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# Association of Quinaldine Red Cation in an Aqueous Solution: The Interaction with Anionic Dyes

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**Abstract**

Association between quinaldine red cation and sulfonephthalein or oxyxanthene anions has been studied experimentally and theoretically. The values of the equilibrium association constants are defined spectrophotometrically in the aqueous solution. Structure and energy characteristics of nanoassociates are determined with the help of semiempirical AM1 method. Analysis of the values of equilibrium constants of association as well as the standard enthalpies of formation of ions and associates has shown that the formation of associates is energetically favorable.

**1. Introduction**

Scientific interest has recently increased in studying heteroassociation processes of molecules of dyes in aqueous and aqueous-organic systems. This is due to the unique spectral and equilibrium properties of nanoassociates and their application in the design of nanomaterials and supramolecular devices, in biotechnology, pharmacy, chemical analysis. For example, the dye heteroassociate (*i.e.* “dissimilar nanoassociate”, this is further named as “nanoassociate”) can serve as an analytical reagent. Nanoassociates are used for the quantitative determination of ionic surfactants in aqueous media [1, 2].

The association of dyes, as a result of the interaction of two different molecules (ions), is accompanied by a change in the color of the aqueous solution, even at small concentrations ( $5 \cdot 10^{-7}$  M and more) of the colored particles. For this reason, the methods of absorption spectroscopy (spectrophotometry, luminescence analysis) are the most informative for studying the properties of nanoassociates.

Cation-anion association is one of the most diverse varieties of the association of dyes. A sufficiently large amount of cationic or anionic dyes is known. However, not all of them are suitable for studying the association in aqueous solutions. The selection of a suitable dye is nanoassociated with a number of conditions. The main conditions are: 1) satisfactory solubility of dye in water; 2) the ease of dissociation of the molecule and the formation of a stable ion; 3) the absence of protolytic transformations at the widest possible pH range (this makes it possible to investigate their association as possible with a larger number of counterions); 4) the ability to nanoassociate at sufficiently low intrinsic concentrations; 5) sufficient intensity of color (luminescence) and the ability to perceptibly change the light absorption (luminescence) in association.

Earlier [2, 3] we investigated in detail the conditions for the association of certain cationic (cyanine) dyes with different classes of anionic dyes. It was shown that the stability of the ionic nanoassociates formed depends on the magnitude of the charge, the spatial and hydrophobic properties of the ion. This report presents the results of a

systematic study of the association of a quinaldine red cation with double-charged anions of bromine-containing sulfonephthaleins and some oxyxanthenes.

Quinaldine red (4-[(E)-2-(1-ethylquinolin-1-ium-2-yl)ethenyl]-N,N-dimethylaniline, QR) corresponds to the conditions specified above. In addition, QR is not subject to dimerization, which allows one to study the association with organic anions in a very wide range of concentrations ( $1 \cdot 10^{-6}$  –  $2 \cdot 10^{-4}$  M). A successful combination of protolytic and spectral properties determines the use of QR for the study of a wide range of objects and systems. Recently, QR has been used to design nanostructured materials [4, 5], in studying the properties of ultramicroheterogeneous systems (mixed micelles) [6], in the chemical analysis of surfactants and metals [7-9], in the study of complex biochemical systems (DNA, RNA, blood plasma) using fluorescent probes and

samples [10-16]. It is noteworthy that the effectiveness of the application of QR is often nanoassociated with its ability to form nanoassociates (ion pairs) in aqueous [9], mixed systems [6] and two-phase systems [7, 8]. Therefore, the study of the cation-anion association of QR with organic counterions is particularly relevant. As anionic dyes, bromine-containing phenolsulfonephthalein derivatives, as well as fluorescein and its halogen derivatives, were investigated.

## 2. Materials and Methods

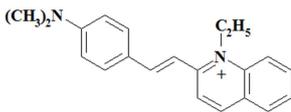
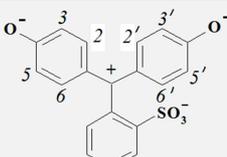
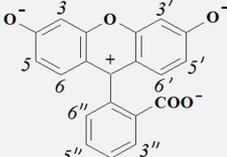
The chloride of QR cation  and sodium salts of anionic dyes (Table 1) were used.

Table 1. Structures of anionic dyes.

