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ASSOCIATION OF THYMOLSULFONEPHTHALEIN AND CRESOLSULFONEPHTHALEIN ANIONS WITH CATIONIC CYANINES IN AQUEOUS SOLUTION

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Abstract. The formation of associates between one- or two-charged anions of sulfonephthalein dyes – thymolsulfonephthalein, cresolsulfonephthalein – and cyanine cations (pinacyanol, quinaldine red) has been considered in aqueous solution. Equilibrium association constants have been determined using spectrophotometric data. By semiempirical methods the enthalpy of formation and the eventual structure of ions and associates have been established.

Keywords: association, aqueous solution, thymolsulfonephthalein, cresolsulfonephthalein, enthalpy of formation, dyes, absorption spectra.

1. Introduction

Phenol red or phenolsulfonephthalein (PS), and other sulfonephthaleins are traditionally applied as acid-base or metalchromic indicators in the quantitative analysis [1, 2]. Recently, attention has been drawn to the use of alkyl PS derivatives: thymolsulfonephthalein (TS) and *o*-cresolsulfonephthalein (CS). These sulfonephthaleins manifest themselves as reagents which are highly sensitive, *e.g.* to the electromagnetic radiation [3] (including UV-radiation [4]), as well as to the content of a number of simple inorganic ions (Pb^{2+} , Cd^{2+} [5], H^+ [6], SO_4^{2-} , PO_4^{3-} [7]), complex multi-functional organic molecules (proteins [8] and antibiotics [9]) in the films [4], in polymer matrices [6] and in solutions [3, 5, 7, 9, 10]. It is important that CS and TS form ion pairs in solutions. For example, the indication of sulfate-ion is based on the formation of ion pairs with squaramide in an acidic medium [10], and spectrophotometric determination of erythromycin is possible due to its association with TS [9]. Analysis of numerous publications demonstrates the need for a more detailed study of the cation-anion interactions leading to the formation of associates with anions (HAn^- , An^{2-}) of CS or TS dyes.

Some facts of PS, CS and TS interactions with single-charged cationic cyanines (Ct^+) were considered

earlier [11-14]. However, the most probable structure of the associates as well as energetics (in particular, the enthalpy of formation, $\Delta_f H^\circ$) were not discussed. In this report, on the basis of the results of spectrophotometric measurements and quantum chemical simulations, we have analyzed the cation-anion interaction leading to the formation of stoichiometric associates between single- or two-charged anions of CS, TS, and single-charged cations of pinacyanol (PNC^+) or quinaldine red (QR^+). Associates of the PS anions are also examined to compare the properties of sulfonephthalein associates. The energetics and the most probable structures of the associates “ $\text{Ct}^+ + \text{HAn}^-$ ”, “ $\text{Ct}^+ + \text{An}^{2-}$ ” are also discussed. Note that the PNC^+ and QR^+ cations have proven themselves as “standard” counterions in studying of the dyes association [11, 12, 14] due to its spectral and protolytic properties.

2. Experimental

2.1. Materials and Equipment

Disodium salts of sulfonephthaleins and chlorides of cyanine dyes («Sigma») have been used. We were convinced spectrophotometrically in good cleanness of each dye taking into consideration the well-known values of molar absorption coefficient (ε_{max} , $\text{l}/(\text{mol}\cdot\text{cm})$) at the maximum absorption band (I_{max}) of the most intensely protolytic forms. The acidity of solutions is created by phosphate, borate or acetate buffer solutions, and the chloride acid or sodium hydroxide in some cases. Supplementary experiments have revealed that additions of buffer solutions did not have a noticeable influence on the association processes. The pH values were monitored by a glass electrode. Ionic strength (I) of photometrical solutions did not exceed 0.004 mol/l . The values of the optical density (A) underlying the calculations of the equilibrium association constant (K_{as}) were in agreement with the basic law of light absorption. The absorption

spectra were measured with a spectrophotometer Hitachi U3210 or “SF-46” at room temperature.

