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Heteroassociation of Dyes in an Aqueous Solution: the Interaction of Cyanine Cations with 3',3'',5',5''-Tetrabromo-m-cresolsulfonephthalein Anions

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Abstract

Heteroassociation of cationic cyanines (quinaldine red, quinaldine blue) with 3',3'',5',5''-tetrabromo-m-cresolsulfonephthalein anions has been studied experimentally and theoretically. The values of the equilibrium association constants in the aqueous solution are determined spectrophotometrically. Geometric and energy characteristics of associates are calculated with the help of AM1 method. The effect of ionic surfactants on associates has been studied.

1. Introduction

It is known [1] that the interactions of intensely colored dye ions with organic counter-ions causes a substantial change in light absorption of the aqueous solution due to the formation of ionic heteroassociates. The heteroassociate can serve as an analytical reagent. This unique ability explains the growing interest in the study of heteroassociates of dyes and is used in solving a number of applied problems. For example, the characteristics of heteroassociates are used for the development of new methods for the quantitative determination of ionic surfactants in aqueous solutions [1, 2].

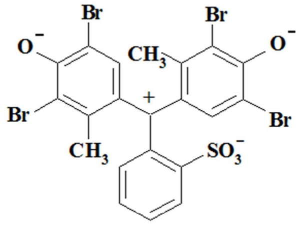
Heteroassociates of sulfonephthalein dyes attract the attention of researchers. Earlier properties of some of them were studied by us in aqueous systems [2]. This paper examines the ability of the 3',3'',5',5''-tetrabromo-m-cresolsulfonephthalein (TBCS) anions to interact with two cationic dyes: (2Z)-1-ethyl-2-[(E)-3-(1-ethylquinolin-1-ium-2-yl)prop-2-enylidene]quinoline, or quinaldine blue (QB), and 4-[(E)-2-(1-ethylquinolin-1-ium-2-yl)ethenyl]-N,N-dimethylaniline, or quinaldine red (QR).

It is known that TBCS is used in the manufacture of sensors of optoelectronic interfaces [3], capillary biosensors of cells [4], chemical sensors [5, 6]. In addition, this sulfonephthalein is used in pharmaceutical formulations to determine antibiotics, antidepressants and other drugs (for example, betaxolol [7], ethambutol [8], prasugrel [9], fluoxetine, clomipramine [10], paliperidone palmitate [11], candesartan [12], mebendazole [13]). It is noteworthy that the use of TBCS in modern spectrophotometric techniques is related to the ability of the dye to form heteroassociates (ion pairs), which are extracted into chloroform or dichloroethane.

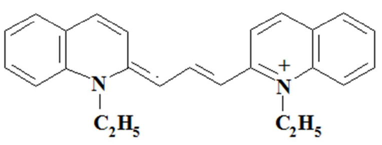
QB and QR were successfully used to study of dyes heteroassociation, including sulfonephthalein [1, 2, 14–16] due to their spectral, structural and protolytic properties.

2. Materials and Methods

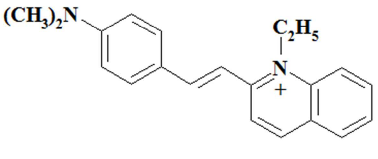
The sodium salt was used for TBCS and chlorides of QR or QB.



$TBCS^{2-}$



QB^{+}



QR^{+}

The content of the main substance was not less than 98%. Cetylpyridinium bromide (CPB) $[C_{16}H_{33}NC_5H_5]Br$ and sodium dodecylsulphate (DDS) $C_{12}H_{25}OSO_3Na$ were used as surfactants. All products were branded "Sigma". Features of the experiment and calculations were presented in the earlier works [2, 15]. The absorption spectra were measured at room temperature immediately after preparation of the solutions.