Sulfonephthaleins	Oxyxanthenes
 <p>Bromothymol blue, BT, (2,2' – CH<sub>3</sub>; 3,3' – Br; 5,5' - <i>i-prop</i>)            Bromocresol purple, BP, (3,3' – CH<sub>3</sub>; 5,5' – Br)            Bromocresol green, BG, (2,2' – CH<sub>3</sub>; 3,3',5,5' – Br)            Bromophenol blue, BB, (3,3',5,5' – Br)</p>	 <p>Fluorescein, FL, all – H            Eosin, EO, (3,3',5,5' – Br; H of the rest)            Erythrosin, ER, (3,3',5,5' – I, H of the rest)            Bengal rose B, BR, (3,3',5,5' – I; 3'',4'',5'',6'' – Cl, H of the rest)</p>

All products were "Sigma" trade mark. The content of the main substance was not less than 98%.

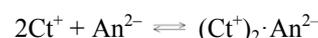
The interaction of the QR cation ( $Ct^+$ ) with anions ( $An^{2-}$ ) have been investigated. The light absorption bands of the cation ( $\lambda_{max} = 528$  nm,  $\epsilon_{max} = 3.1 \cdot 10^4$  l/(mol·cm),  $pK_a = 2.63$ ) and  $An^{2-}$  of sulfonephthaleins are well spectrally different. For example,  $\Delta\lambda_{max}$  is 63 nm in the case of  $Ct^+$  and BP, and 88 nm in the case of  $Ct^+$  and BT (see Table 2; data are generalized from [1-3]). This makes it possible to minimize complications due to overlapping of the light absorption bands of counterions. The anions of oxyxanthene dyes also proved to be suitable counterions, since they have a high intensity ( $\epsilon_{max}$ ) of light absorption.

Table 2. Properties of the anionic dyes.

Anion, $An^{2-}$	$pK_{a2}$	$\lambda_{max}$ , nm	$\epsilon_{max} \cdot 10^{-3}$ , l/(mol·cm)
BT	7.3	616	41.3
BP	6.4	588	43.0
BG	4.9	617	40.0
BB	4.2	591	80.0
FL	6.8	491	88.0
EO	3.75	514	96.7
ER	5.3	525	94.6
BR	5.72	548	93.0

The absorption spectra were measured at room temperature immediately after preparation of the solutions.

Formation of association was interpreted as an equilibrium process:



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

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

The molar equilibrium concentrations of the nanoassociate  $[(Ct^+)_2 \cdot An^{2-}]$  were determined from the spectral data by the equation:

$$[(Ct^+)_2 \cdot An^{2-}] = \frac{\epsilon_{Ct} \times C_{Ct} \times l - A}{(2\epsilon_{Ct} - \epsilon_{As}) \times l}$$

where  $C_{Ct}$  is the analytical concentration of 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 thickness of absorbing layer;  $\epsilon_{Ct}$  and  $\epsilon_{as}$  are the molar absorption coefficients of the cation and nanoassociate, respectively.

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

The semiempirical AM1 method has been used to estimate

the values of  $\Delta H_f^\circ$  for ions and nanoassociates. The parameters of this method were selected so that they allow us to reproduce the experimental values of  $\Delta H_f^\circ$  of organic substances in the best way. The AM1 method was used to determine the most probable structure of nanoassociates. Other features of the experiment and principles of implementing quantum-chemical simulations of the structures of dyes, nanoassociates, and the interpretation of the obtained results are presented previously [2, 3, 17].

### 3. Results and Discussion

#### 3.1. Protolytic Features of QR and Anionic Dyes in Water

The acid-base transformations of the investigated sulfonephthalein and oxyxanthene dyes as three-base acids can be represented in the form of such a scheme:



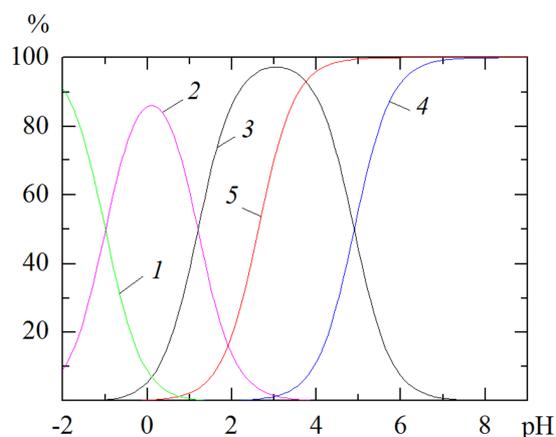
Single-charged cation of QR is significantly discolored in strongly acidic and alkaline media, due to hydrolysis:



and



The acidity of the solution should ensure the coexistence of only the corresponding ionic forms when studying the interaction of  $Ct^+$  with  $An^{2-}$ . Otherwise, the interpretation of spectral changes is difficult due to possible interactions involving other particles. The optimal conditions were determined for the association and the fractional contents were calculated for all particles taking into account the data on the  $pK_{a2}$  values of protolytic properties of anionic dyes (Table 1). For example, as follows from Figure 1, the interaction of  $Ct^+$  with  $An^{2-}$  of BG should be investigated at pH 7 or more.



**Figure 1.** Correlation between content of protolytic forms of BG (1 –  $H_3An^+$ , 2 –  $H_2An$ , 3 –  $HAn^-$ , 4 –  $An^{2-}$ ) or  $Ct^+$  cation of QR (5) and pH values of aqueous solution.

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 anionic dyes  $5.0 \cdot 10^{-6} - 2.5 \cdot 10^{-4}$  M, and QR  $1.0 \cdot 10^{-6} - 1.0 \cdot 10^{-4}$  M. For QR example, linear regression equations of this law (two series of independent determinations, 9–10 concentrations in each series) have the form:

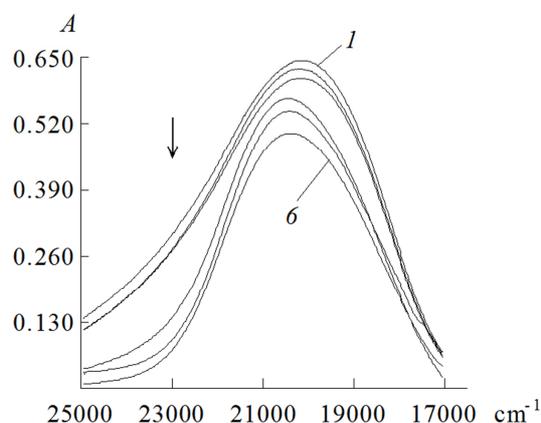
$$A_{528} = -0.0038_{(0.015)} + 3.37 \cdot 10^4_{(324)} \times C_{QR}, \text{ correlation coefficient } 0.9996_{(0.033)},$$

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.

In fact,  $A = k \times C$ , since the free term of the regressions is a statistical zero. A similar course of the dependencies is characteristic of anionic dyes. Thus, it can be considered that the QR and anionic dyes do not dimerize in the indicated concentration ranges.

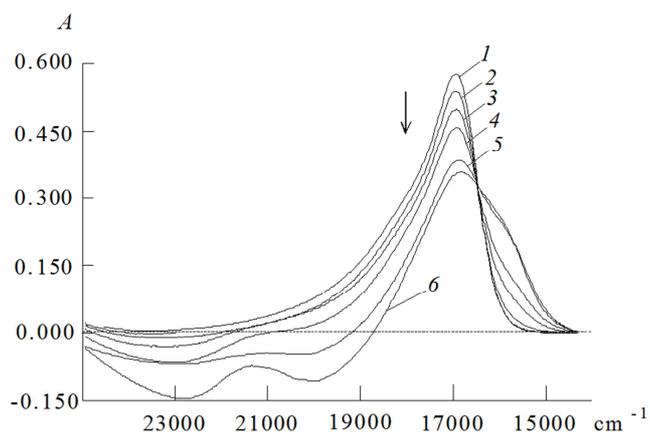
#### 3.2. Interaction Between $Ct^+$ and $An^{2-}$ Structure and Energy of Nanoassociates

A characteristic feature of the association between  $Ct^+$  and  $An^{2-}$  is a significant decrease in the intensity of light absorption. This decrease is clearly observed when an increasing quantity of sulfonephthalein or oxyxanthene is added to the unchanged QR content (Figure 2, curves 1–6, arrow indicates the direction of spectral shifts with increasing of TBCS concentration).



**Figure 2.** Light absorbance in the system «QR + BT». Concentrations, M, of QR: 1...6 –  $2.1 \cdot 10^{-5}$ ; of BT: 1 – 0; other spectra –  $5.9 \cdot 10^{-6} \dots 1.3 \cdot 10^{-4}$ . pH 9.2. Blank solutions are BT at the same concentrations. The thickness of absorbing layer is 1.00 cm.

