# Heteroassociates of singly- and doubly-charged anions of alizarin red S with the pinacyanol cation

*S. A. Shapovalov*

*V. N. Karazin Khar´kov National University,*
*4 pl. Svobody, 61077 Khar´kov, Ukraine.*
*Fax: +380 (57) 707 5130. E-mail: serghey.a.shapovalov@univer.kharkov.ua*

The formation of heteroassociates of singly- and doubly-charged anions of alizarin red S with the cation of the cyanine dye pinacyanol in an aqueous solution was considered. The most probable structure of the heteroassociates was proposed on the basis of the data of spectrophotometry and theoretical calculations (quantum chemical methods of determination of the geometry of the structures and the enthalpy of formation). The destructive effect of the ionic surfactants on the heteroassociates was established, and the kinetics of their destruction was studied.

**Key words:** dye, absorption spectra, association, enthalpy of formation, semiempirical methods, alizarin red S, pinacyanol, solution, ionic surfactants, kinetics.

Association of dye ions of various classes (heteroassociation, or heterogeneous association[1]) in solutions causes a substantial change in light absorption and is of both theoretical and practical interest. Heteroassociation in aqueous systems is especially important, because water serves as a medium in which interacting protolytic and aggregation forms of particles manifest unique spectral luminescence properties.[1,2] Under certain conditions, heteroassociates of dyes can act as analytical reagents, color markers, and bioprobes. This finds use in the solution of many urgent problems of quantitative chemical analysis, biochemistry, pharmacy, and biomedicine.[1,3,4] The ability of alizarin and its derivatives, first of all, alizarin red S (AR) (sodium salt of 9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracenesulfonic acid) as the most water-soluble reagent, to associate has recently been established. Alizarin red is known as the acid-base metallochromic indicator and a reagent for photometric and extraction-photometric determinations of inorganic ions[5]; AR was among the first dyes used as a highly sensitive (submicromolar) fluorescent sensor for identification of boron-containing acids.[6] The use of AR in the development of optical chemical sensors[7] and receptors[8] and in the construction of biocomposite nanofibers (tissue engineering)[9,10] was efficient. An analysis of the literature data show that this dye is rather efficient and promising as a reagent for quantitative determination of many drugs as ionic heteroassociates (ion pairs), for example, antibiotics (determination of trimethoprim[11]), vitamins (ascorbic acid[12]), amino acids (cysteine[13]), proteins,[14,15] polyphosphates,[16] hypolipidemic preparations (atorvastatin[17]), bactericidal drugs (norfloxacin[18]), and antidepressants (clomipramine[19]). However, for the rational use of the properties of a dye for similar purposes, it is necessary to know the spectral, equilibrium, and thermodynamic characteristics of processes of its association.

In the present work, the interaction of singly- and doubly-charged AR anions with the singly-charged cation of pinacyanol (PNC, 1-ethyl-2-[3-(1-ethyl-1*H*-quinolin-2-ylidene)propenyl]quinolinium) was discussed in more detail, and the properties and probable structure of the heteroassociates were discussed. Due to its spectral, structural, and protolytic properties, this cyanine turned out to be appropriate for studying the ability to dissociation of dyes of various classes, *e.g.*, sulfophthaleins, hydroxyxanthenes, azo dyes, *etc*.[1,4,20—22] The interaction of AR with cyanine cations was not studied earlier. In addition, the influence of ionic surfactants on heteroassociates was revealed, and the kinetics of their destruction was studied.

## Experimental

The AR preparation (analytical purity grade) was recrystallized from ethanol. Pinacyanol chloride (Sigma, the content of the main substance at least 95%) was used. Surfactants, *viz.*, cetylpyridinium bromide (CPB) $[C_{16}H_{33}NC_5H_5]Br$ and sodium dodecyl sulfate (SDS) $C_{12}H_{25}OSO_3Na$, contained at least 90% of the main substance. The influence of surfactants on the associates was studied in the ranges of CPB and SDS concentrations $1 \cdot 10^{-6}$—$9 \cdot 10^{-4}$ and $1 \cdot 10^{-6}$—$9 \cdot 10^{-3}$ mol $L^{-1}$, respectively, taking into account their critical micelle concentrations (CMC) equal to $(6.6—9.0) \cdot 10^{-4}$ and $8.1 \cdot 10^{-3}$ mol $L^{-1}$, respectively.[23] Specific features of calculations have been described pre-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 1, pp. 87—95, January, 2011.

viously.[24–27] The acidity in the medium was created by buffer solutions and the addition of HCl or NaOH. Additional experiments showed that the components of the used buffer solutions exert no noticeable effect on the studied processes of heteroassociation. Dilute solutions of the dyes, whose ionic strength ($I$) did not exceed 0.001—0.008 mol $L^{-1}$, were used in experiments.

Absorption spectra were measured at ~20 °C on Hitachi-U3210 and SF-46 spectrophotometers immediately after the solutions were prepared.*

## Results and Discussion

**State of the dyes in an aqueous solution.** The equilibrium of AR in solution as a tribasic acid can be presented as follows:

$$H_3An \rightleftharpoons H_2An^- \rightleftharpoons HAn^{2-} \rightleftharpoons An^{3-}.$$

Since an AR molecule contains the sulfo group, the electroneutral species exists in noticeable amounts only in a strongly acidic medium (pH <1). At a lower acidity of an aqueous solution, AR dissociates stepwise to form singly- (yellow color), doubly- (pink), and triply-charged (violet) anions. Their absorption bands are rather well discernible (Tables 1 and 2; $pK_{a_2}$ = 5.53 (see Ref. 31) and $pK_{a_3}$ = 11.20 (see Ref. 31), 10.71 (see Ref. 33) refer to solutions containing no additives of background salts). Solutions containing the singly-charged cation ($Ct^+$) of cyanine are appreciably decolorized in strongly acidic and strongly alkaline media due to the formation of species $HCt^{2+}$ and CtOH, respectively.

When studying the interaction of $H_2An^-$ and $HAn^{2-}$ with $Ct^+$, one should maintain such an acidity of the medium that provides the coexistence of only reacting ionic forms (in the opposite case, it is difficult to interpret spectral changes, because other species participate in association). To reveal the optimal conditions of association, we calculated the fraction ($x$) of the considered ions in the system (Fig. 1) taking into account the above listed protolytic process that occur in aqueous solutions. Based on this, we established the appropriate values of pH. It seems reasonable to study the interaction of $H_2An^-$ with $Ct^+$ at pH 4.1, and that of $HAn^{2-}$ with $Ct^+$ should be studied at pH 7.6—9.3. We failed to create conditions of the simultaneous presence of $An^{3-}$ and $Ct^+$ in solution, since the cyanine cation is almost completely hydrolyzed at the acidity providing the predomination of the triply-charged AR cations.

The interpretation of the spectral changes in the framework of the equilibrium approach, which considers cation-anionic interactions in terms of the law of acting masses, implies the fulfillment of the main law of light absorption by the protolytic forms of the dyes. It was found that the linear dependence of the absorbance ($A$) on the molar concentration of the dye in solution ($C$) obeys satisfactorily in rather wide concentration ranges for each anionic form of AR (Table 3) and takes the form $A_\lambda = kC$ (the free term of the regressions is statistical zero).

