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# Dissimilar Associates of Dyes in Aqueous Solutions: Experimental Study and Computer Simulation [1]

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Dissimilar cation-anionic association of dyes («cyanine+oxyxanthene», «cyanine+sulfonepthalein») has been regularly investigated in aqueous solutions. Experimental (by spectrophotometry) and theoretical (by semiempirical) methods were used. The basic regularities of association processes have been discussed. It is shown that the change in the stability of associates has a systematic character both in the series of singly charged and doubly charged anions. The experimentally determined values (of equilibrium constant of association) and simulated values (of standard enthalpy of hydration of associates) are mutually consistent. The standard enthalpy of formation and the most probable structures of associates have been determined.

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## Introduction

The processes of association of dye molecules have a significant effect on the light absorption and luminescence of aqueous solutions [1-4]. The formation of dimers and more associated structures (self-associates) is recorded at concentrations of $5 \cdot 10^{-5}$ mol/L and higher [5-11]. The cation-anion association, as a kind of association between dyes of different structures, leads to the formation of fairly stable stoichiometric compounds at concentrations of polyatomic particles of $1 \cdot 10^{-6}$ – $1 \cdot 10^{-5}$ mol/L. Such association is characterized by a variety of spectral effects, including the appearance of absorption bands or their shifts. In practical terms, the association is considered as an effective factor for changing the spectral-luminescent characteristics of solutions.

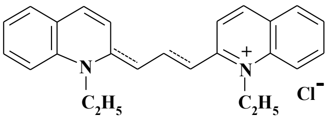
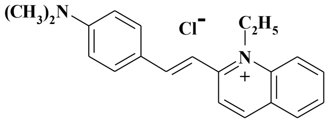
Extending the notion of the association of polyatomic particles is important for the development of scientific fields, such as chemical analysis, analytical chemistry of pharmaceuticals, surface chemistry, cell and DNA biochemistry [12-20]. For this reason, the study of regularities of cation-anionic dye association is relevant, as well as determination of the influence of several factors (first of all, the structure and charge of the ions) on the stability of associates.

Electronic spectroscopy, theoretical methods and computer simulation have been used successfully for the study of complex supramolecular systems. They allow one to study and interpret the formation of associates at particle concentrations of not more than $1 \cdot 10^{-5}$ mol/L [21-25].

In this paper, the equilibrium properties of cation-anion associates are considered, their most probable structures are discussed, and the agreement between the experimental data and computer simulation is analyzed. Associates had in their composition cations of cyanine dyes and anions of sulfonephthaleins and oxyxanthenes.

## Experimental part

*Materials*

Pinacyanol chloride (PNC)  and quinaldine red  (QR) were used as the cationic cyanine dyes ($Ct^+$).

The well-known phenol red (PR), cresol red (CR), thymol blue (TB), bromothymol blue (BTB), bromocresol purple (BCP), bromocresol green (BCG), bromophenol blue (BPB) were used as anionic sulfonephthaleins. The well-known fluorescein (FL), eosin (EO), ethyleosin (EE), tetrabromophenylfluoron (TBPF), erythrosine (ER), Bengal Rose B (BRB) have been investigated as oxyxanthene anions. The preparations of the dyes were of the "Sigma" trade mark with the 95 % contents of the main substance. The chemical purity of the dyes was checked spectrophotometrically using known values of the molar extinction coefficient.

*Methods*

The intrinsic absorption of individual forms of dyes was taken into account when determining the spectrophotometric characteristics of dissimilar associates.

