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ASSOCIATION OF COMPLEX FERRUMCYANIDE ANIONS WITH PINACYANOL CATION IN AQUEOUS SOLUTION

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Abstract. The possibility of associates formation between complex ferrumcyanide anions $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and cationic polymethine dye pinacyanol in aqueous solution has been investigated. Energetic characteristics and the structures of associates were determined and the influence of ionic surfactants on the associates has been considered.

Keywords: association, aqueous solution, complex ferrumcyanide anions, surfactants, absorption spectra, pinacyanol.

1. Introduction

It is well known [1, 2] that the interactions of intensely colored dye ions with large counterions may lead to the formation of associates in solutions. Recently this phenomenon has been studied in detail. It has a special importance in connection with the processes of heteroassociation [1-3], aggregation [4] and intercalation [5, 6] of dyes in the objects with complex chemical composition. A number of "standard" dyes as well as colourless organic ions are used for more detailed investigation of cationic-anionic association in water. They include quinaldine blue and its structural analogues [7, 8], quinaldine red [8], astraphloxin [9, 10] (as cyanines), tetrabromophenylfluoron [11] (as oxyxanthene dye), rhodamin 110 [12] (as aminoxanthene dye), phenol red [13-15] (as sulfonephthalein dye), tetraphenylborat anion (TPB^-), tetraphenylarsonium ion (TFA^+) [10, 12, 15, 16], and tetrabutylammonium ion (as colourless ions). Accumulation of experimental data on equilibrium properties of associates not only promotes development of the theory of intermolecular interactions but also allows predicting the thermodynamic and spectral properties of complex species which are formed in solutions [17]. For this reason, the interactions between dyes and complex ions of metals are of special scientific interest. However, the study of association with these particles is only starting [18, 19].

Complex ferrumcyanide anions $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ (An^{i-}) differ in their characteristics from other "standard" anions. They are known as electrochemical redox systems and are used for indirect determination of thermodynamic characteristics of solvation of individual ions or division of complex interionic interactions into components (Coulomb – non Coulomb) [20-22]. The similarity of the geometric structure (right octahedron) and chemical composition makes it possible to explain the differences in the thermodynamic properties of these ions by the different manifestations of electrostatic (Coulomb) interactions only.

In this report we analyzed the cationic-anionic interactions that lead to the formation of associates between An^{i-} and single charged cation of pinacyanol (PNC^+) as a polymethine dye on the basis of the results of spectrophotometric measurements and quantum chemical simulations. Energetic characteristics, the most probable structure of associates of type "$Ct^+ + An^{i-}$" and the influence of ionic surfactants on associates have been discussed as well. It should be noted that in the study of dyes association processes [7, 13, 19] due to its spectral and protolytic properties PNC^+ has already proven itself as a "standard" cation.

2. Experimental

2.1. Materials and Equipment

"Sigma" pinacyanol chloride was used (the basic substance content was not less than 99 %). The quality of ferrumcyanide salts $K_3[Fe(CN)_6]$) and $K_4[Fe(CN)_6]$ was "chemically pure" (without additional purification). The samples of cationic surfactant $[C_{16}H_{33}NC_5H_5]Br$, cetylpirydinium bromide, (CPBr) and anionic surfactant $C_{12}H_{25}OSO_3Na$, dodecylsulphate sodium (NaDS) contained at least 90 % of the basic substance. The acidity of the solutions was created by phosphate, borate, and acetate buffer solutions and supplements HCl or NaOH were used in some cases. Supplementary experiments have established that additions of buffer solutions did not have a noticeable influence on the association between An^{i-} and the dye.

The pH values were monitored by glass electrode. The absorption spectra were measured by using Hitachi U3210 or SF 46 spectrophotometers at a room temperature. The measurement error was ± 0.5 nm for wavelength (λ) in 400–690 nm intervals.

2.2. Experimental Procedure

The preparation technique of dye solutions as well as other reagents was presented in the prior publications [9, 11, 14]. Throughout the course of the study of An^{i-} interaction with the dye the acidity of the solution was kept at the level that ensured coexistence of the corresponding ionic forms. Ionic strength of aqueous photometric solutions was ≤0.004 mol/l under these conditions. Original preparations of ferrumcyanide salts and PNC chloride were considered as completely dissociated in aqueous solution at all used concentrations.

The surfactants influence on the associates was investigated in the concentration ranges of $(1 \cdot 10^{-6})$–$(9 \cdot 10^{-4})$ mol/l for CPBr and $(1 \cdot 10^{-6})$–$(8.5 \cdot 10^{-3})$ mol/l for NaDS, taking into account the value of critical micelle concentration (CMC), $(6.6–9.0) \cdot 10^{-4}$ and $8.1 \cdot 10^{-3}$ mol/l, respectively [23].