Coincidence of the correlation coefficient with unity indicates that the dimerization processes of the singly- and doubly-charged anions in water are not characteristic at the studied AR concentrations. Note that in other media (for instance, the media containing from 5 to 70% of the organic component in mixtures of water with methanol, DMF, acetonitrile, and DMSO) no formation of AR dimers was observed.[32]

Unlike AR, for pinacyanol the main law of light absorption is fulfilled only at low concentrations, since the $Ct^+$ cation is prone to self-association (the logarithm of the equilibrium dimerization constant is 4.79±0.06; the properties of PNC in an aqueous solutions have earlier[22,29] been considered in more detail). The increase in the cyanine concentration in solution is manifested in the elec-

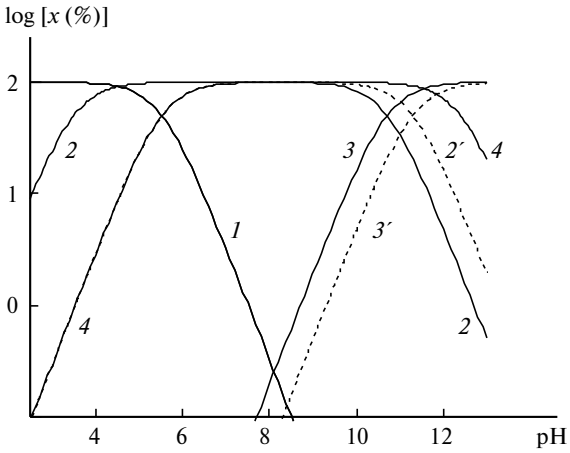



**Fig. 1.** Fraction ($x$) of the anionic protolytic forms of AR: $H_2An^-$ (*1*), $H_2An^-$ (*2*), $An^{3-}$ (*3*), and cation $PNC^+$ (*4*) *vs* pH of an aqueous solution. Curves *1—4* were obtained with allowance for $pK_{a_2}$ = = 5.53 and $pK_{a_3}$ = 10.71 (see Ref. 33), and curves *2′* and *3′* were obtained with allowance for $pK_{a_2}$ = 5.53 and $pK_{a_3}$ = 11.20 (see Ref. 31).

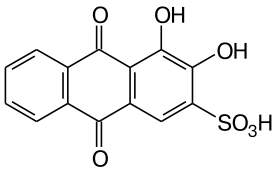
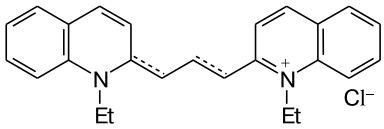
**Table 1.** Spectral characteristics of the studied anions and cations

| Characteristic* | $H_2An^-$ | $HAn^{2-}$ | $An^{3-}$ | $Ct^+$ |
|---|---|---|---|---|
| $\lambda_{max}$/nm | 421 | 518—519 | 560 | 600 (α-band); 550 (β-band); 510 (γ-band) |
| $\varepsilon_{max}$ /L $mol^{-1}$ $cm^{-1}$ | $4.9 \cdot 10^3$ | $7.7 \cdot 10^3$ | $14.4 \cdot 10^3$ | $1.3 \cdot 10^5$ (α-band) |

* The spectral characteristics of $Ct^+$ were taken from Refs 28—30. The inaccuracy of $\lambda_{max}$ is ±1 nm, and that of $\varepsilon_{max}$ is ±500 L $mol^{-1}$ $cm^{-1}$.

* Ya. Svishcheva took part in measurements of light absorption.

**Table 2.** Protolytic characteristics of the studied dyes

| Characteristic* | Alizarin red S | Pinacyanol chloride |
|---|---|---|
| Formula |  |  |
| $pK_{a_1}$ | — | 3.5** |
| $pK_{a_2}$ | 5.53 ($I \longrightarrow 0$); 4.72±0.03 ($I \longrightarrow$ 0.1 mol $L^{-1}$ $KNO_3$) | — |
| $pK_{a_3}$ | 10.08±0.03 ($I \longrightarrow$ 0.1 mol $L^{-1}$ $KNO_3$); 10.71, 11.20 ($I \longrightarrow 0$) | — |

* The values of $pK_{a_2}$ and $pK_{a_3}$ are taken from Refs 31—33; and $I$ is the ionic strength of the solution.
** The value of $pK_a$ refers to the dissociation of the cation $HCt^{2+}$ (see Ref. 30).

tronic absorption spectrum as a weakening of the intensity of the α-band and an increase in the intensity of the β-band (see Table 1) due to cation dimerization, and the further increase in the PNC concentration results in the appearance of aggregated particles (the increase in the intensity of the γ-band). In the present work, the concentration of the cyanine dye was not higher than $4 \cdot 10^{-6}$ mol $L^{-1}$.

**Association of $Ct^+$ with $H_2An^-$ and $HAn^{2-}$ and the structures and energies of the associates.** An analysis of changes in the electronic spectra reveals that the spectral bands are not additive. Non-additivity is observed in the fact that the absorption intensity of a mixture of counterions is systematically lower than that total light absorption of individual ions of the dyes. As AR was added to PNC, whose amount remained unchanged, we distinctly observed a decrease in the absorption intensity of $Ct^+$ (Fig. 2), mainly, in the long-wavelength α-band (spectra *2*—*6*), reaching more than 40% of the initial spectrum (spectrum *1*). This pattern is characteristic of various initial concentrations of pinacyanol. In similar cases, the decrease in the long-wavelength band intensity (Fig. 3, curve *1*) due to heteroassociate formation is accompanied by an increase in the absorbance in the shorter-wavelength of the spec-

**Table 3.** Equations of linear regressions for the fulfillment of the main law of light absorption

| Ion | Equation* | Correlation coefficient |
|---|---|---|
| $H_2An^-$ | $A_{421} = -0.022_{(0.009)} + 4.85 \cdot 10^3{}_{(5.5)} \cdot C$, $C = 5.0 \cdot 10^{-6}$—$1.5 \cdot 10^{-4}$, $n = 9$ | $0.9995_{(0.0001)}$ |
| | $A_{421} = -0.031_{(0.027)} + 4.96 \cdot 10^3{}_{(6.5)} \cdot C$, $C = 1.3 \cdot 10^{-4}$—$2.5 \cdot 10^{-3}$, $n = 8$ | $0.9996_{(0.0001)}$ |
| $HAn^{2-}$ | $A_{518} = -0.014_{(0.016)} + 7.74 \cdot 10^3{}_{(1.5)} \cdot C$, $C = 7.5 \cdot 10^{-6}$—$1.8 \cdot 10^{-4}$, $n = 9$ | $0.9999_{(0.0001)}$ |
| | $A_{518} = -0.028_{(0.022)} + 7.69 \cdot 10^3{}_{(3.5)} \cdot C$, $C = 1.2 \cdot 10^{-4}$—$2.5 \cdot 10^{-3}$, $n = 8$ | $0.9998_{(0.0001)}$ |

* The subscripts at the values of absorbance ($A$) correspond to the wavelengths (λ/nm) at which the dependence was established; the subscripts in parentheses are the standard deviations of the corresponding values; $C$/mol $L^{-1}$ is the initial concentration of the dye ion; and $n$ is the sampling volume of the values of $C$.