Using previously obtained data on the composition of the associates [25], the cation-anionic interactions of the dyes were considered in accordance with such equilibria:

$$\mathrm{Ct^+ + HAn^-} \rightleftarrows \mathrm{Ct^+ \cdot HAn^-}$$

and

$$\mathrm{2Ct^+ + An^{2-}} \rightleftarrows \mathrm{(Ct^+)_2 \cdot An^{2-}}.$$

Equilibrium constants of association ($K_{\mathrm{as}}$) were calculated according to the law of acting masses respectively:

$$K_{as} = \frac{[\mathrm{Ct^+ \cdot HAn^-}]}{(C_{\mathrm{HAn^-}} - [\mathrm{Ct^+ \cdot HAn^-}]) \times (C_{\mathrm{Ct^+}} - [\mathrm{Ct^+ \cdot HAn^-}])}$$

and

$$K_{as} = \frac{[(\mathrm{Ct^+})_2 \cdot \mathrm{An^{2-}}]}{(C_{\mathrm{An^{2-}}} - [(\mathrm{Ct^+})_2 \cdot \mathrm{An^{2-}}]) \times (C_{\mathrm{Ct^+}} - 2[(\mathrm{Ct^+})_2 \cdot \mathrm{An^{2-}}])^2}$$

where the equilibrium concentrations of the associates are:

$$[\mathrm{Ct^+ \cdot HAn^-}] = \frac{\varepsilon_{\mathrm{Ct^+}} \times C_{\mathrm{Ct^+}} \times l - A}{(\varepsilon_{\mathrm{Ct^+}} - \varepsilon_{\mathrm{as}}) \times l}$$

and

$$[(\mathrm{Ct^+})_2 \cdot \mathrm{An^{2-}}] = \frac{\varepsilon_{\mathrm{Ct^+}} \times C_{\mathrm{Ct^+}} \times l - A}{(2\varepsilon_{\mathrm{Ct^+}} - \varepsilon_{\mathrm{as}}) \times l}.$$

Notation: $C$ is the initial molar concentrations of the cation or anion; $l$ is the absorbing layer thickness; $A$ is the optical density of the solution at the fixed wavelength; and ε is the molar extinction coefficient of the cation or the associate. The numerical $A$ values which form the basis for calculating the $K_{\mathrm{as}}$ were checked for compliance with the basic law of light absorption.

For the calculation of the association constants, the equilibrium concentrations of the associate were determined from the spectral data in the region of $\nu_{\mathrm{max}}$ of cation. The search for $[\mathrm{Ct^+ \cdot HAn^-}]$ or $[(\mathrm{Ct^+})_2 \cdot \mathrm{An^{2-}}]$ values is substantially facilitated by the fact that the association is pronounced. And it is not necessary to create of large excesses of the $\mathrm{HAn^-}$ or $\mathrm{An^{2-}}$ concentrations. The intrinsic light absorption of anionic dyes in the absorption region of the cation is very small due to the use of low initial concentrations of anions and a significant difference in the $\nu_{\mathrm{max}}$ values between cation and anion (for example, $\nu_{\mathrm{max}} = 16670\ \mathrm{cm^{-1}}$ for $\mathrm{Ct^+}$ of PNC [23] and $\nu_{\mathrm{max}} = 16670\ \mathrm{cm^{-1}}$ for $\mathrm{HAn^-}$ of PR [25]). So, the formulas do not take into account the absorption of $\mathrm{HAn^-}$ or $\mathrm{An^{2-}}$ because their contribution in was not substantial under analysis.

Very dilute solutions of dyes were used and the ionic strength ($I$) of photometric solutions did not exceed 0.001–0.008 mol/L. So, the concentration association constant is actually thermodynamic at such values of $I$. The details of the measurement procedure are set out earlier [25].