3. Results and Discussion

3.1. An^{i-} and Ct^{+} Association

In the pH range of 4.5–9.5 PNC mainly exists in the form of single-charged cation (an exponent of equilibrium dissociation constant is 3.5 for two-charge cation [24]). The dye is protonized in strong acidic solution and significantly hydrolyzed at pH over 10. Protonization and hydrolysis processes are accompanied by breakdown of the chromophore system, and, consequently, lead to discoloration of the solution. For this reason the acidity of aqueous solutions was kept within the pH range of 4.5–9.5. It provided the required coexistence of protolytic forms of the dye and ferrumcyanide salts.

A characteristic feature of PNC is its significant dependence on its concentration. Redistribution of intensities of absorption bands takes place when concentration of PNC increases from $3.8 \cdot 10^{-6}$ mol/l up to $5.6 \cdot 10^{-5}$ mol/l (or more). The intensity of long-wavelength band (α-band, $l_{\max} = 600$ nm (16670 cm^{-1})) decreases and intensity of the near located band (β-band, $l_{\max} = 550$ nm (18180 cm^{-1})) increases. This course of changes is stipulated by the transformation of monomer to dimer (logarithm of the equilibrium constant of PNC dimerization is equal to 4.79 ± 0.06; more detailed spectral features are discussed in a number of publications [25-27]).

We experimentally determined that α- and β-band of cation decrease light absorbance when adding increasing amounts of $[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}$ to a constant content of PNC in the solution. Additionally, a new short-wavelength band appears with $\lambda_{\max} = 475$ nm (21050 cm^{-1}). Corresponding spectral shifts (marked by arrows) are presented as examples for the system "$K_3[Fe(CN)_6]$ + PNC" in Figs. 1 and 2.

Notably, the spectral changes occur regardless of the initial concentration of the dye. Thus, the PNC concentrations in Figs. 1 and 2 differ more than twice (in Fig. 2 the dimer fraction of the dye is larger than the monomer fraction as compared with Fig. 1, because the ratio of intensities of bands $\beta : \alpha$ is higher in the case of Fig. 2). Optical density (A) changes occur at relatively low contents of An^{i-}, which are even less than the contents of Ct^{+} (see spectra 2 in Figs. 1 and 2). Apparently, the character of spectral changes in "$An^{i-} + Ct^{+}$" systems is

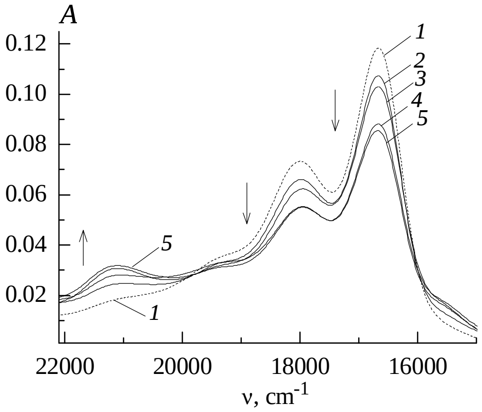

Fig. 1. Light absorbance in the "$K_3[Fe(CN)_6]$ + PNC" system. Concentrations of $K_3[Fe(CN)_6]$ (mol/l): 0 (*1*); $1.0 \cdot 10^{-6}$ (*2*); $2.0 \cdot 10^{-6}$ (*3*); $4.0 \cdot 10^{-6}$ (*4*); $2.0 \cdot 10^{-5}$ (*5*); of PNC: $1.5 \cdot 10^{-6}$ (*1–5*). The thickness of absorbing layer is 1 cm, pH 6.9. Blank solutions are water

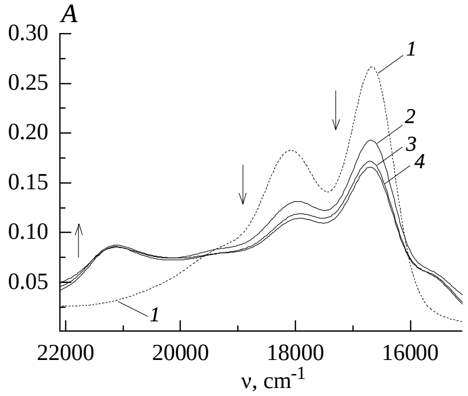

Fig. 2. Light absorbance in the "$K_3[Fe(CN)_6]$ + PNC" system. Concentrations of $K_3[Fe(CN)_6]$ (mol/l): 0 (*1*); $3.0 \cdot 10^{-6}$ (*2*); $6.0 \cdot 10^{-6}$ (*3*); $1.0 \cdot 10^{-5}$ (*4*); of PNC: $3.6 \cdot 10^{-6}$ (*1–4*). The thickness of absorbing layer is 1 cm, pH 6.9. Blank solutions are water

explained by the possibility of formation of compounds of different stoichiometry. Appearance of short-wavelength band in the spectra along with the decreasing of *A* in the long-wavelength region (15625–15270 cm^{-1}, see Figs.) and experimentally established fact of appearance of the solid phase at higher concentrations of counterions ($\geq 6.0 \cdot 10^{-5}$ mol/l Ct^+ and $\geq (1–3) \cdot 10^{-4}$ mol/l An^{i-}) in the solution testify to this assumption.