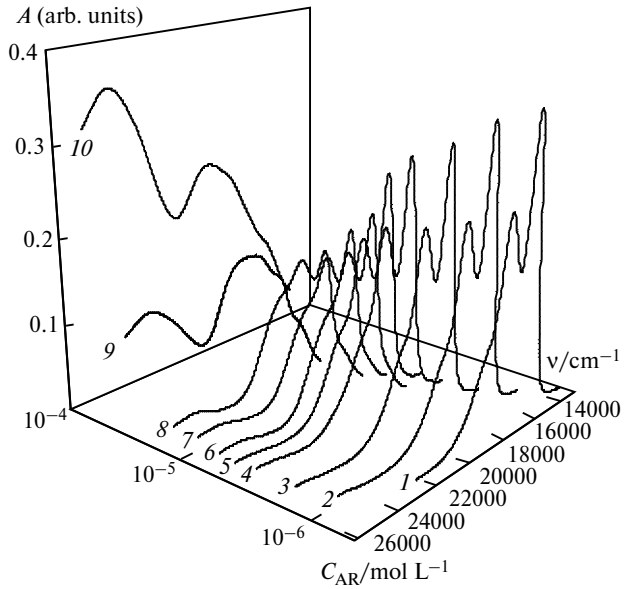



**Fig. 2.** Absorbance ($A$) of a solution of PNC ($C_{PNC} = 1.7 \cdot 10^{-6}$ mol $L^{-1}$) *vs* concentration of AR ($C_{AR}$): $C_{AR} = 0$ (*1*), $2.0 \cdot 10^{-6}$ (*2*), $4.0 \cdot 10^{-6}$ (*3*), $6.0 \cdot 10^{-6}$ (*4*), $8.0 \cdot 10^{-6}$ (*5*), $1.2 \cdot 10^{-6}$ (*6*), $1.4 \cdot 10^{-6}$ (*7*), $2.0 \cdot 10^{-5}$ (*8*), $5.0 \cdot 10^{-5}$ (*9*), and $1.0 \cdot 10^{-4}$ mol $L^{-1}$ (*10*). Here and in Fig. 3, the absorbing layer thickness is 1.00 cm, pH 3.6, and water as a reference solution.

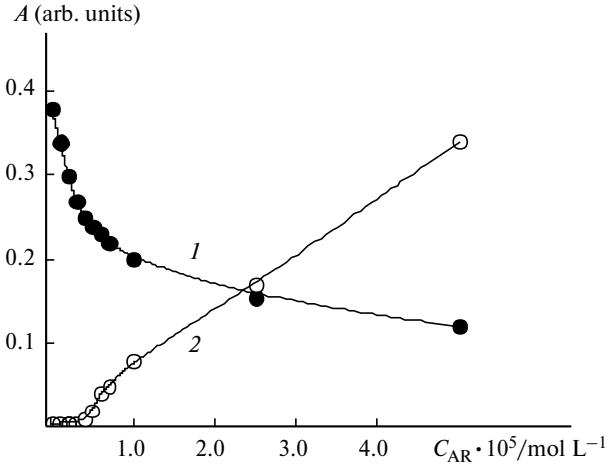



**Fig. 3.** Absorbance ($A$) of a solution of PNC ($C_{PNC}$ = = $1.7 \cdot 10^{-6}$ mol L$^{-1}$) *vs* concentration of AR ($C_{AR}$) at λ = 600 (16 670 cm$^{-1}$) (*1*) and 421 nm (23 750 cm$^{-1}$) (*2*). The conditions are indicated in the caption to Fig. 2.

trum (see Fig. 3, curve *2*; see also Fig. 1, spectra *9* and *10*) due to an increase in the AR content in a mixture of the dyes. It is noteworthy that the absorption of AR can be almost imperceptible both visually and instrumentally (the value of $A$ does not exceed 0.02 arbitrary units at the AR concentration lower than $5 \cdot 10^{-6}$ mol L$^{-1}$; see Fig. 3, curve *2*), but hypochromism of the absorption bands of PNC is appreciable (a sharp decrease in $A$ is observed with an increase in $C_{AR}$; see Fig. 3, curve *1*).

It was established by the methods of determination of the composition that the AR anions can form with the PNC cation $Ct^+$ compounds of the stoichiometric compositions $Ct^+ \cdot H_2An^-$ and $(Ct^+)_2 \cdot HAn^{2-}$. The measure of stability of these compounds is the equilibrium association constant $K_{as}$ (in fact, the thermodynamic value because of the low ionic strength of the solutions) determined from the law of acting masses. For the equilibrium

$$Ct^+ + H_2An^- \rightleftharpoons Ct^+ \cdot H_2An^-$$

this constant can be expressed as follows:

$$K_{as} = [Ct^+ \cdot H_2An^-] \cdot (C_{H_2An} - [Ct^+ \cdot H_2An^-])^{-1} \cdot (C_{Ct} - [Ct^+ \cdot H_2An^-])^{-1},$$

while for the equilibrium

$$2\,Ct^+ + HAn^{2-} \rightleftharpoons (Ct^+)_2 \cdot HAn^{2-}$$

can be expressed in the form

$$K_{as} = [(Ct^+)_2 \cdot HAn^{2-}] \cdot (C_{HAn} - [(Ct^+)_2 \cdot HAn^{2-}])^{-1} \cdot (C_{Ct} - 2[(Ct^+)_2 \cdot HAn^{2-}])^{-2},$$

where the equilibrium concentrations of the associates are $[Ct^+ \cdot H_2An^-] = (\varepsilon_{Ct} C_{Ct} l - A) \cdot (\varepsilon_{Ct} - \varepsilon_{as})^{-1} \cdot l^{-1}$ and $[(Ct^+)_2 \cdot HAn^{2-}] = (\varepsilon_{Ct} C_{Ct} l - A) \cdot (2\varepsilon_{Ct} - \varepsilon_{as})^{-1} \cdot l^{-1}$; $C$/mol L$^{-1}$ are the initial concentrations of the cation or anion; $l$/cm is the absorbing layer thickness; $A$ is the absorbance of the solution at the fixed wavelength; and $\varepsilon_{Ct}$ and $\varepsilon_{as}$/L mol$^{-1}$ cm$^{-1}$ are molar absorption coefficients of $Ct^+$ and the associate, respectively. We determined that for the associate of the singly-charged AR anion log $K_{as}$ = = 6.12±0.10, while for the associate $(Ct^+)_2 \cdot HAn^{2-}$ log $K_{as}$ = 10.92±0.10. It is noteworthy that the associate $H_2An^-$ is somewhat more stable than the associate of analogous composition of unsubstituted sulfophthalein: phenol red (PR) for which log $K_{as}$ = 5.83±0.10, whereas the $HAn^{2-}$ associates are close in stability to the corresponding associate of PR (log $K_{as}$ = 11.81±0.10).[20] At the same time, these AR associates are less stable than the pinacyanol associates of the series of the bromosubstituted derivatives of phenol red[34]: bromocresol green (log $K_{as}$ = = 6.74±0.04 and 12.09±0.09, respectively) and bromophenol blue (log $K_{as}$ = 6.88±0.05 and 13.73±0.10, respectively). This is related, most likely, to the planar chromophoric system of the AR anions, unlike the propeller-like structure of phenol red, and hence, they interact more efficiently with the flattened structure of pinacyanol. At the same time, unlike the listed phenolsulfophthalein derivatives, AR contains no bromine atoms, which enhance the hydrophobicity of the anion and thus favor the enhancement of the cation-anionic interactions.[1,4,25]

The probable structure of the associate $(Ct^+)_2 \cdot HAn^{2-}$ calculated by the AM1 semiempirical method[35,36] (calculation conditions: the Polak-Ribiere convergence algorithm; the convergence gradient of two successive iterations not higher than 2 kJ mol$^{-1}$) is presented in Fig. 4. To obtain the optimized structure of the heteroassociate, it is important to find the global energy minimum (this procedure has earlier been described in more detail[34]). We tested 6-7 different starting mutual positions of counterions in the heteroassociate (one of the variants of the initial arrangement of the ions is shown in Fig. 4, *a*; 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 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