Software applications "HyperChem 8.0", "MOPAC 2012", (evaluation or license versions) were used to determine the characteristics of associates. To estimate the values of the standard enthalpy of hydration, $\Delta H°_f$, the AM 1 semiempirical method was used. Method AM 1 is one of the extended variants of the MNDO method. This method has been parametrized in such a way that the experimental values of $\Delta H°_f$ of organic compounds would be reproduced most adequately The average inaccuracy of the AM 1 method in the calculation of $\Delta H°_f$ is 25 kJ/mol. Note that similar nonempirical simulations give inaccuracies of the values of $\Delta H°_f$ exceeding 100 kJ/mol even for small molecules. With an increase in the number of atoms in the molecule, the inaccuracies in the calculated values of $\Delta H°_f$ increase more and gain a systematic character [26-28]. The MOPAC procedure essentially accelerates the calculations by using the AM 1 method, and the application "HyperChem 8.0" makes it possible to visualize the structure of ions and associates.

## Results and discussion

*Experimental study of dyes association*

A significant decrease in the intensity of light absorption is a characteristic feature of a dissimilar association. This decrease is clearly seen as the addition of increasing amounts of one dye to the unchanged content of the other. The most typical cases are presented in **Figure 1** (decrease in the absorption intensity) and **Figure 2** (shifts of the absorption band and the appearance of a new band).

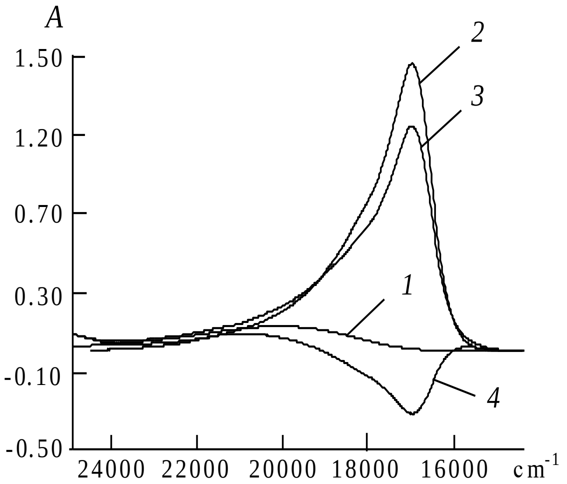


**Figure 1.** Light absorption of aqueous solutions containing QR and BTB. Concentrations, mol/L, of QR: *1, 3* – $2\cdot10^{-5}$, *2* – 0; of BTB: *1* – 0, *2, 3* – $4\cdot10^{-5}$, *4* – is nonadditivity curve. The reference solution is water. The absorbing layer thickness is 0.2 cm. pH 7.0.

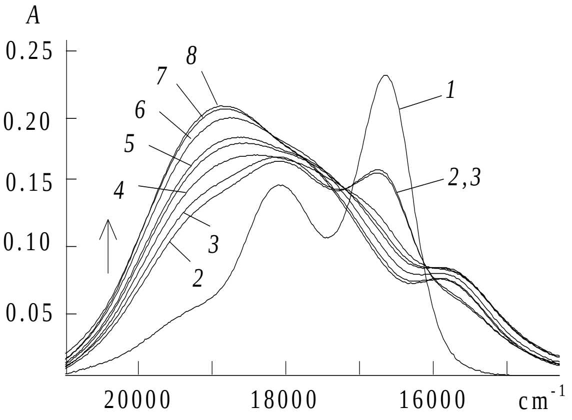


**Figure 2.** Light absorption of aqueous solutions containing PNC and BTB. Concentrations, mol/L, of PNC: *1–8* – $4.9\cdot10^{-6}$, of BTB: *1* – 0, *2* – $4\cdot10^{-6}$, *3* – $4.5\cdot10^{-6}$, *4* – $5\cdot10^{-6}$, *5* – $1\cdot10^{-5}$, *6* – $1.25\cdot10^{-5}$, *7* – $1.5\cdot10^{-5}$, *8* – $2\cdot10^{-5}$. The reference solution is water. The absorbing layer thickness is 1.0 cm. pH 3.6.

Analysis of the absorption spectra reveals the nonadditivity of the spectral bands. It consists in that the intensity of *A* values of a mixture of counterions is systematically less than the total light absorption of individual ions (curve *4* in **Figure 1**). Areas with a negative value of $A$ indicate a tangible interaction of counterions and the formation of ionic associates. A similar situation is observed in the association of rhodamines or indopolycarbocyanines [25].

