon_{An} \times l = (C_{An} - [(Ct^+]_j \cdot An^-]) \times \varepsilon_{An} \times l,
\]

\[
A_{as} = [(Ct^+]_j \cdot An^-] \times \varepsilon_{as} \times l,
\]

where \( l \) is the thickness of the absorbing layer, cm.

For \( l = 1 \) cm, it turns out:

\[
[(Ct^+]_j \cdot An^-) = \frac{C_{Ct} \times \varepsilon_{Ct} + C_{An} \times \varepsilon_{An} - A}{l \times \varepsilon_{Ct} + \varepsilon_{An} - \varepsilon_{as}}.
\]

In general, it is possible to use different ratios of cation and anion concentrations. However, when one of the dyes is susceptible to dimerization, then it is necessary to measure the optical density of the mixture at a constant concentration of this dye (for example, QB) and a varying concentration of the second dye (BP). In fact, the cationic dye is “titrated” by the anion, and then \( C_{Ct} \times \varepsilon_{Ct} \times l = \text{const} \). If the absorption bands of the cation and the anion are well separated (\( \Delta \lambda_{max} = |\lambda_{max Ct} - \lambda_{max An}| \geq 80 \ldots 100 \) nm), then the light absorption of the anion, \( A_{An} \), at the selected wavelength \( \lambda_{max Ct} \) barely differs from zero, since \( \varepsilon_{An} \approx 0 \). Then:

\[
[(Ct^+]_j \cdot An^-) = \frac{C_{Ct} \times \varepsilon_{Ct} - A}{l \times \varepsilon_{Ct} - \varepsilon_{as}},
\]

where \( A \) is the measured value of the optical density of the dye mixture.

Data for \( K_{as} \) were obtained at \( C_{Ct}^+ \approx 6 \cdot 10^{-7} \) mol/L for several \( C_{An}^- \) values and at three wavelengths (see Table 2).

### Table 2. The \( \lg K_{as} \) values of BP associates.

| Cation | \( \lg K_{as} \)   |
|--------|-------------------|
|        | \( Ct^+ \cdot HAn^- \) | \( (Ct^+)_2 \cdot An^2^- \) |
| QB     | 6.61 ± 0.07       | 11.16 ± 0.11     |
| QR     | 4.84 ± 0.06       | 8.29 ± 0.05      |

The obtained data on the logarithmic values of the association constant are in good agreement with the values of \( K_{as} \), which were defined earlier by us [59] (QB: 6.67 ± 0.05 \( (Ct^+ \cdot HAn^-) \), 11.07 ± 0.10 \( ((Ct^+)_2 \cdot An^2^-) \); QR: 4.78 ± 0.06 and 8.23 ± 0.04, respectively) for slightly different concentration ranges of \( Ct^+ \) and BP. This fact confirms the validity of considering the indicated stoichiometry of a dissimilar association from the position of an equilibrium model. However, it should be noted that turbidity may appear in more concentrated solutions of mixtures of dyes. This phenomenon indicates the formation of associates of more complex stoichiometry, which are sparingly soluble in water: \( (Ct^+)_j \cdot An^- + kAn^- (Ct^+)_j \cdot (An^-)_k+1 \). Thus, it is possible to form associates of complex composition by a cooperative mechanism, when the counterion interacts not only with the dye, but with the dissimilar associate. Similar facts were set earlier for tetraphenylborate...
anion by spectrophotometrically [67] and for “daunomycin + ethidium bromide” [68] or “acridine orange + caffeine” [69] by $^1$H NMR spectroscopy.

Comparison of the values of $\lg K_{as}$ (see Table 2) show that QB associates of BP are more stable than QR associates. This is probably due to the lower hydrophobicity of QR compared to QB. The octanol–water partition ratio is the most common way of expressing the hydrophobicity of a compound ($P$), and it is defined as the ratio of the concentration of a solute in a water-saturated octanolic phase to its concentration in an octanol-saturated aqueous phase. The correlation between hydrophobicity and activity has provoked the extensive use of the octanol–water partition ratio, among others, as a descriptor in quantitative structure–activity/property relationships [70–73]. The higher the $P$ parameter, the more hydrophobic the molecule is. Indices of hydrophobicity are $\log P_{QR} = 5.15 \pm 0.12$ and $\log P_{QB} = 5.69 \pm 0.12$ according to [74]. So, the manifestation of hydrophobic interactions in QR associates is reduced. In addition, the positive charge is localized mainly on the heteroatom of the nitrogen-containing heterocycle in QR, while the positive charge is delocalized in QB.