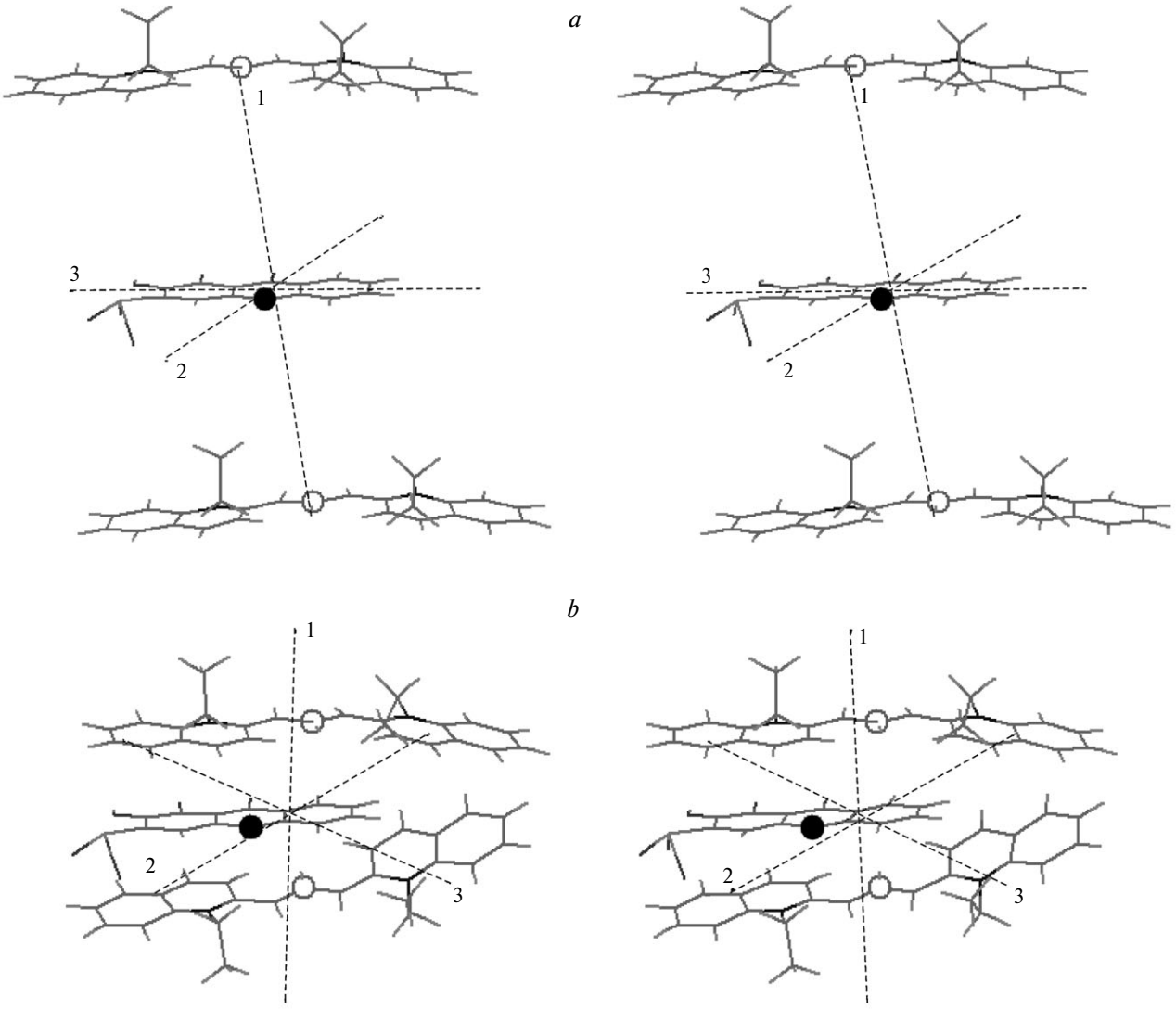



**Fig. 4.** The starting (*a*) and optimized (*b*) arrangements of the cations PNC and AR in the heteroassociate $(Ct^+)_2 \cdot HAn^{2-}$ (stereo images). The distance between the marked atom of AR (black circle) and atoms of PNC (light circles) is 8.5 Å (*a*, upper or bottom atoms of PNC); 4.5 Å (*b*, upper atom) and 4.9 Å (*b*, bottom atom). The central angle at the vertex at the marked atom of AR is 161° (*a*) and 91° (*b*). The length of PNC in the direction of the polymethine chain is 18.8 Å, and the length of $HAn^{2-}$ along the chromophore plane is 7.5 Å.

RMS gradient but is almost completed already at 0.01 kJ mol$^{-1}$ Å$^{-1}$ and is accompanied by the shortening of the distance between the counterions. The heteroassociate $(Ct^+)_2 \cdot HAn^{2-}$ has a sandwich structure. This mutual arrangement of ions results in the enhancement of dispersion and π-electronic interactions as driving forces of heterogeneous association of dyes.[1,22,25] Their manifestation is indicated by a noticeable deformation of the initially planar π-electronic system of the cation (see Fig. 4, *b*).

The appreciable cation-anionic interaction is indicated by the results of calculations of the enthalpies of formation ($\Delta H^o_f$, standard conditions) of the associates. To estimate the values of $\Delta H^o_f$, we used the AM1 semiempirical method as one of the extended variants of the MNDO method and the PM3 method.[35,36] These methods were parametrized in such a way that the experimental values of $\Delta H^o_f$ of organic compounds would be reproduced most adequately (for instance, the average inaccuracy of the AM1 method in the calculation of $\Delta H^o_f$ is 25 kJ mol$^{-1}$).[35] Note that similar nonempirical calculations give inaccuracies of the values of $\Delta H^o_f$ exceeding 100 kJ mol$^{-1}$ even for small molecules.[37,38] With an increase in the number of atoms in the molecule, the inaccuracies in the calculated values of $\Delta H^o_f$ increase more and gain a systematic character.[38]

The characteristics of ions of the dyes and heteroassociates of AR are shown as examples in Figs 5 and 6 (figures

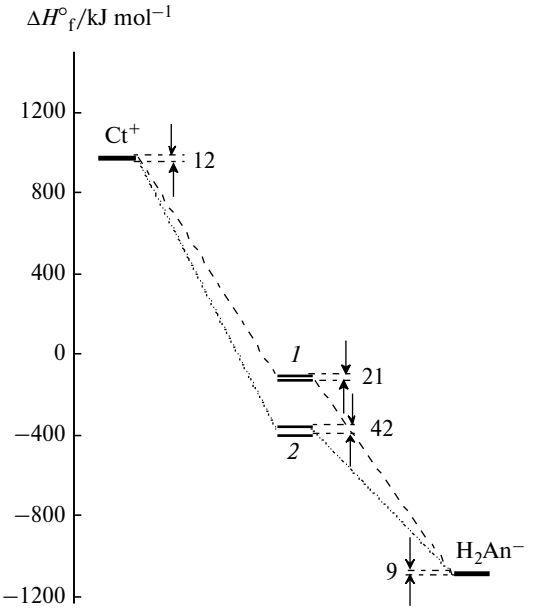



**Fig. 5.** Enthalpies of formation ($\Delta H^o_f$) of the ions $Ct^+$ and $H_2An^-$; the algebraic sum of $\Delta H^o_f$ of the ions composing the associate (*1*); and $\Delta H^o_f$ of the associate $Ct^+ \cdot H_2An^-$ (*2*). Calculation by the PM3 method.