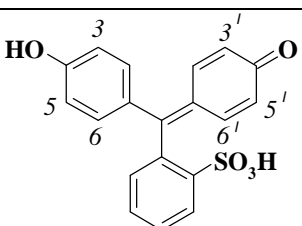
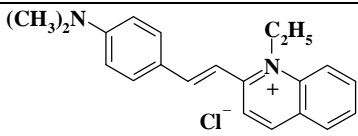
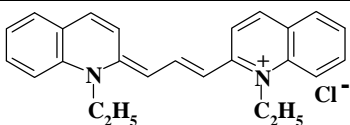
2.2. Procedure

Technique of preparation of dyes mixtures and the calculations of the spectral and equilibrium characteristics of the associates are given in prior publications [11-13]. General principles of quantum-chemical simulations of dyes structures and ion associates have been described previously [15]. Studying the interaction HAn^- (or An^{2-}) with Ct^+ the acidity of the solution that would ensure the

coexistence of the ionic forms was observed (otherwise, the interpretation of spectral changes is complicated due to possible interactions with other particles). By creating the optimum acidity the numerical values of $\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$ have been taken into account (see Table 1; characteristics of dyes are given for $I \rightarrow 0$ according to [16-19]; $\text{p}K_{\text{a}}$ error values are equal to $\pm(0.03-0.08)$; values of $\text{p}K_{\text{a1}}$ for QR and PNC are given for the dissociation process of the HCT^{2+} cation). For example, the data in Table 1 indicate that the interaction of a single charged anion of CS^- with PNC^+ should be investigated at pH 5.0–6.5, and the same is at 5.5–7.2 for TS^- anion.

Table 1

Spectral and protolytic properties of dyes

Dye	$\text{p}K_{\text{a1}}$ (λ_{max} , nm HAn^- or Ct^+)	$\text{p}K_{\text{a2}}$ (λ_{max} , nm An^{2-})
Sulfonephthaleins: 		
<i>o</i> -cresolsulfonephthalein (CS), 5,5' – CH_3	1.05 (433)	8.46 (572)
thymolsulfonephthalein (TS), 3,3' – $\text{CH}(\text{CH}_3)_2$; 6,6' – CH_3	1.50 (438)	9.20 (537)
phenolsulfonephthalein (PS), 3,3',5,5',6,6' – H	1.03 (430)	8.00 (558)
Cyanines:		
quinaldine red (QR^+) 	2.63 (528)	
pinacyanol (PNC^+) 	3.5 (600, α -band 550, β -band)	

3. Results and Discussion

3.1. Equilibria of Dyes in Aqueous Solutions

The molecules of sulfonephthalein dyes dissociate as polybasic acids: $\text{H}_3\text{An}^+ \rightleftharpoons \text{H}_2\text{An}^0 \rightleftharpoons \text{HAn}^- \rightleftharpoons \text{An}^{2-}$. Cationic and neutral protolytic forms are observed only in strongly acidic medium. Anions, especially An^{2-} , have the most intense coloring; the absorption band HAn^- and An^{2-}

are well separated spectrally (see I_{max} data in Table 1). These properties are favorable for the experimental study of ionic association of dyes even at very low (at $1 \cdot 10^{-6}$ mol/l) concentrations of species. Significant differences in values of $\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$ allow creating the acidity of the solution, in which there is only one- (or two-charged) anion.

Aqueous solutions of cationic cyanines noticeably lose color in highly acidic or alkaline solutions due to protonization (formation of HCT^{2+}) or hydrolysis (CtOH appearance) processes, respectively.

The interpretation of spectral changes based on the equilibrium approach (using the law of mass action) includes keeping the basic law of light absorption of the protolytic forms of interacting dyes. We found that the equations of the law $A = B + kC$ (where A is the optical density at I_{\max} for protolytic forms HAn, An^2 or Ct^+ , C is a molar concentration of the dye) have a linear character under $5 \cdot 10^{-6} - 1 \cdot 10^{-4}$ mol/l of CS, $5 \cdot 10^{-6} - 2.5 \cdot 10^{-4}$ mol/l of TS, $2 \cdot 10^{-6} - 8 \cdot 10^{-5}$ mol/l of PS, and $2 \cdot 10^{-6} - 8.5 \cdot 10^{-5}$ mol/l of QR. The parameter B is the statistical zero, the values of the angular coefficient k are practically equal to ϵ_{\max} of corresponding protolytic forms, and the correlation coefficients are 0.97–0.99. These facts suggest that sulfonephthaleins and QR do not form dimers actually in the investigated concentration ranges. Unlike other dyes, the basic law of the light absorption for PNC is observed only at small (less than $3 \cdot 10^{-6}$ mol/l) concentrations, since this cyanine is notably prone to self-association [19]. Dimerization of PNC is characterized spectrally by a sharp absorption weakening of α -bands and by increasing the intensity of the β -band (Table 1).