According to the spectrophotometric data and the above formulas, the $K_{as}$ values were calculated for dissimilar associates of PNC (**Table 1**). EE and TBPF do not form doubly charged anions. The solutions containing singly charged cations of dyes in strongly acidic and basic media are considerably decolorized in consequence of the processes $Ct^+ + H^+ \rightarrow HCt^{2+}$ and $Ct^+ + OH^- \rightarrow CtOH$ correspondingly due to the disturbance of the conjugation of the polymethine chain of the chromophore. Therefore, the fact of the interaction of single-charged BCG and BPB anions, as well as the double-charged anion of a TB with a cation $Ct^+$ of PNC is not experimentally determined. In addition, the existence of these sulfonephthalein anions is possible at pH values that do not coincide with the area of existence of the PNC cation.

**Table 1.** Values of log $K_{as}$ for PNC associates

| Dye | log $K_{as}$ | |
|---|---|---|
| | $Ct^+\cdot HA^-$ | $(Ct^+)_2\cdot An^{2-}$ |
| PR | 5.83 ± 0.10 | 11.81 ± 0.10 |
| CR | 4.59 ± 0.03 | 10.96 ± 0.10 |
| TB | 5.29 ± 0.05 | |
| BTB | 5.95 ± 0.11 | 10.89 ± 0.09 |
| BCP | 6.67 ± 0.04 | 11.07 ± 0.10 |
| BCG | | 12.09 ± 0.09 |
| BPB | | 13.73 ± 0.10 |
| FL | 4.58 ± 0.11 | 9.75 ± 0.10 |
| EE | 5.45 ± 0.09 | – |
| TBPF | 6.38 ± 0.11 | – |
| EO | | 11.25 ± 0.10 |
| ER | | 11.84 ± 0.10 |
| BRB | | 13.46 ± 0.11 |

The study of the interaction of PNC with singly-charged anions of EO, ER, BRB is also difficult. Due to the proximity of the values of p$K_{a1}$ and p$K_{a2}$ of these oxyxanthenes, no 100 % yield of the singly charged anion can be obtained at any pH value. Therefore, associates of the $Ct^+\cdot HA^-$ composition of these oxyxanthenes have not been studied.

The data of the table indicate a statistically significant difference in the values of $K_{as}$ for associates of the same stoichiometric composition. In all cases, the $K_{as}$ values are comparable with the known values of the equilibrium complexation constants [10, 11], when, unlike the association process, new valence bonds arise between the reacting particles.

*Computer simulation of dyes association*

The obtained experimental results allow us to conclude that alkyl substituents in the sulfonephthalein or oxyxanthene structures contribute to a decrease of $K_{as}$ values, while the halogen atoms, in contrast, increase of $K_{as}$ values. To explain the course of the $K_{as}$ change, a number of design characteristics have been tested, among them the effective area of the molecule, its volume, the hydrophobicity index. However, the standard enthalpy of hydration

$\Delta H°_{hydr}$ reflects the state of the ion in the solution to the greatest extent. Let's consider it on an example of PNC associates.

The values of $\Delta H°_{hydr}$ (kJ/mol, in brackets) are located for the anions of sulfonephthaleins in the following sequence:

$HAn^{–}$: CR (-45.4) < TB (-29.8) < BTB (-27.4) < BCP (-26.0),

$An^{2–}$: BTB (-25.6) ≈ CR (-24.4) < BCP (-9.7) < BCG (-2.5) < BPB (-1.3).

The changes in the $\Delta H°_{hydr}$ of oxyxanthene anions are:

$HAn^{–}$: FL (-60.9) < EE (-2.3) < TBPF (-0.8),

$An^{2–}$: FL (-45.3) < EO (+1.0) < ER (+7.4) < BRB (+26.6).