The formation of associates in solutions is more characteristic for dyes with a flat molecule shape and developed π-electronic fragments, which enhances the component of noncovalent interactions. Such properties have some thiacyanines, porphyrins, spiropyran and squaraines [75–78]. However, sulfonephthaleins do not have a flat structure in contrast to these structures. However, the cation–anionic interactions for BP are significantly expressed as they follow from the determined values of $K_{as}$. Based on experimental data on stoichiometry, it can be assumed that the polymethine cation coordinates with the single-charge BP anion (or two cations coordinate with one double-charged BP anion). Using quantum chemical calculations, we considered the energy state (value of the standard enthalpy of formation, $\Delta_f H^o$) of each of the counterions and associates in more detail, and also determined their most probable structure.

4.2. Energy and Structural Properties of Dissimilar Associates

The semi-empirical PM3 method was used to estimate $\Delta_f H^o$ values of ions and dissimilar associates. The parameters of this method most correctly reproduce the experimental values of $\Delta_f H^o$ of organic compounds. It should be noted that $\Delta_f H^o$ calculations for organic molecules by non-empirical methods lead to errors exceeding 100 kJ/mol even for small molecules, while the average error of the PM3 method in calculating $\Delta_f H^o$ is only 25 kJ/mol [79,80]. In advance, the geometry of all structures was optimized by the method of molecular mechanics MM+ (by the minimum value of the total energy $E$). This significantly simplified the further determination of $\Delta_f H^o$ by the semi-empirical method.

It is important to find the global energy minimum from a set of local minima to obtain the correct values of $\Delta_f H^o$. To do this, we tested several different starting locations (more often 5–6) of counterions in the associate. From the received calculated set of energy minima, the smallest was chosen; the energy of this structure corresponded to the global energy minimum. For example, Figure 4 shows three variants of the initial location of the two-charged ion in the association of An$^{2−}$ with two cations of QR.

Different (1 and 2) starting positions of ions in an associate can lead to practically identical optimized values of $E$. However, in comparison with curve 3, this indicates that only a local energy minimum has been achieved, since in case 3 the energy results in being even lower. Thus, curve 3 corresponds to the variant with the energy of the global minimum $E = 123$ kJ/mol.
Figure 4. Energy dependences on the RMS value for three variants (1–3) of different locations of ions in the (Ct$^+$)$_2$·An$^{2-}$ associate.

Note that the total energy gradient is calculated as a root mean square (RMS, kJ/(mol·Å)) value. The gradient is the rate of change (first derivative) of total energy ($E$) with respect to the displacement of each atom in the $x$, $y$, and $z$ directions; the local minimum of the potential energy of the structure is considered reached when RMS = 0. The process of finding the optimized variant of the associate structure was considered complete when the $E$ or standard enthalpy of formation $\Delta_H^o$ ceased to depend on the RMS values. This is indicated by the flatness of the area of the corresponding graphical dependence (Figure 5).

Figure 5. Changes in $\Delta_H^o$ from RMS values for Ct$^+$·HAn$^{2-}$ associate of BP with QB, PM3 method.

Table 3 shows the dependence of $\Delta_H^o$ on RMS values, as well as changes in the location of ions during the optimization process (the numbers on the curve, Figure 5, correspond to the location of dyes from initial 1 to final 5 state; stereo images are presented, and 1, 2, 3 are the directions of the coordinate axes; the position of BP (BP is over) is conditionally fixed for clarity).
Table 3. Dependence of $\Delta fH^o$ on RMS values and change of mutual arrangement of BP and QR dyes in Ct$^+$-HAn$^-$ associate.

| State | Arrangement of BP and QB Ions |
|-------|--------------------------------|
| 1     | ![Diagram 1](image1.png)       |
| 2     | ![Diagram 2](image2.png)       |
| 3     | ![Diagram 3](image3.png)       |
| 4–5   | ![Diagram 4](image4.png)       |

The optimization process is accompanied by a decrease in the distance between the dyes (the distance between the ions along the axis 1 is from 6.8 Å (initial state 1) to 4.2 Å (final state 5), a certain deformation π-electronic dye system, and is almost finalized with $\Delta fH^o = 202$ kJ/mol at RMS$_{\text{min}} = 0.025$.