Heteroassociation was interpreted as an equilibrium process:

$$j\mathrm{Ct}^{+} + \mathrm{An}^{j-} \rightleftarrows (\mathrm{Ct}^{+})_j \cdot \mathrm{An}^{j-}$$

The association constants, K_{as}, were determined by the law of the effective masses:

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

$$= \frac{[(\mathrm{Ct}^{+})_j \cdot \mathrm{An}^{j-}]}{(C_{\mathrm{An}} - [(\mathrm{Ct}^{+})_j \cdot \mathrm{An}^{j-}]) \times (C_{\mathrm{Ct}} - j \times [(\mathrm{Ct}^{+})_j \cdot \mathrm{An}^{j-}])^{j}}$$

For the calculation of the association constants, the molar equilibrium concentrations of the associate $[(Ct^{+})_j \cdot An^{j-}]$ were determined from the spectral data by the equation:

$$[(\mathrm{Ct}^{+})_j \cdot \mathrm{An}^{j-}] = \frac{\varepsilon_{\mathrm{Ct}} \times C_{\mathrm{Ct}} \times l - A}{(j \times \varepsilon_{\mathrm{Ct}} - \varepsilon_{\mathrm{As}}) \times l}$$

where C_{Ct} is the analytical concentration of QB or QR (which does not vary in a single series of measurements); A is the optical density for the current value of the analytical concentration of the anion (C_{An}); l is the length of absorbing layer; ε_{Ct} and ε_{as} are the molar absorption coefficients of the cation and associate, respectively.

Very dilute solutions of dyes were used, the ionic strength (I) of photometric solutions did not exceed 0.001–0.008 M. So, the concentration association constant is actually thermodynamic at such values of I.

The principles of implementing quantum-chemical simulations of the structures of dyes, heteroassociates, and the interpretation of the obtained results are presented previously [2, 15]. It is known that *ab initio* simulations result in the errors in ΔH^{o}_{f} values larger than 100 $kJ \cdot mol^{-1}$ even for small molecules. This is due to the incompleteness of the basis set used and to the fact that the electron correlation energy is not taken into account. An increase in the size of molecules leads to an increase in the error of ΔH^{o}_{f} calculated by the *ab initio* method and these errors are to a great extent systematic in character. Hence, to estimate the values of ΔH^{o}_{f} for ions and heteroassociates, we used the semiempirical AM1 method as one of extended variants of the MNDO method. The parameters of this method were selected so that they allow us to reproduce the experimental values of $\Delta H°f$ of organic substances in the best way. The average error in calculation of $\Delta H°f$ is 25 $kJ \cdot mol^{-1}$.

The AM1 method was used to determine the most probable structure of heteroassociates (conditions of simulations: the Polak-Ribiere convergence algorithm; the convergence gradient of two successive iterations not higher than 2 $kJ \cdot mol^{-1}$). To obtain the optimized structure of the heteroassociate, it is important to find the global energy minimum. Six or seven different starting mutual positions of counterions in the heteroassociate were tested (each counterion was also preliminarily geometrically optimized). The lowest minimum was chosen from the calculated set of energy (so-called local) minima; and the energy of this structure was accepted as corresponding to the global energy minimum. Then the additional geometric optimization of the heteroassociate structure was performed, during which a series of decreasing values of the convergence gradient of successive iterations was specified (as a rule, from 0.1 to $5 \cdot 10^{-3}$ – $1 \cdot 10^{-4}$ $kJ \cdot mol^{-1}$). The process of searching for the optimized arrangement of the counterions in the heteroassociate was completed in the absence of geometric parameters from the specified values of the convergence gradient (so-called the RMS-gradient (root mean square value): the rate of changing the energy (the first derivative) with the change in the arrangement of each atom in three mutually perpendicular directions). As shown by the calculations, the optimization of geometry of the structure depends substantially on the values of the RMS gradient but is almost completed already at 0.01 $kJ\cdot mol^{-1}\cdot Å^{-1}$ and is accompanied by the shortening of the distance between the counterions.