For anions of sulfonephthaleins, an increase in the stability of associates is in agreement with an increase in the $\Delta H°_{hydr}$ anions (log $K_{as}$ values are set in brackets):

$HAn^{–}$: CR (4.59) < TB (5.29) < BTB (5.95) < BCP (6.67),

$An^{2–}$: BTB (10.89) < CR (10.96) ≈ BCP (11.07) < BCG (12.09) < BPB (13.73).

Associates of oxyxanthene anions are arranged in stability in the following sequence:

$HAn^{–}$: FL (4.58) < EE (5.45) < TBPF (6.38),

$An^{2–}$: FL (9.75) < EO (11.25) < ER (+11.84) < BRB (+13.46).

These sequences also correlate well with the corresponding of the increase in the $\Delta H°_{hydr}$ values. Thus, the satisfactory agreement between the experimentally $K_{as}$ values with theoretically determined of $\Delta H°_{hydr}$ values is observed for sulfonephthaleins or oxyxanthenes dissimilar associates.

Note that the association is inherent in dyes, which have a planar form of the molecule. Hydrophobicity, the presence of developed π-conjugated electron fragments significantly enhance dispersion interactions and also promote association. However, the investigated anionic dyes are not flat π-electronic systems, in contrast to cations of cyanines. However, as follows from the experimental data, a significant interaction occurs between $Ct^{+}$ and anions. It can be assumed that the planar cation is coordinated by a singly charged anion or two cations by a single doubly charged anion. The most probable structures of stoichiometric associates were defined and the values of the standard enthalpy of formation of associates were determined.

Finding a global energy minimum is necessary for the correct determination of the $\Delta H°_{f}$. For this, 6-7 different starting mutual positions of counterions in the associate were tested. Each of the counterions was geometrically optimized previously. From the set of energy (so-called local) minima, the smallest has been chosen. The energy of this structure was assumed to correspond to the global energy minimum. As an example, **Figure 3** shows the dynamics of $\Delta H°_{f}$ changes depending on the values of the RMS-gradient for the associates of QR with BCG.

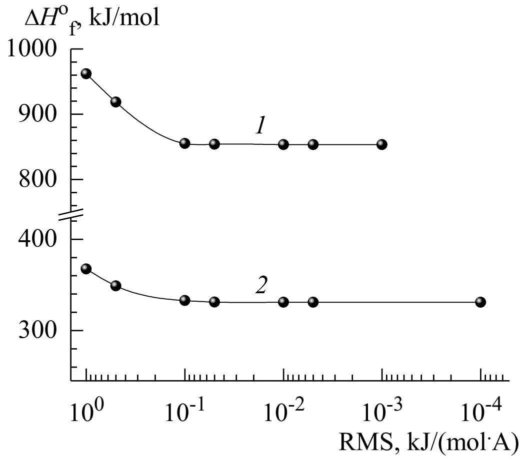


**Figure 3.** The change in $\Delta H^{\circ}_{f}$ as a function of RMS-gradient values. *1* – $(QR^{+})_2{\cdot}BCG^{2-}$ associate; *2* – $QR^{+}{\cdot}BCG^{-}$ associate.

Note, that the RMS-gradient, kJ/(mol·Å), is the rate of change of energy with a change in the arrangement of each atom in three mutually perpendicular directions.

The optimized arrangement ions in the associate $(QR^{+})_2{\cdot}BCG^{2-}$ is presented in **Figure 4** (stereo-image, hydrogen atoms are not shown).