The obtained data make it possible to build energy diagrams. The properties of the associate of the HAn$^-$ anion with the QB cation are considered in Figure 6 as an example (numbers near the arrows indicate the range of variation of the values of $\Delta fH^o$, kJ/mol).
The values of $\Delta fH^0$ for ions (QB+, BP) and the Ct+·HAn− associate.

The values of $\Delta fH^0$ 980.8 . . . 968.7 kJ/mol and $-584.5 . . . -609.6$ kJ/mol correspond to Ct+ and HAn− ions. Their algebraic sum (Σ) can take values from 980.8 − 584.5 = 396.3 kJ/mol to 968.7 − 609.6 = 359.1 kJ/mol, that is it varies within 396.3 − 359.1 = 37.2 kJ/mol (level 1). The values of $\Delta fH^0$ for the Ct+·HAn− associate (level 2) are 220.4 . . . 202.4 kJ/mol, that is these values differ by 18.0 kJ/mol (level 2). The differences between levels 1 and 2 are from 359.1 − 220.4 = 138.7 kJ/mol to 396.3 − 202.4 = 193.9 kJ/mol, which significantly exceeds the above systematic error of semi-empirical calculations. In this case, the relative error (δ) of the $\Delta fH^0$ estimate is no more than (193.9 − 138.7)/100% = 28%. These data indicate that the formation of an associate between dye ions is an energetically favorable process. The $\Delta fH^0$ and δ values are given for all dissimilar associates in Table 4 (rounded values).

Table 4. Values of $\Delta fH^0$, Σ − $\Delta fH^0$ and δ for BP dissimilar associates.

| An Associate | Σ, kJ/mol | $\Delta fH^0$, kJ/mol | Σ − $\Delta fH^0$, kJ/mol/δ, % |
|--------------|-----------|-----------------------|---------------------------------|
| QB⁺·BP⁻      | 359       | 202                   | 157/28                          |
| QR⁺·BP⁻      | 303       | 107                   | 194/14                          |
| (QB⁺)₂·BP²⁻  | 1367      | 703                   | 664/6                           |
| (QR⁺)₂·BP²⁻  | 1254      | 525                   | 729/7                           |

The analysis of the results leads to an important conclusion. The value of $\Delta fH^0$ for associates of bromine-containing dyes is systematically higher in comparison with associates that do not contain bromine. For example, in the case of an associate of cresolsulfonphthalein (CS) with these polymethines, the lg $K_{as}$ values are 4.59 ± 0.03 (associate QB⁺·CS⁻) and 10.96 ± 0.10 (associate (QB⁺)₂·CS²⁻), and in the case of thymolsulfonphthalein (TS) they are 4.1 ± 0.1 (associate QR⁺·TS⁻) and 5.9 ± 0.1 (associate (QR⁺)₂·TS²⁻) [57,60]. Obviously, bromine atoms, located in the plane of benzene rings, have virtually no effect on the geometry of BP, but significantly enhance the non-Coulomb component of intermolecular interactions, primarily the hydrophobicity of the molecule [81,82]. Thus, the introduction of halogen atoms into the structure of sulfonphthalein promotes the formation of cation–anionic associates between dyes.
5. Conclusions

The interaction between single- or double-charged anions of BP and cyanine cations has been investigated at dye concentrations of $5.0 \times 10^{-7} – 4.0 \times 10^{-5}$ mol/L. The obtained results indicate that the processes of dye association are accompanied by a rather complex combination of different interactions, including non-Coulomb and π-electronic. The study of these processes is appropriate in terms of comparing the results of spectrophotometric measurements with computer simulation data.

Semi-empirical PM3 simulations are in agreement with the spectrophotometric data and indicate that the association of dye into an associate is possible and accompanied by a significant gain in energy. The study of the cation–anion association develops the concept of intermolecular interactions in solutions and creates a basis for further practical use of the spectral and equilibrium properties of associates.

Further study of the dissimilar association of dyes is aimed at finding the relationship between the structure of the dye and its ability to associate with organic ions. There is a need to develop theoretical provisions on the basis of which it would be possible to predict the stability ($K_{as}$ values) of associates and their spectral properties based on the structure of interacting ions. Dye associates can be very useful for chemical analysis; the regulation of the completeness of the association can be considered an effective means of changing the absorption characteristics of solutions.

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