3. Results and Discussion

3.1. Properties of the Dyes in Water

The TBCS dye is a tribasic acid, and the TBCS equilibrium can be represented as a scheme:

$$H_3An^+ \rightleftarrows H_2An^0 \rightleftarrows HAn^- \rightleftarrows An^{2-}.$$

The H_3An^+ particles have a red color (in dehydrated acetonitrile). The neutral form of TBCS forms a colorless tautomer like other bromoderivatives of sulfonephthaleins [16, 17]. The TBCS preparation has a flesh color if it is recrystallized with concentrated ethanic acid. HAn^- and An^{2-} forms are more colored, their absorption bands are well spectrally different, as seen in Table 1 (errors of the parameters are: λ_{max} ± 1 nm, ε_{max} ± 500, pK ± 0.03–0.08; pK_0 = –0.99 for TBCS; the value of pK_{a1} for QB and QR refers to the dissociation of a doubly charged cation). This favors the spectral study of ionic association in the region of very low concentrations (at a level of $1\cdot10^{-6}$ M).

Table 1. *Properties of the Dyes.*

Characteristics	**An ion**			
	$TBCS^-$	**$TBCS^{2-}$**	**QB^+**	**QR^+**
λ_{max}, nm	444	617	600 (α-band), 550 (β-band), 510 (γ-band)	528
ε_{max}	$1.8\cdot10^4$	$3.9\cdot10^4$	$1.3\cdot10^5$ (α-band)	$3.1\cdot10^4$
	A molecule			
	TBCS		QB	QR
pK_{a1}	1.2 TBCS, $I = 0.15$		3.5	2.63
pK_{a2}	4.90		–	–

Single-charged cations (Ct^+) of QR and QB significantly discolored in strongly acidic and alkaline media, due to hydrolysis:

$$Ct^+ + H^+ \rightleftarrows HCt^{2+}$$

and

$$Ct^+ + OH^- \rightleftarrows CtOH.$$

When studying the interaction of HAn^- and An^{2-} with Ct^+, the acidity of the solution should ensure the coexistence of only the corresponding ionic forms.

Otherwise, the interpretation of spectral changes is difficult due to possible interactions involving other particles. It was found out the optimal conditions for the association and calculated the fractional content of all the particles studied, taking into account the data on the pK values of protolytic processes (Figure 1). For example, as follows from Figure 1, the interaction of Ct^+ with HAn^- should be investigated at pH 3.5–4.2, and Ct^+ with An^{2-} at pH 7 or more.

In addition, the basic law of light absorption must be observed by each protolytic form for the correct calculation of the constants of the association (see below). Such ranges of concentrations were used for dyes: TBCS $5.0\cdot10^{-6}$ – $2.5\cdot10^{-4}$ M, and QR $1.0\cdot10^{-6}$ – $1.0\cdot10^{-4}$ M. Linear regression equations of this law (two series of independent determinations, 9–10 concentrations in each series) have the form:

$$A_{617} = 0.00078_{(0.0038)} + 7.73\cdot10^3_{(45.2)}\times C_{TBCS}, \text{ correlation coefficient } 0.99988_{(0.010)};$$

$$A_{528} = -0.0038_{(0.015)} + 3.37\cdot10^4_{(324)}\times C_{QR}, \text{ correlation coefficient } 0.9996_{(0.033)},$$

where A is the optical density at the indicated wavelength, C is the initial molar concentration of the dye, and the standard deviation of the each parameter is indicated by the brackets.

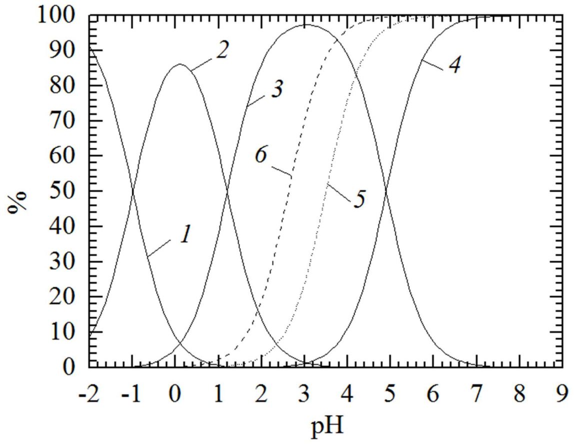


Figure 1. *Consistence of protolytic forms of TBCS (1 – H_3An^+, 2 – H_2An, 3 – HAn^-, 4 – An^{2-}), and cations of QB (5) and QR (6) in correlation with pH value.*