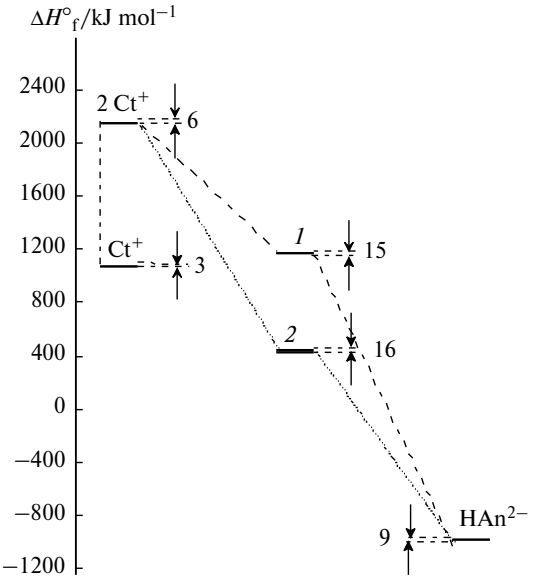



**Fig. 6.** Enthalpies of formation ($\Delta H^o_f$) of the ions $Ct^+$ and $HAn^{2-}$; the algebraic sum of $\Delta H^o_f$ of the ions composing the associate (*1*); and $\Delta H^o_f$ of the associate $(Ct^+)_2 \cdot HAn^{2-}$ (*2*). Calculation by the AM1 method.

at arrows designate the range of variation of $\Delta H^o_f$/kJ mol$^{-1}$ for the corresponding species). In Fig. 5 (PM3 method) the ions $Ct^+$ and $H_2An^-$ are characterized by the values of $\Delta H^o_f$ ranging from 980 to 968 and from −1085 to −1094 kJ mol$^{-1}$, respectively. The algebraic sum of the values of $\Delta H^o_f$ for the cation and anion ranges from −126 to −105 kJ mol$^{-1}$ (energy level *1*) and exceeds $\Delta H^o_f$ of the associate $Ct^+ \cdot H_2An^-$, which ranges from −356 to −398 kJ mol$^{-1}$ (energy level *2*), by 293—230 kJ mol$^{-1}$. Similarly, in Fig. 6 (AM1 calculation) the ions $Ct^+$ and $HAn^{2-}$ are characterized by the values of $\Delta H^o_f$ ranging from 1076 to 1073 and from −976 to −985 kJ mol$^{-1}$, respectively. The algebraic sum of $\Delta H^o_f$ of two cations and the anion is 1161—1176 kJ mol$^{-1}$ (energy level *1*). Since the value of $\Delta H^o_f$ of the associate $Ct^+ \cdot H_2An^-$ was found to be 448—432 kJ mol$^{-1}$ (level *2*), the excess of the algebraic sum of the values of $\Delta H^o_f$ of the counterions over $\Delta H^o_f$ of the heteroassociate is 744—713 kJ mol$^{-1}$.

The energy characteristics of the ions and heteroassociates of AR are given in Table 4. This table also contains the values of Σ (algebraic sum of the values of $\Delta H^o_f$ of the corresponding ions in the associate $Ct^+ \cdot H_2An^-$ or $(Ct^+)_2 \cdot HAn^{2-}$ determined as $\Sigma = i\Delta H^o_f$ (cation) + $\Delta H^o_f$ (anion), where *i* is the number of cations in the composition of the associate) and the difference $\Sigma - \Delta H^o_f$; the ranges of changing (variation range) are indicated for each characteristic. The values of $\Delta H^o_f$ of the pinacyanol cation almost coincide with those obtained previously[34] when the cation-anionic association involving the sulfophthalein anions was studied. It is noteworthy that the enthalpies of formation of the anions and especially the values of the difference $\Sigma - \Delta H^o_f$ determined by different method coincide.

An analysis of the data in Table 4 suggests that the formation of heteroassociates of anions of alizarin red S is energetically favorable. This agrees with rather high values of the association constants determined experimentally.

**Table 4.** Energy characteristics ($\Delta H^\circ_f$/kJ mol$^{-1}$ and Σ/kJ mol$^{-1}$) of the ions and heteroassociates

| Method | Characteristic | $Ct^+$ | $H_2An^-$ | $HAn^{\sim 2-}$ | $Ct^+ \cdot H_2An^-$ | $(Ct^+)_2 \cdot HAn^{2-}$ |
|---|---|---|---|---|---|---|
| AM1 | $\Delta H^\circ_f$ | 1076—1073 | −1052÷−1060 | −976÷−985 | −193÷−235 | 448—432 |
| | Σ | | | | 13—24 | 1161—1176 |
| | $\Sigma - \Delta H^\circ_f$ | | | | 259—206 | 744—713 |
| PM3 | $\Delta H^\circ_f$ | 980—968 | −1085÷−1094 | −1006÷−1014 | −356÷−398 | 180—151 |
| | Σ | | | | −126÷−105 | 922—954 |
| | $\Sigma - \Delta H^\circ_f$ | | | | 293—230 | 803—742 |

The energy gain characterized by the value of $\Sigma - \Delta H^o_f$ substantially exceeds the average inaccuracy of calculation methods for the calculation of $\Delta H^o_f$ and the variation range of the obtained values of $\Delta H^o_f$. The listed facts indicate that the formation of associates in solutions is characteristic of dyes with the flattened shape of the molecule[1,29,39] and the presence of π-conjugated electronic systems enhancing the contribution of dispersion interactions similarly to squaranines,[40,41] spiropyrans,[42] pyrazines,[43] porphyrins,[44] and others.

**Interaction of the heteroassociates with the surfactants.** Additives of sodium dodecyl sulfate (SDS) or cetylpyridinium bromide (CPB) to the associates $Ct^+ \cdot H_2An^-$ and $(Ct^+)_2 \cdot HAn^{2-}$ induce spectral changes, indicating the destruction of the associates. Similar effects have earlier been observed for heteroassociates of sulfophthaleins, hydroxyxanthenes, rhodamines, and other dyes.[1,22,45–49] The recovery of the band contours of each dye and an increase in the light absorption intensity with an increase in the content of the ionic surfactant in the solution are observed in the absorption spectra of mixtures of the dyes in the presence of surfactants. The most complete destruction of the associate occurs in surfactant micelles. Figure 7 presents the absorption spectra of a solution containing pinacyanol and AR (associate $(Ct^+)_2 \cdot HAn^{2-}$, curve *1*). The contour of the absorption spectra of a mixture of the dyes upon the addition of SDS changes substantially (curves *2*—*4*) and consists in fact of the light absorption of PNC (resembles the long-wavelength part of spectrum *1* in Fig. 2 with the pronounced α- and β-bands; see Table 1) and AR in surfactant micelles. Note that in SDS or CPB micelles the dyes are colored more intensely and their absorption bands undergo shifts. This is characteristic, to a greater extent, of the cyanine cation (for example, the bathochromic shift of the α- and β-bands for SDS micelles is approximately 7 nm).

Upon the introduction of CPB additives, the spectral shifts begin to appear (under other equivalent conditions) at lower surfactant concentrations compared to the PNC—AR system containing SDS. In Fig. 8 this is illustrated by smoother plots (curves *2* and *4*) of the absorbance *vs* SDS concentration (*cf.* curves *1* and *3*). Nonequivalence of this effect of the surfactant on the heteroassociates is related, evidently, to the fact that the above presented value of CMC of the cationic surfactant is considerably lower than that of SDS. At micellar concentrations of the ionic surfactants, the destruction of the associates can be presented as follows:

$$Ct^+ \cdot H_2An^- + (x + y)\ Surf \longrightarrow (Ct^+)_{x\,Surf} + (H_2An^-)_{y\,Surf};$$

$$(Ct^+)_2 \cdot HAn^{2-} + (x + y)\ Surf \longrightarrow 2\,(Ct^+)_{x\,Surf} + (HAn^{2-})_{y\,Surf},$$

where ions of the dyes form no heterogeneous associates but are solubilized by micelles of the ionic surfactant and are almost isolated from each other.