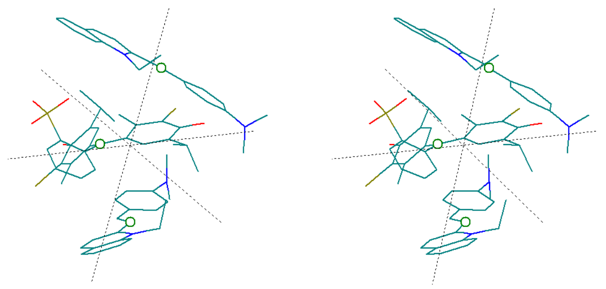


**Figure 4.** The arrangement of ions in the $(QR^{+})_2{\cdot}BTB^{2-}$ associate ($BTB^{2-}$ is at the center; the distance between the isolated middle atom and the upper one is 6.7 Å, the mean and the lower is 4.6 Å, the central angle is 97°).

The progress of structural optimization depends significantly on RMS values, but is practically finalized already at 0.01 kJ/mol and is accompanied by a decrease in the distance between counterions.

The energy diagrams of dyes and an $(Ct^{+})_2{\cdot}An^{2-}$ associate between QR and BPB are shown as an example in **Figure 5** (the numbers at the arrows denote the range of variation of the values of $\Delta H^{\circ}_{f}$).

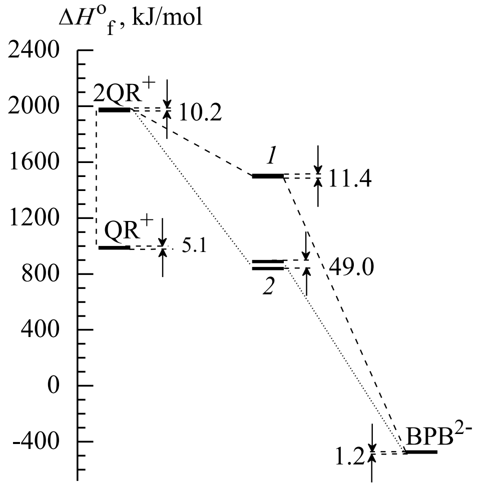


**Figure 5.** The $\Delta H^{\circ}_{f}$ values of the $QR^{+}$, $BPB^{2-}$ ions and associate. *1* – The algebraic sum of the counters ions; *2* – $\Delta H^{\circ}_{f}$ of the associate.

The excess of the algebraic sum of the $\Delta H^{\circ}_{f}$ values of counterions (1494 kJ/mol, level *1*) with respect to $\Delta H^{\circ}_{f}$ of associate (839 kJ/mol, level *2*) is 655 kJ/mol. This excess of the $\Delta H^{\circ}_{f}$ value is significantly higher than the average error (is about 25 kJ/mol) of the simulation AM1 method [26, 27].

Calculations also show that the similar excesses of the $\Delta H^{\circ}_{f}$ value are higher for associates of PNC cation. Thus, $\Delta H^{\circ}_{f}$ excess is 649 kJ/mol for “PNC + $BTB^{2-}$” associate, but $\Delta H^{\circ}_{f}$ excess is only 605 kJ/mol for “$QB^{+}$ + $BTB^{2-}$” associate. Since the error of $\Delta H^{\circ}_{f}$ is no higher than the mentioned average error of the method, we can state that the formation of all associates is energetically advantageous, especially in the association of dyes with structures containing developed π-electron systems, where the advantage is ~150–160 kJ/mol (for $Ct^+ \cdot HA^-$ associates) and 605–700 kJ/mol (for $(Ct^+)_2 \cdot An^{2-}$ associates).

## Conclusions

Unobvious experimental and theoretical results have been obtained in the study of the formation of dissimilar associates of dyes in aqueous solutions. Association of polyatomic particles was interpreted as part of an equilibrium model of intermolecular interactions. The satisfactory agreement between the experimentally $K_{as}$ values with theoretically determined of $\Delta H^\circ_{hydr}$ values has been revealed. The combination of instrumental and theoretical methods made it possible to establish spectral and equilibrium regularities of the cation-anionic association of dyes, as well as to get the $\Delta H^\circ_f$ values and a design of the most probable structure of associates.

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