In fact, $A = k\times C$, since the free term of the regressions is a statistical zero. Thus, it can be considered that the TBCS and QR dyes do not dimerize in the indicated concentration ranges. On the contrary, for QB, the basic law of light absorption is observed in a very narrow range of concentrations ($3\cdot10^{-7}$ – $2\cdot10^{-6}$ M), since QB is prone to self-association (in more detail, the properties of QB in aqueous solution are considered in [18]).

3.2. Association of Ions. Structure and Energy of Associates

An analysis of the changes in the electronic absorption spectra reveals the nonadditivity of the spectral bands. This is because the absorption intensity of the counterion mixture is systematically less than the total light absorption of the individual dye ions. A characteristic feature of the association is a significant decrease in the intensity of absorption. This decrease is clearly observed when an increasing quantity of TBCS is added to the unchanged cyanine content (Figure 2, curves *1–6*, arrows indicate the directions of spectral shifts with increasing of TBCS concentration). The dye QB has a more developed vibrational structure (the presence of sufficiently intense α and β absorption bands, see the data in Table 1), and the spectral changes for QB are more distinct than for QR. As we can see, the spectral changes are quite complex. These changes may be accompanied by the formation of associates of different stoichiometry (as indicated by curves *7–10*) and even slightly soluble aggregates, when the turbidity is formed in the solution (curve *11*).

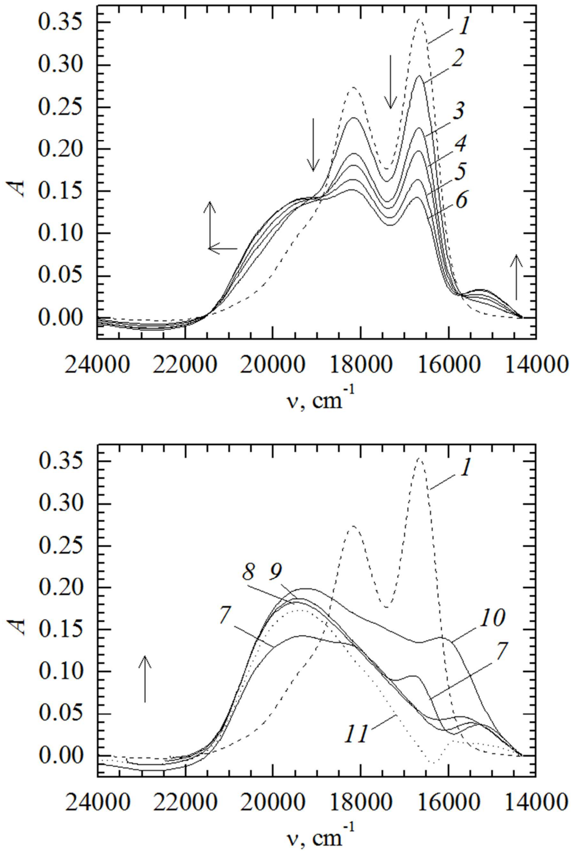


Figure 2. *Light absorbance in the system «QB + TBCS». Concentrations, M, QB: 1…11 – $4.9\cdot10^{-6}$; TBCS: 1 – 0; 2 – $1.0\cdot10^{-6}$; 3 – $1.5\cdot10^{-6}$; 4 – $2.0\cdot10^{-6}$; 5 – $2.5\cdot10^{-6}$; 6 – $3.0\cdot10^{-6}$; 7 – $1.5\cdot10^{-5}$; 8 – $2.0\cdot10^{-5}$; 9 – $5.0\cdot10^{-5}$; 10 – $7.4\cdot10^{-5}$; 11 – $9.9\cdot10^{-5}$. pH 9.2. Blank solutions are TBCS at the same concentrations. The thickness of absorbing layer is 1.00 cm.*