This is also evidenced by negative sections of the optical density  $A$  in the difference spectral series and the character of the dependence of the light absorption of the mixture “ $Ct^+ + An^{2-}$ ” at a variable concentration of QR and constant contents of the anionic dye (Figure 3). The change in the optical density of the QR solution reaches 50% from the initial value at the maximum of the absorption band.



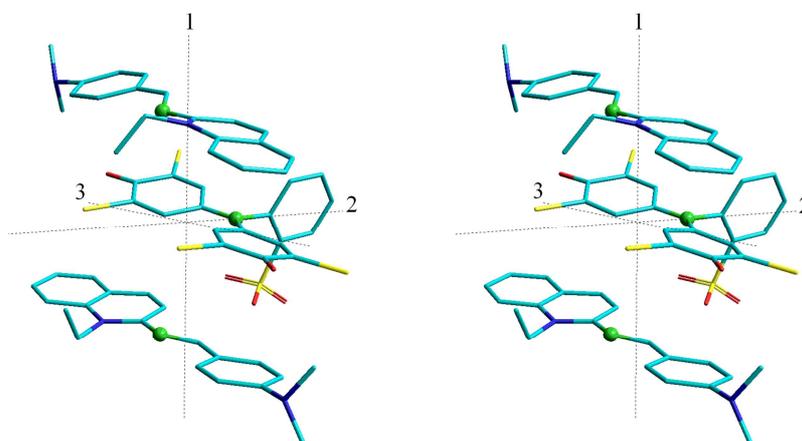
**Figure 3.** Light absorbance in the system «BB + QR». Concentrations, M, of BB: 1...6 –  $5.0 \cdot 10^{-6}$ ; of QR: 1 – 0; 2 –  $2.5 \cdot 10^{-5}$ ; 3 –  $4.5 \cdot 10^{-5}$ ; 4 –  $6.0 \cdot 10^{-5}$ ; 5 –  $9.9 \cdot 10^{-5}$ ; 6 –  $1.2 \cdot 10^{-4}$ . pH 9.2. Blank solutions are QR at the same concentrations. The thickness of absorbing layer is 1.00 cm.

Besides of them, 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  $\text{Ct}^+ + \text{An}^{2-}$ . Similar spectral changes were observed for all the systems studied.

As we can see, the spectral changes are quite complex. These changes may be accompanied by the formation of nanoassociates of different stoichiometry and even slightly soluble aggregates, when the turbidity is formed in the solution (like as a curve 6 on Figure 3). However, these phenomena occur at higher concentrations of interacting particles ( $5 \cdot 10^{-4}$  M and more).

As defined by spectrophotometric methods of composition determination [2, 3, 17], the QR cation can form stoichiometric nanoassociates  $(\text{Ct}^+)_2 \cdot \text{An}^{2-}$  at the considered concentrations ( $2.1 \cdot 10^{-5} - 1.2 \cdot 10^{-4}$  M of QR and  $1 \cdot 10^{-5} - 5 \cdot 10^{-4}$  M of anionic dye). The value of the equilibrium constant of the association,  $K_{\text{as}}$ , is a measure of the stability of nanoassociates:  $2\text{Ct}^+ + \text{An}^{2-} \rightleftharpoons (\text{Ct}^+)_2 \cdot \text{An}^{2-}$ . Such a scheme is also confirmed by the fact that attempts to calculate the value of  $K_{\text{as}}$ , based on 1:1 stoichiometry, lead to negative values of  $K_{\text{as}}$  that have no physical meaning.

The values of  $K_{\text{as}}$  differ from each other (Table 3).



**Figure 4.** The stereo image of  $(\text{QR}^+)_2 \cdot \text{BB}^{2-}$  structure. Hydrogen atoms are not shown.

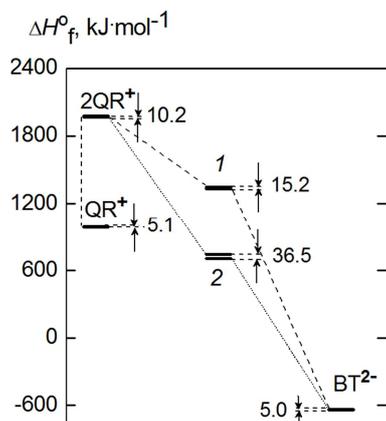
**Table 3.** The  $\log K_{\text{as}}$  values of the quinaldine red nanoassociates  $(\text{Ct}^+)_2 \cdot \text{An}^{2-}$ .