However, a non-evident specific feature is observed in the interaction of the heteroassociates with the ionic sur-

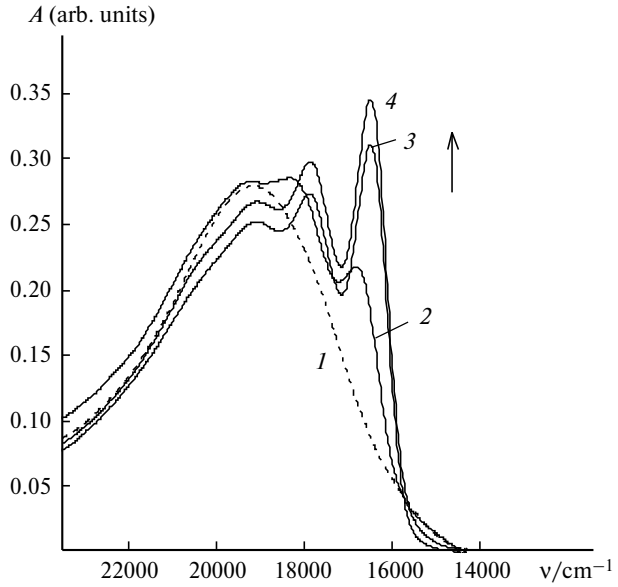



**Fig. 7.** Absorbance (*A*) of a solution containing PNC ($C_{PNC}$ = $= 1.2 \cdot 10^{-6}$ mol L$^{-1}$) and AR ($C_{AR} = 1.5 \cdot 10^{-5}$ mol L$^{-1}$) *vs* concentration of SDS: $C_{SDS} = 0$ (*1*), $1.8 \cdot 10^{-3}$ (*2*), $3.6 \cdot 10^{-3}$ (*3*), and $9.0 \cdot 10^{-3}$ mol L$^{-1}$ (*4*). Here and in Fig. 9 the absorbing layer thickness is 1.00 cm, pH 6.8, and water as a reference solution.

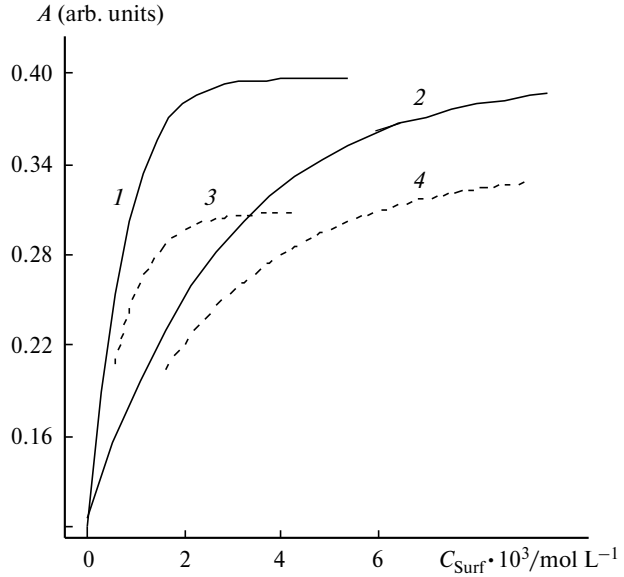



**Fig. 8.** Absorbance (*A*) of a solution containing AR ($C_{AR}$ = $= 1.5 \cdot 10^{-5}$ mol L$^{-1}$) and PNC ($C_{PNC} = 1.2 \cdot 10^{-6}$ mol L$^{-1}$) *vs* concentration of ionic surfactant ($C_{Surf}$): *1* and *3*, CPB; *2* and *4*, SDS; λ = 607 (*1*, *2*) and 553 nm (*3*, *4*). The absorbing layer thickness is 1.00 cm, pH 9.1.

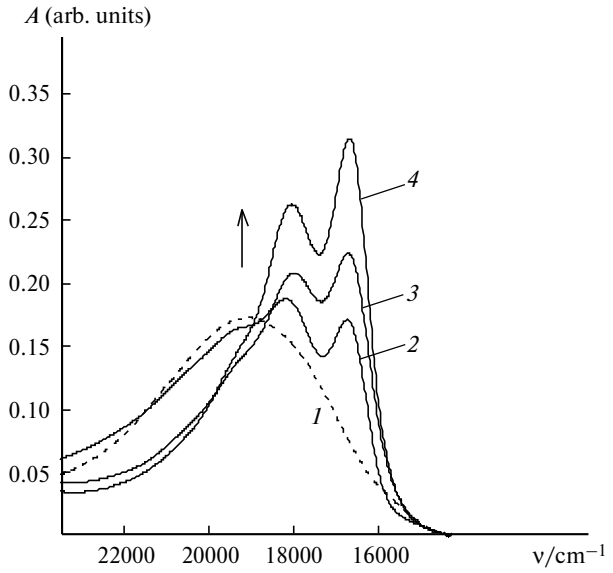



**Fig. 9.** Absorbance ($A$) of a solution containing PNC ($C_{PNC}$ = $= 1.2 \cdot 10^{-6}$ mol $L^{-1}$, *1–4*), AR ($C_{AR} = 1.5 \cdot 10^{-5}$ mol $L^{-1}$, *1–4*), and CPB ($C_{CPB} = 2.2 \cdot 10^{-4}$ mol $L^{-1}$, *2–4*) *vs* time ($t$): $t = 0$ (*1*, *2*), 600 (*3*), and 1560 s (*4*). The conditions are indicated in the caption to Fig. 7.

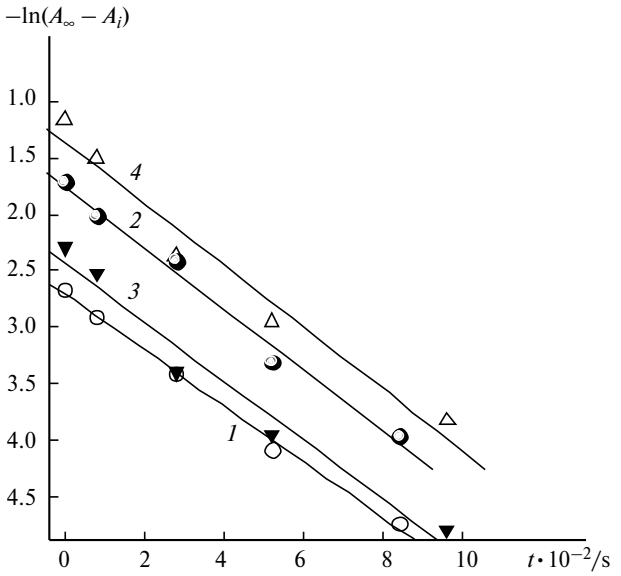



**Fig. 10.** Dependence of $\ln(A_\infty - A_t)$ on time ($t$) for the system $Ct^+ \cdot H_2An^-$ —CPB at various concentrations of the components: $C_{PNC} = 1.4 \cdot 10^{-6}$ (*1–4*), $C_{AR} = 2.7 \cdot 10^{-5}$ (*1–4*), and $C_{CPB} = 4.4 \cdot 10^{-4}$ (*1*, *2*) and $8.8 \cdot 10^{-4}$ mol $L^{-1}$ (*3*, *4*); $\lambda = 551$ (*1*, *3*) and 602 nm (*2*, *4*).

factants. At the surfactant concentrations close to the values of CMC, the associates decompose not immediately, but this process lasts for a certain time (Fig. 9). We studied this phenomenon in more detail.