By the methods of composition determination [1, 2], the TBCS anions can form stoichiometric compounds $Ct^{+}\cdot HAn^{-}$ and $(Ct^{+})_2\cdot An^{2-}$. The value of the equilibrium constant of the association, K_{as}, is a measure of the stability of these associates:

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

and

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

The values of K_{as} were calculated (as described above) for heteroassociates using the law of acting masses:

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

and

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

The values of K_{as} for the associates of QB and QR differ from each other. Associations of the QB are more stable than the associates of the QR. This can be explained by the fact that dispersion interactions, and not just Coulomb forces, promote to the association of large organic ions. Dispersion interactions are manifested to a greater extent for developed π-electron systems. Due to the structural features, they are more characteristic for QB^{+} than for QR^{+}.

The log K_{as} value is equal to 12.09±0.09 for the associate $(QB^{+})_2\cdot TBCS^{2-}$, while the same value for $(QR^{+})_2\cdot TBCS^{2-}$ is equal to 8.64±0.07. The associates of the singly charged TBCS anion for QB are also more stable (log K_{as} = 6.74±0.09 for $QB^{+}\cdot TBCS^{-}$ and log K_{as} = 5.04±0.07 for $QR^{+}\cdot TBCS^{-}$). It is noteworthy that the difference in the K_{as} values of the TBCS associates is already known for the associates of single- and double-charged anions of phenol red [15].

The probable structure of the $(QB^{+})_2\cdot TBCS^{2-}$ associate is shown on Figure 3 (conditions of simulation: semiempirical method *AM1*, each ion is surrounded by 7 water molecules; the gradient of convergence of two successive iterations according to the Polak-Ribiere algorithm is no more than 2 kJ·mol⁻¹, the anion of sulfonephthalein is located in the center; the distance between the designated central and peripheral atoms is 5.0–5.6 angstroms; the central angle with the vertex on the carbon atom $TBCS^{2-}$ is 170°, the length of the QB^{+} in the direction of the polymethine chain is 17 angstroms).

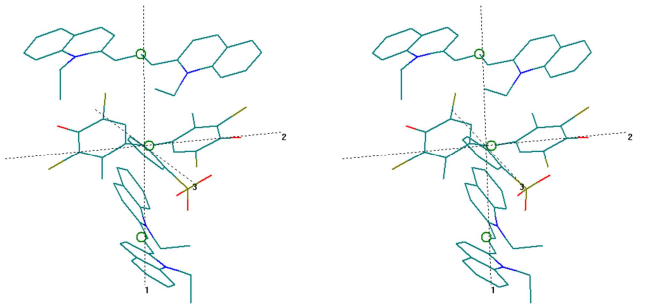


Figure 3. *The structure of $(QB^{+})_2\cdot TBCS^{2-}$ associate (for stereo viewing). Hydrogen atoms are not shown.*

The geometry of the cation and anion is significantly different. Despite of it, a tangible interaction occurs between the counterions in the aqueous solution. This is evidenced both by the spectral measurements and by the values of the standard enthalpies of associates formation (ΔH^{o}_{f}) (see Table 2, *AM1* method, geometric optimization of structures is analogous to the case of Figure 3 in the absence of water molecules). In this case, Σ is the algebraic sum of the values of ΔH^{o}_{f} of corresponding ions in the $Ct^{+}\cdot An^{-}$ or $(Ct^{+})_2\cdot An^{2-}$ associate. For the $TBCS^{-}$, $TBCS^{2-}$, QB^{+} and QR^{+} ions, the values of ΔH^{o}_{f} are equal to -478, -479, 1073 and 984 $kJ\cdot mol^{-1}$, respectively, and the range of variation of the values of ΔH^{o}_{f} is from 8 to 12 $kJ\cdot mol^{-1}$.