Anion, $\text{An}^{2-}$	$\log K_{\text{as}}$
BT	$7.85 \pm 0.09$
BP	$8.23 \pm 0.04$
BG	$8.64 \pm 0.07$
BB	$8.86 \pm 0.08$
FL	$7.94 \pm 0.07$
EO	$9.60 \pm 0.09$
ER	$10.05 \pm 0.05$
BR	$11.07 \pm 0.04$

Associations of halogen derivatives of the FL are more stable than the nanoassociates of the sulfonephthalein dyes. This can be explained by the fact that dispersion and hydrophobic interactions, and not just Coulomb forces, promote to the association of large organic ions [2, 3, 17]. Dispersion interactions are manifested to a greater extent for developed  $\pi$ -electron systems with hydrophobic halogen atoms (structures of BG, BB, ER, BR). The intensification of interactions between counterions (and hence an increase in the  $K_{\text{as}}$  value) should be assumed in those cases when the chromophores maximally approach each other. This can be expected to a greater extent if the structure of the chromophores is flattened. Such properties are possessed by oxyxanthenes, and not by propeller-like sulfonephthaleins. A similar situation was previously observed experimentally for nanoassociates of indopolycarboyanines [2]. It is noteworthy that the difference in the  $K_{\text{as}}$  values of the nanoassociates is already known for the nanoassociates of single- and double-charged anions of phenol red [3]. Due to the structural features (cation flatness, first of all) nanoassociates of pinacyanol cation are more stable than of QR cation.

The probable structure of the  $(\text{QR}^+)_2 \cdot \text{BB}^{2-}$  nanoassociate is shown on Figure 4 (conditions of optimization: semiempirical method *AMI*; the gradient of convergence of two successive iterations according to the Polak-Ribiere algorithm is no more than  $2 \text{ kJ} \cdot \text{mol}^{-1}$ ). The anion of sulfonephthalein is located in the center; the distance between the designated central and peripheral atoms is 4.9 angstroms; the central angle with the vertex on the carbon atom  $\text{BB}^{2-}$  is  $102^\circ$ , the length of the QR in the direction of the polymethine chain is 13.9 angstroms.

As we can see, the geometry of the cation and anion is 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 nanoassociates formation ( $\Delta H_f^\circ$ ). The characteristics of dye ions and BT nanoassociate are shown in Figure 5 as an example.



**Figure 5.** The values of  $\Delta H_f^\circ$  of  $QR^+$  and  $BT^{2-}$  ions, and the algebraic sum of  $\Delta H_f^\circ$  of ions composing the nanoassociate (1) and  $\Delta H_f^\circ$  of the nanoassociate  $(QR^+)_2 \cdot BT^{2-}$  (2), AM1 method (2).

The  $QR^+$  and  $BT^{2-}$  ions are characterized by  $\Delta H_f^\circ$  984.2 kJ·mol<sup>-1</sup> and -639.8 kJ·mol<sup>-1</sup>, whereas two cations  $QR^+$  have the energy of 1968.4 kJ·mol<sup>-1</sup>. The algebraic sum ( $\Sigma$ ) of  $\Delta H_f^\circ$  of counter ions is 1328.6 kJ·mol<sup>-1</sup> (level 1). Since  $\Delta H_f^\circ$  of the nanoassociate was found to be equal to 703.5 kJ·mol<sup>-1</sup> (level 2), the surplus of the algebraic sum of  $\Delta H_f^\circ$  of counter ions over  $\Delta H_f^\circ$  of the nanoassociate is  $1328.6 - 703.5 = 625.1$  kJ·mol<sup>-1</sup>. Note that the error of calculation of  $\Delta H_f^\circ$  value is about 25 kJ·mol<sup>-1</sup> [18]. Since  $\Sigma - \Delta H_f^\circ$  value is higher than this average error of the AM1 method we can assert that the formation of nanoassociates is energetically favorable. We note that a similar situation was observed in the case of the nanoassociates of single- and doubly-charged phenol red anions [3].

## 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. The obtained data on association confirm the necessity of search of correlations between structural features of dye molecules and properties of nanoassociates. Further study of such systems is based on a comparison of the results of spectral measurements with computer simulation data.

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