3.2. Association Ct^+ with HAn^- and Ct^+ with An^{2-}

Analysis of changes in electronic absorption spectra of Ct^+ with HAn^- and Ct^+ with An^{2-} mixtures reveals nonadditivity of spectral bands. Nonadditivity is the fact that the intensity of the mixture absorption of interacting counterions is systematically lower than the total light absorption of individual dye ions. A characteristic feature of the association is also an essential decrease of the absorption bands intensity. It is clearly observed at the addition of increasing amounts of sulfonephthalein to the constant concentration of cyanine. Moreover, such a phenomenon occurs regardless the initial concentrations of anions or cations (in the above molar ranges). Thus, the initial concentrations of PNC in Figs. 1 and 2 differ approximately in 100 times. α -Band has the intensity greater than β -band for PNC in Fig. 1, and the situation is contrary in Fig. 2 (system $\text{Ct}^+ + \text{HAn}^-$ and $\text{Ct}^+ + \text{An}^{2-}$ respectively; arrows indicate the direction of spectral shifts). Hypochromic shifts of Ct^+ absorption bands without the appearance of new bands allow to suggest the solvation-separated structure of associates (in accordance with the general features of the spectral shifts for systems of dye associates [20]).

By the methods of evaluation of stoichiometric composition (similar to [12, 13]) it was found that CS and TS anions can form $\text{Ct}^+ \cdot \text{HAn}^-$ or $(\text{Ct}^+)_2 \cdot \text{An}^{2-}$ associates under certain conditions (initial concentrations of counterions or molar concentrations ratio). A measure of the stability of these compounds is K_{as} . The value of concentration K_{as} is numerically not different from the thermodynamic value because $I \leq 0.004$. The K_{as} value is calculated on the basis

of the mass action law (in accordance with [13]) for $\text{Ct}^+ + \text{HAn}^- \rightleftharpoons \text{Ct}^+ \cdot \text{HAn}^-$ and $2\text{Ct}^+ + \text{An}^{2-} \rightleftharpoons (\text{Ct}^+)_2 \cdot \text{An}^{2-}$ equilibria. The values of $K = [\text{Ct}^+ \cdot \text{HAn}^-] \cdot [\text{Ct}^+]^{-1} \cdot [\text{HAn}^-]^{-1}$ and $K_{\text{as}} = [(\text{Ct}^+)_2 \cdot \text{An}^{2-}] \cdot [\text{Ct}^+]^{-2} \cdot [\text{An}^{2-}]^{-1}$ are presented in Table 2 (the molar equilibrium concentrations of the species are in square brackets; they were determined by a spectrophotometric method).

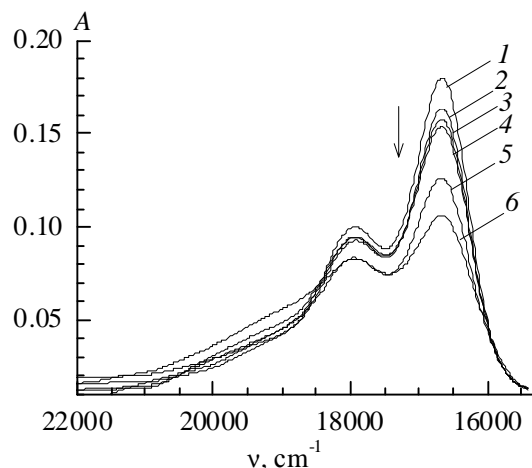


Fig. 1. Light absorbance in the “PNC + CS” system. Concentrations (mol/l) of PNC is $5.0 \cdot 10^{-7}$ (1–6); of CS: 0 (1), $5.1 \cdot 10^{-6}$ (2), $7.6 \cdot 10^{-6}$ (3), $1.5 \cdot 10^{-5}$ (4), $2.0 \cdot 10^{-5}$ (5) and $2.5 \cdot 10^{-5}$ (6). The thickness of absorbing layer is 5.00 cm, pH is 5.3. Blank solutions are: water (1) and CS at the corresponding concentrations (2–6).