The destruction of the associate can be considered as an almost irreversible reaction. The determination of the reaction order is related to the search for kinetic dependences of the linear character in the corresponding coordinates of variables.[50,51] The equation $\exp(-kt) = C_t C_0^{-1}$ obeys for similar reactions of the first order, *i.e.*, the dependence of the property of the system (in this case, the absorbance ($A$) at a chosen wavelength ($\lambda$)) *vs* time can be presented as follows:

$$\exp(-kt) = (A_t - A_\infty) \cdot (A_0 - A_\infty)^{-1}$$

or in the form

$$\ln(A_\infty - A_t) = -kt + \ln(A_\infty - A_0).$$

In the general case,

$$Y = B + kt,$$

where $k$ is the reaction rate constant; $C_t$ and $C_0$ are the molar concentration of the substance at the moment $t$ and the initial ($t = 0$) concentration, respectively; $A_0$, $A_t$, and $A_\infty$ are the absorbances of the solution at a certain wavelength at the initial moment $t = 0$ (the associate itself has this value), at the given moment $t$, and at $t = \infty$, respectively. As can be seen from Fig. 10, the interaction of the surfactant with the associate $Ct^+ \cdot H_2An^-$ induces an almost linear change in $Y$ with time at both different surfactant concentrations and different absorption wavelengths (Table 5).

The constant values of $k$ and the satisfactory correlation coefficient of the dependences for the CPB concentrations close to the CMC indicate that the destruction of the associate $Ct^+ \cdot H_2An^-$ in micellar aqueous solutions of CPB is described by the kinetic equation of the first order

$$V = k[Ct^+ \cdot H_2An^-],$$

where $V$ is the rate of the reaction of the associate with the CPB micelles. Under the conditions of considerable excess of surfactant over the dyes and associates, the destruction scheme can be presented as follows:

$$Ct^+ \cdot H_2An^- \xrightarrow{CPB_{(exc)}} (Ct^+)_{CPB} + (H_2An^-)_{CPB},$$

where $(Ct^+)_{CPB}$ and $(H_2An^-)_{CPB}$ are the ions of the dyes solubilized by CPB micelles.

This scheme and the first order of the reaction with respect to the cation $Ct^+$ are confirmed not only by the spectra (the appearance of solubilized forms of the dyes in the solution). We checked the hypothesis of correspondence of $k$ to the second reaction order for which the following equation is valid:

$$k = ([Ct^+ \cdot H_2An^-] - [Ct^+]) \cdot ([Ct^+ \cdot HAn^-] \cdot t[Ct^+])^{-1},$$

where the equilibrium concentrations of the associate and cyanine cation determined from the spectrophotometry data are given in brackets. It turned out that the values of

**Table 5.** Parameters of the kinetic dependences of the type $Y = -kt + B$ at various CPB concentrations and absorption wavelengths (λ) for the system $Ct^+ \cdot H_2An^-$—CPB

| Parameter | Value | | | |
|---|---|---|---|---|
| | $C_{CPB} = 4.4 \cdot 10^{-3}$ mol L$^{-1}$ | | $C_{CPB} = 8.8 \cdot 10^{-3}$ mol L$^{-1}$ | |
| | I | II | I | II |
| $-B$ | $2.63_{0.06}$ | $1.64_{0.09}$ | $2.40_{0.16}$ | $1.31_{0.11}$ |
| $k \cdot 10^3$/s$^{-1}$ | $1.58_{0.06}$ | $1.47_{0.10}$ | $1.53_{0.18}$ | $1.71_{0.17}$ |
| $-r$ | $0.998_{0.09}$ | $0.995_{0.14}$ | $0.988_{0.20}$ | $0.986_{0.22}$ |
| $n$ | 7 | 6 | 6 | 7 |

*Note*. $C_{PNC} = 1.4 \cdot 10^{-6}$ mol L$^{-1}$; $C_{AR} = 2.7 \cdot 10^{-5}$ mol L$^{-1}$; $Y = \ln (A_\infty - A_t)$; $B = \ln(A_\infty - A_0)$; $k$ is the rate constant; $r$ is the correlation coefficient; $n$ is the sampling volume of the values of $\ln(A_\infty - A_t)$; the subscript designates the standard deviation of the corresponding parameter; I: at λ = 551 nm, and II: at λ = 602 nm.

$k$ calculated within one series (the contents of the dyes and surfactant are unchanged) for the associate $Ct^+ \cdot H_2An^-$ differ by a factor of 8—12. Therefore, for this assumption $k \neq$ const, and the scheme of destruction of the associates formally does not correspond to the second-order reaction. Similar kinetic dependences are characteristic of SDS as well.

The results obtained confirm the earlier established[1,20—22,46,47] facts of the destruction influence of the ionic surfactants on the heterogeneous associates of dyes of various compositions. Further they can find practical use and form the basis for the development of the testing (semi-quantitative) estimation of the content ionic surfactants in an aqueous solution based on the visual perception of a change in the color of the solution. A characteristic feature of similar developments can be the high contrast of determinations of surfactants, which is caused by the presence in the solution of two dyes (for example, the pinacyanol cation and the anion $H_2An^-$) having well resolved intrinsic absorption bands with an appropriate intensity and forming colored associates.

The systematic study of the heteroassociates of the singly- and doubly-charged anions of AR with the pinacyanol cation shows that the π-electronic interactions play a substantial role in the association of polyatomic particles in addition to the Coulomb interactions. The further study of the association processes assumes to analyze the electronic absorption spectra and computer simulation data.