Table 2. *Energetic characteristics of associates of TBCS.*

Associate	**ΔH^{o}_{f}, $kJ\cdot mol^{-1}$**	**Σ, $kJ\cdot mol^{-1}$**	**$\Sigma - \Delta H^{o}_{f}$ $kJ\cdot mol^{-1}$**
$QB^{+}\cdot TBCS^{-}$	376	595	219
$QR^{+}\cdot TBCS^{-}$	320	506	186
$(QB^{+})_2\cdot TBCS^{2-}$	1073	1667	594
$(QR^{+})_2\cdot TBCS^{2-}$	952	1490	538

Analysis of the data of Table 2 leads to the conclusion that the formation of associates of TBCS with QB is more energetically favorable than associates of TBCS with QR. We note that a similar situation was observed in the case of the associates of single- and doubly-charged phenol red anions [15].

3.3. Effect of Ionic Surfactants

The addition of CPB or DDS to the $Ct^{+}\cdot HAn^{-}$ and $(Ct^{+})_2\cdot An^{2-}$ associates causes significant spectral changes. In all cases, the shape of the bands of each of the dyes is restored in the absorption spectra and the intensity of light absorption is increased (Figure 4).

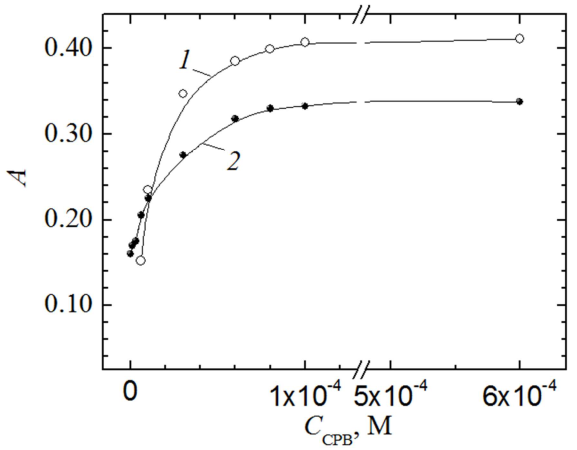


Figure 4. *Dependence of optical density from concentration of CPB in solution. 1 – 600 nm wave length; 2 – 550 nm wave length. Concentrations, M, QB: 4.6·10⁻⁶; TBCS: 8.0·10⁻⁵. Comparative solutions are 8.0·10⁻⁵ M of TBCS solutions. The thickness of absorbing layer is 1.00 cm; pH 9.2.*

Thus, they indicate the destruction of associates. Analysis of spectral changes leads to the conclusion that the destruction of associates at premicellar surfactant concentrations can be represented in general form as:

$$(Ct^{+})_n \cdot An^{n-} + xDDS^{-} \rightarrow (Ct^{+})_n \cdot (DDS^{-})_x + An^{n-}$$

or

$$(Ct^{+})_n \cdot An^{n-} + xCPB^{+} \rightarrow nCt^{+} + (CPB^{+})_x \cdot An^{n-}$$ (in the simplest case $x = 1$).

In micelles of ionic surfactants:

$$(Ct^{+})_n \cdot An^{n-} + (x + y)\mathrm{surfactant} \rightarrow (nCt^{+})_{x\,\mathrm{surfactant}} + (An^{n-})_{y\,\mathrm{surfactant}} ,$$

where the dye ions are no longer associated in fact.

The obtained data are in agreement with the previously established facts [1, 2] of the effect of ionic surfactants on associates. The development of a test (semiquantitative) assessment of the content of ionic surfactants can be the next step in the study of heteroassociation and the effect of surfactant on it in aqueous solution. The combination of a very high sensitivity (at the level of $1\cdot10^{-6}$ M) of the color reaction and its contrast will be a feature of this development. Such a prediction is based on the fact that heteroassociates are formed by such dye ions that have well distinguishable absorption bands such as, for example, QB and TBCS.

4. Conclusion

A systematic study of cation-anion heteroassociation shows that interactions of polyatomic particles of dyes are carried out due to a complex combination of Coulomb, hydrophobic and dispersion forces. Further study of such systems is based on a comparison of the results of spectral measurements with computer simulation data.

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