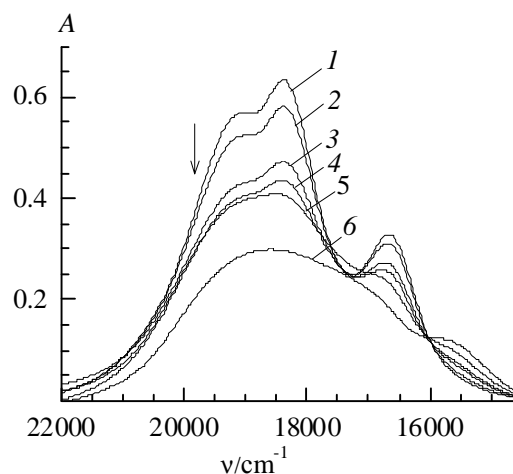


Fig. 2. Light absorbance in the “PNC + CS” system. Concentrations (mol/l) of PNC is $4.9 \cdot 10^{-5}$ (1–6); of CS: 0 (1), $5.0 \cdot 10^{-5}$ (2), $7.5 \cdot 10^{-5}$ (3), $1.0 \cdot 10^{-4}$ (4), $1.5 \cdot 10^{-4}$ (5) and $2.5 \cdot 10^{-4}$ (6). The thickness of absorbing layer is 0.20 cm, pH is 5.3. Blank solutions are: water (1) and CS at the corresponding concentrations (2–6).

The obtained data indicate that PNC associates are more stable than QR associates. We can assume that the reason for this phenomenon is related to different

contribution of hydrophobic and dispersion interactions in the association processes. Dispersion interactions are more typical for an advanced electronic system for PNC than for QR. By comparing the values of K_{as} it is also observed that the alkyl substituents hinder the association of counterions. Moreover, the unsubstituted PS associates are more stable than the associates of substituted CS or TS. Probably this is due to the fact that the alkyl groups degrade planarity of the molecule and prevent the convergence of the ions. The dispersion interactions important for the association of dyes [13, 20] are weakened as a consequence.

Table 2

The $\lg K_{as}$ values of sulphonephthaleins associates

Sulpho-nephtalein	$\lg K_{as}$			
	PNC ⁺		QR ⁺	
	Ct ⁺ ·HAn ⁻	(Ct ⁺) ₂ ·An ²⁻	Ct ⁺ ·HAn ⁻	(Ct ⁺) ₂ ·An ²⁻
PS	5.83 ± 0.10	11.81 ± 0.10	5.13 ± 0.09	8.64 ± 0.09
CS	4.59 ± 0.03	10.96 ± 0.10	4.0 ± 0.10	6.1 ± 0.10
TS	5.29 ± 0.05	11.0 ± 0.1	4.1 ± 0.10	5.9 ± 0.10

The formation of associates in solutions is typical for dyes having flat shape of the molecule [19, 20]. But sulfonephthalein anions are not flat π -electronic systems. Nevertheless, as it follows from the K_{as} values, the interaction between Ct⁺ and anions is quite noticeable. On the basis of experimental data as to the associate composition it can be assumed that the planar polymethine cation is coordinated by a single charged anion (or two cations are coordinated with a twocharged anion). We examined the energy states (the $\Delta_f H^\circ$ values) of each ion and associate in more detail and determined the most likely structure with the use of quantum chemical simulations.