## References


1. A. A. Ishchenko, S. A. Shapovalov, *Zh. Prikl. Spektrosk.*, 2004, **71**, 557 [*J. Appl. Spectr.* (*Engl. Transl.*), 2004, **71**].
2. *Voda: struktura, sostoyanie, sol´vatatsiya. Dostizheniya poslednikh let* [*Water: Structure, State, Solvation. Achievements of the Recent Years*], Ed. A. M. Kutepov, Nauka, Moscow, 2003, 404 pp. (in Russian).
3. V. I. Larin, S. A. Shapovalov, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 2004, **70**, 10 (in Ukrainian).
4. S. A. Shapovalov, *Zh. Fiz. Khim.*, 2008, **82**, 1685 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2008, **82**].
5. I. M. Korenman, *Organicheskie reagenty v neorganicheskom analize* [*Organic Reagents in Inorganic Analysis*], Khimiya, Moscow, 1980, 448 pp. (in Russian).
6. S. Arimori, C. J. Ward, T. D. James, *Chem. Commun.*, 2001, 2018.
7. S. B. Savvin, V. V. Kuznetsov, S. V. Sheremet´ev, A. V. Mikhailova, *Ros. Khim. Zh.* (*Zh. Ros. Khim. Obshch. im. D. I. Mendeleeva*) [*Russ. Chem. J.*], 2008, **52**, No. 2, 7 (in Russian).
8. M. J. Bonné, E. Galbraith, T. D. James, M. J. Wasbrough, K. J. Edler, A. T. A. Jenkins, M. Helton, A. McKee, W. Thielemans, E. Psillakis, F. Marken, *J. Mater. Chem.*, 2010, **20**, 588.
9. D. W. Green, *Biomed. Mater.*, 2008, **3**, 1.
10. N. Nakiboğlu, İ. Şahin, N. Ertaş, *Analyt. Lett.*, 2008, **41**, 2621.
11. A. L. El-Ansary, Y. M. Issa, W. Selim, *Analyt. Lett.*, 1999, **32**, 955.
12. M. Nejati-Yazdinejad, *Int. J. Food Sci. Technol.*, 2007, **42**, 1402.
13. F.-Y. Wu, W.-S. Liao, Y.-M. Wu, X.-F. Wan, *Spectrosc. Lett.*, 2008, **41**, 393.
14. Z. Wang, X. Liu, W. R. G. Baeyens, J. R. Delanghe, J. Ouyang, *J. Proteome Res.*, 2008, **7**, 5075.
15. J.-M. Liu, H. Gao, F.-M. Li, Y.-L. Liu, J. Liu, M.-L. Ouyang, H.-X. Wang, S.-Q. Lin, C.-Q. Lin, Z.-M. Li, *Analyt. Lett.*, 2010, **43**, 300.
16. A. Nonaka, S. Horie, T. D. James, Y. Kubo, *Org. Biomol. Chem.*, 2008, **6**, 3621.
17. N. Erk, *Analyt. Lett.*, 2003, **36**, 2699.
18. C. Hong, *Chin. J. Spectrosc. Lab.*, 2004, **21**, 959.
19. N. Rahman, N. Afaq, *Anal. Methods*, 2010, **2**, 513.
20. S. A. Shapovalov, Ya. S. Kiseleva, *Zh. Fiz. Khim.*, 2008, **82**, 1105 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2008, **82**].
21. S. A. Shapovalov, M. A. Dobriyan, T. V. Sakhno, Ya. S. Kiseleva, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 2008, **74**, 71 (in Ukrainian).
22. S. A. Shapovalov, *Zh. Prikl. Khim.*, 2008, **81**, 1082 [*Russ. J. Appl. Chem.* (*Engl. Transl.*), 2008, **81**].

23. *Poverkhnostno-aktivnye veshchestva. Spravochnik* [*Surfactants. Manual*], Ed. A. A. Abramzon and G. M. Gaevoi, Khimiya, Leningrad, 1979, 376 pp. (in Russian).
24. S. A. Shapovalov, *Ukr. Khim. Zh.* [*Ukrainian Chemical Journal*], 2004, **70**, 25 (in Ukrainian).
25. S. A. Shapovalov, V. L. Koval, T. A. Chernaya, A. Yu. Pereversev, N. A. Derevyanko, A. A. Ishchenko, N. O. Mchedlov-Petrossyan, *J. Brazil. Chem. Soc.*, 2005, **16**, 232.
26. S. A. Shapovalov, *Zh. Fiz. Khim.*, 2005, **79**, 565 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2005, **79**].
27. S. A. Shapovalov, E. A. Samoilov, V. V. Ivanov, *Izv. Vuzov. Khim. Khim. Tekhnol.* [*Bulletin of Higher Education School. Chemistry and Chemical Technology*], 2006, **49**, No. 7, 39 (in Russian).
28. S. E. Sheppard, *Rev. Modern Phys.*, 1942, **14**, 303.
29. S. A. Shapovalov, E. A. Samoilov, *Izv. Akad. Nauk, Ser. Khim.*, 2008, 1379 [*Russ. Chem. Bull., Int. Ed.*, 2008, **57**, 1405].
30. H. Herz, *Photogr. Sci. Eng.*, 1974, **18**, 207.
31. E. M. Adamova, *Tez. dokl. XVI Mezhdunar. konf. studentov, aspirantov i molodykh uchenykh "Lomonosov"* [*Abstrs XVI International Conf. of Students, Post-Graduates, and Young Scientists "Lomonosov"*] (*Moscow, April 14—17, 2009*), MAKS Press, Moscow, 2009, p. 1 (in Russian).
32. A. Niazi, A. A. Rezaei, F. Shahhosseini, *Annali di Chimica (Ital.)*, 2007, **97**, 199.
33. J. J. Cruywagen, J. B. B. Heyns, E. A. Rohwer, *South African J. Chem.*, 1999, **52**, 15.
34. S. A. Shapovalov, *Zh. Obshch. Khim.,* 2010, **80**, 783 [*Russ. J. Gen. Chem.* (*Engl. Transl.*), 2010, **80**].
35. M. J. S. Dewar, D. M. Storch, *J. Am. Chem. Soc.*, 1985, **107**, 3898.
36. J. J. P. Stewart, *MOPAC 2000. Users Manual*, Fujitsu Limited, New York, 2000, 433 pp.
37. K. Ya. Burshtein, P. P. Shorygin, *Kvantovo-khimicheskie raschety v organicheskoi khimii i molekulyarnoi spektroskopii* [*Quantum Chemical Calculations in Organic Chemistry and Molecular Spectroscopy*], Nauka, Moscow, 1989, 104 pp. (in Russian).
38. S. A. Astakhov, V. I. Baranov, L. A. Gribov, *Theory and Methods of Computational Vibronic Spectroscopy*, Nova Science Publishers, New York, 2008, 87 pp.
39. Yu. M. Kessler, A. L. Zaitsev, *Sol´vofobnye effekty. Teoriya, eksperiment, praktika* [*Solvophobic Effects. Theory, Experiment, and Practice*], Khimiya, Leningrad, 1989, 312 pp. (in Russian).
40. K. Saito, *J. Phys. Chem. B.*, 2001, **105**, 4235.
41. M. Tian, M. Furuki, I. Iwasa, Y. Sato, L. S. Pu, S. Tatsuura, *J. Phys. Chem. B.*, 2002, **106**, 4370.
42. P. Uznanski, *Synth. Metals,* 2000, **109**, 281
43. F. Peral, E. Gallego, *Spectrochim. Acta. A. Mol. Biomol. Spectr.*, 2003, **59**, 1223.
44. R. Rubires, J.-A. Farrera, J. M. Ribo, *Chem. Eur. J.*, 2001, **7**, 436.
45. S. A. Shapovalov, V. L. Koval´, N. O. Mchedlov-Petrosyan, V. N. Kleshchevnikova, N. A. Derevyanko, A. A. Ishchenko, *Dokl. Nat. Akad. Nauk Ukr.* [*Reports of the National Academy of Sciences of Ukraine*], 1999, 156 (in Ukrainian).
46. S. A. Shapovalov, Ya. A. Svishcheva, V. I. Larin, *Izv. Vuzov. Khim. Khim. Tekhnol.* [*Bulletin of Higher Education School. Chemistry and Chemical Technology*], 2002, **45**, No. 4, 37 (in Russian).
47. S. A. Shapovalov, Ya. A. Svishcheva, *Zh. Prikl. Khim.*, 2002, **75**, 463 [*Russ. J. Appl. Chem.* (*Engl. Transl.*), 2002, **75**].
48. S. A. Shapovalov, *Zh. Fiz. Khim.*, 2010, **84**, 2098 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2010, **84**].
49. S. A. Shapovalov, *Zh. Fiz. Khim.*, 2011, **85**, 13 [*Russ. J. Phys. Chem.* (*Engl. Transl.*), 2011, **85**].
50. N. M. Emanuel´, D. G. Knorre, *Kurs khimicheskoi kinetiki* [*The Course of Chemical Kinetics*], Vysshaya Shkola, Moscow, 1984, 463 pp. (in Russian).
51. S. A. Shapovalov, *Zh. Fiz. Khim.*, 2005, **79**, 1786 [*Russ. J. Phys. Chem. (Engl. Transl.*), 2005, **79**].

*Received August 26, 2010;*
*in revised form November 2,2010*