3.3. Energetics and Structures of Sulfonephthalein Associates

We used semi-empirical AM1 and PM3 methods to determine $\Delta_f H^\circ$ for ions and associates. The parameters of these methods have been chosen so that one should reproduce the experimental $\Delta_f H^\circ$ values of organic compounds best of all. For example, the average error of the AM1 method for calculating the enthalpy is 25 kJ/mol [21, 22]. It should be noted that such *ab initio* simulation leads to $\Delta_f H^\circ$ errors that exceed 100 kJ/mol even for small molecules. This is due to the incompleteness of the used basis and the neglect of electron correlation energy. If the number of atoms in the molecule increases, the errors of $\Delta_f H^\circ$ values are even greater, and they acquire systematic character [23].

An convergence RMS gradient (Root Mean Square gradient is the rate of change (first derivative) of total energy at displacement of each atom in x, y, and z directions; the

RMS gradient of zero means the structure is at a local minimum in the potential energy surface). The gradient of the convergence of successive iterations decreased from 4.2 to 0.04 kJ/mol. The data in Table 3 ascertain a satisfactory convergence of results within each method of simulation. The scale of variation of $\Delta_f H^\circ$ values does not exceed 20 kJ/mol (for PS, AM1 methods) and 26 kJ/mol (for CS, PM3 method); hereinafter the most negative values of $\Delta_f H^\circ$ are accepted as the final ones. A comparison between absolute $\Delta_f H^\circ$ values of two semi-empirical methods shows that the obtained differences are not fundamental problems in the context of the investigation. For example, the largest AM1 and PM3 difference is 44 kJ/mol for the PS²⁻ ion.

Table 3

The $\Delta_f H^\circ$ values, kJ/mol, of dye ions

Ions	Method	
	PM3	AMI
CS ⁻	(-656)–(-682)	(-647)–(-661)
CS ²⁻	(-597)–(-606)	(-569)–(-570)
TS ⁻	(-746)–(-763)	(-730)–(-746)
TS ²⁻	(-702)–(-712)	(-667)–(-671)
PS ⁻	(-575)–(-586)	(-556)–(-576)
PS ²⁻	(-534)–(-536)	(-479)–(-492)
PNC ⁺	980–968	1077–1073
QR ⁺	918–912	989–984

It is very important to determine non local but global energy minimum to obtain correct $\Delta_f H^\circ$ values of associates. We tested 6–7 different starting arrangements of counterions at the process of geometric optimization of the associate structure; previously each of the counterions has been geometrically optimized as described above. The energy state with the lowest energy corresponded to the global energy minimum. Then additional geometric structure optimization of the associate has been done by reducing RMS values, usually from 0.1 to (5·10⁻³–1·10⁻⁴) kJ/mol. The finishing point of optimization was determined at the absence of $\Delta_f H^\circ$ changes from the RMS values. It occurred at RMS = 5.0·10⁻²–5.0·10⁻³ kJ/mol often. Initial and final locations of the ions in the (QR⁺)₂·TS²⁻ associate are shown in Figs. 3 and 4 as examples (stereo; position of the anion has been arbitrarily fixed for the observer; the hydrogen atoms are omitted in Fig. 4). Distances between the carbon atom at TS²⁻ and each carbon atom at QR⁺ are equal to 6.5 Å, the central angle with vertex on the carbon atom of TS²⁻ is equal to 152° (see Fig. 3). Distance between the carbon atom at TS²⁻ and upper carbon atom of QR⁺ is 5.5 Å, and the same is 4.9 Å for the bottom carbon atom of QR⁺; the central angle with vertex on the carbon atom of TS²⁻ is equal to 116° (see

Fig. 4). Geometry of the structure strongly depends on the RMS values for sulfonephthalein associates. The optimization process is also characterized by decreasing the distance between the counterions and deformation of the π -electronic systems of dyes. The process has been practically completed at RMS = 0.01 kJ/mol yet.

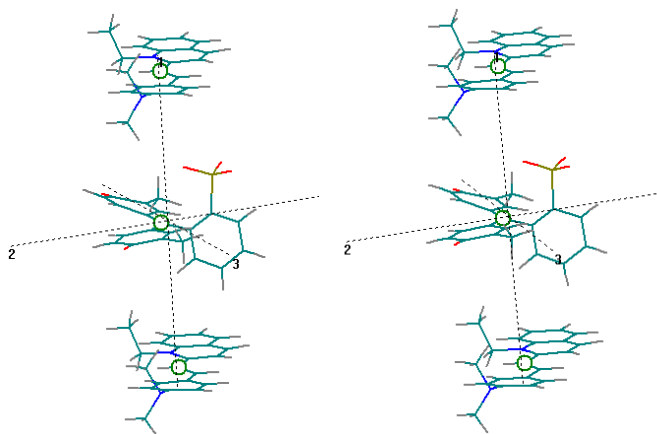


Fig. 3. Initial position of TS^{2-} anion (in the middle) and two QR^+ cations

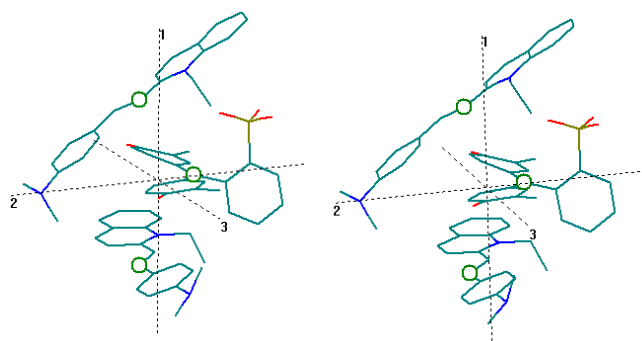


Fig. 4. Position of QR^+ and TS^{2-} ions in $(\text{QR}^+)_2 \cdot \text{TS}^{2-}$ associate

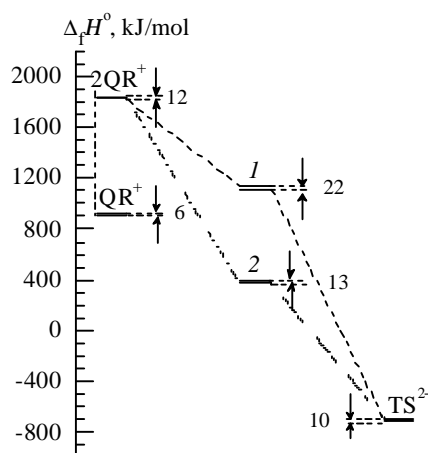


Fig. 5. The $\Delta_f H^\circ$ values of QR^+ and TS^{2-} ions: the $\Delta_f H^\circ$ value as the algebraic sum of ions (1) and the $\Delta_f H^\circ$ value of $(\text{QR}^+)_2 \cdot \text{TS}^{2-}$ associate (2)

Energy characteristics of the ions QR^+ , TS^{2-} and $(\text{QR}^+)_2 \cdot \text{TS}^{2-}$ associate are presented as an example in Fig. 5 (PM3 method; the numbers near arrows indicate the range of variation values of $\Delta_f H^\circ$, kJ/mol).

QR^+ and TS^{2-} ions are characterized by the $\Delta_f H^\circ$ values 918–912 and (–702)–(–712) kJ/mol respectively (see Table 3). The algebraic sum of $\Delta_f H^\circ$ value of two QR^+ cations and TS^{2-} anion is equal to 1134–1112 kJ/mol (level 1). It exceeds the $\Delta_f H^\circ$ value of $(\text{QR}^+)_2 \cdot \text{TS}^{2-}$ associate 388–375 kJ/mol (level 2), and the energy excess is 759–724 kJ/mol. Similarly, the $\Delta_f H^\circ$ values have been calculated for other associates. These data are presented in Table 4. This table also contains the following values: Σ is the algebraic sum of the $\Delta_f H^\circ$ values of ions in an associate, ($\Sigma = i \cdot \Delta_f H^\circ(\text{Ct}) + \Delta_f H^\circ(\text{An})$, where i is the number of cations in an associate); $\Sigma - \Delta_f H^\circ$ values; maximum relative error of $\Delta_f H^\circ$ values. The calculation of Σ values was carried out with the involvement of $\Delta_f H^\circ$ ions (from Table 3).

Table 4

**The energetic properties of the associates
(PM3 method)**

Associates	Σ , kJ/mol	$\Delta_f H^\circ$, kJ/mol	$\Sigma - \Delta_f H^\circ$, kJ/mol	Relative error of $\Delta_f H^\circ$, %
$\text{PNC}^+ \cdot \text{CS}^-$	287	104	183	36
$\text{QR}^+ \cdot \text{CS}^-$	230	62	168	23
$(\text{PNC}^+)_2 \cdot \text{CS}^{2-}$	1331	630	701	18
$(\text{QR}^+)_2 \cdot \text{CS}^{2-}$	1219	476	743	7
$\text{PNC}^+ \cdot \text{TS}^-$	205	24	181	24
$\text{QR}^+ \cdot \text{TS}^-$	149	–45	194	25
$(\text{PNC}^+)_2 \cdot \text{TS}^{2-}$	1225	514	711	10
$(\text{QR}^+)_2 \cdot \text{TS}^{2-}$	1113	375	738	20
$\text{PNC}^+ \cdot \text{PS}^-$	382	134	248	9
$\text{QR}^+ \cdot \text{PS}^-$	326	122	204	8
$(\text{PNC}^+)_2 \cdot \text{PS}^{2-}$	1400	688	712	7
$(\text{QR}^+)_2 \cdot \text{PS}^{2-}$	1288	518	770	4

Analysis of the data from Table 4 and the obtained results lead to several conclusions. It can be argued that the formation of associates is energetically favourable because an error of calculated $\Sigma - \Delta_f H^\circ$ values is not above mentioned average error of the method for calculating $\Delta_f H^\circ$ (the error highest value is 36 % for $\text{PNC}^+ \cdot \text{CS}^-$ associate; errors are less than 25 % for the rest associates). The gain reaches about 168–204 kJ/mol (single charged associates) and 701–770 kJ/mol (two charged associates).

It should be noted that changes in values $\Delta_f H^\circ$ (vacuum) and K_{as} (solution) do not necessarily correspond to each other, since the semi-empirical simulation cannot take into consideration certain interactions (e.g., hydrophobic interactions which are characteristic for bulky

polyatomic counterions [10, 12]). Nevertheless, the variation of $\Delta_f H^\circ$ (values are in parentheses), turned out to be the same as well as to K_{as} . For PNC⁺ associates: PNC⁺·TS⁻ (24) < PNC⁺·CS⁻ (104) < PNC⁺·PS⁻ (134), (PNC⁺)₂·TS²⁻ (514) < (PNC⁺)₂·CS²⁻ (630) < (PNC⁺)₂·PS²⁻ (688),

and for QR⁺ associates:

QR⁺·TS⁻ (-45) < QR⁺·CS⁻ (62) < QR⁺·PS⁻ (122), (QR⁺)₂·TS²⁻ (375) < (QR⁺)₂·CS²⁻ (476) < (QR⁺)₂·PS²⁻ (518).

4. Conclusions

Thus, the identified differences of K_{as} and $\Delta_f H^\circ$ values have a regular character in the series of the same type on the associates' structure. The obtained results also indicate that the processes of dyes association are accompanied by a rather complicated combination of various interactions including dispersive and π -electronic interactions. The effective investigation of these processes will imply a comparison of the results of spectral measurements with the data of computer simulation in the future.

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АСОЦІАЦІЯ АНІОНІВ ТИМОЛСУЛЬФОФТАЛЕЇНА І КРЕЗОЛСУЛЬФОФТАЛЕЇНА З КАТІОННИМИ ЦІАНІНАМИ У ВОДНОМУ РОЗЧИНІ

Анотація. Розглянуто утворення у водному розчині асоціатів між одно- або двозарядними аніонами сульфогфталейнових барвників – тимолсульфогфталейну, крезолсульфогфталейну – і катіонами ціанінів (пінаціанол, хінальдиновий червоний). За допомогою спектрофотометричних даних визначено рівноважні константи асоціації. Нанівемпіричними методами розрахована ентальпія утворення йонів і асоціатів, встановлено їх ймовірну будову.

Ключові слова: асоціація, водний розчин, тимолсульфогфталейн, крезолсульфогфталейн, ентальпія утворення, барвники, спектри поглинання.