It should be noted that the spectral changes that occur in "ferrumcyanide anion + PNC cation" systems are similar to those that were earlier observed for "dye cation + TFB^-" [12], "dye anion + TFA^+" [10], and "dye cation + dye anion" [3, 8, 19, 28, 29] systems. Similar changes are interpreted as the formation of heterogeneous (dissimilar) associates between counterions.

3.2. Energetics and Structure of Associates

We established a number of energy states of "An^{i-} + Ct^+" type associates of various stoichiometric compositions. Based on the values of formation enthalpy $\Delta_f H^o$ of PNC^+, $[Fe(CN)_6]^{3-}$, and $[Fe(CN)_6]^{4-}$ ions (*i.e.* 908, 1410 and 2182 kJ/mol, respectively) the difference between the algebraic sum $\Sigma\ \Delta_f H^o(nCt^+, An^{i-})$ of the components ($\Delta_f H^o_{/sum}$) and the calculated $\Delta_f H^o$ value for the associates was established. The obtained data are presented in the Table (all formation enthalpy values – 298 K, method PM6, vacuum; $\Delta_f H$ variation magnitude is equal to 4–7 kJ/mol [18]; Y. Samoilov took part in the calculations).

Table

Energetic characteristics of the associates

Composition of associate	$\Delta_f H^o$, kJ/mol	$-(\Delta_f H^o - \Delta_f H^o_{/sum})$, kJ/mol
$3K^+ + [Fe(CN)_6]^{3-} + Ct^+ + Cl^-$	565	–
$[Fe(CN)_6]^{3-} + 2Ct^+$	2583	643
$[Fe(CN)_6]^{3-} + 3Ct^+$	2350	1784
$[Fe(CN)_6]^{4-} + 2Ct^+$	1816	2182
$[Fe(CN)_6]^{4-} + 3Ct^+$	2531	2375
$[Fe(CN)_6]^{4-} + 4Ct^+$	2968	2846

As we can see from the table, the $\Delta_f H^o - \Delta_f H^o_{/sum}$ values testify to different energetic advantage of type $(Ct^+)_2 \cdot An^{i-}$ and $(Ct^+)_3 \cdot An^{i-}$ compounds formation. More advantageous formation of such associates is for $[Fe(CN)_6]^{4-}$ anion. In Figure 3 relative position of counterions in the associate with $[Fe(CN)_6]^{4-}$ anion and three PNC^+ cations is presented as an example (see Fig. 3).

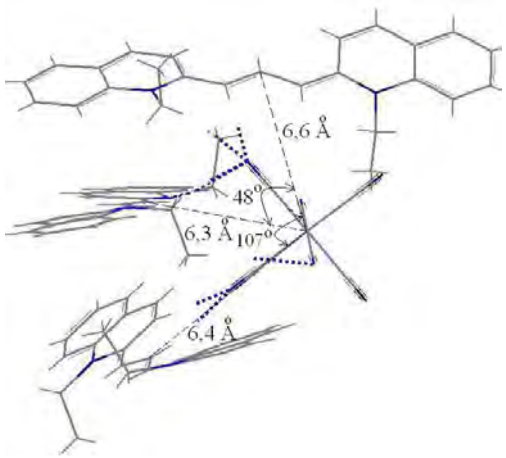

Fig. 3. Relative position of ions in "$[Fe(CN)_6]^{4-}$ + $3Ct^+$" associate. Hydrogen bond is marked by short dots

Calculations show that varying of the relative position of counterions in a model "$3K^+ + [Fe(CN)_6]^{3-} + Ct^+ + Cl^-$" system does not cause an essential change of $\Delta_f H^o$. However, it can lead to incorrect result, that is the formation of covalent bonds between the anion and the cation. In general, the final versions of the geometric optimization of "An^{i-} + Ct^+" structures are characterized by a number of local energy minima, which are very close in numerical values.

One of the associates' features under considered is the fact that strong polar $-C{\equiv}N$ groups of ferrumcyanide anions induce the formation of intermolecular hydrogen bonds (Fig. 3) with hydrogen atoms of polymethine chain or with heteroatoms of polymethine dye.

3.3. Influence of Ionic Surfactants on Associates

Additives NaDS or CPBr to mixtures of "An^{i-} + Ct^+" cause spectral changes that testify to associates destruction (see Figs. 4 and 5). The most complete destruction of associate occurs in surfactant micelles. Restoration of PNC bands contours and increasing of light absorbance with increasing content of ionic surfactant in solution in the absorption spectra is observed. Thus, the initial contour of absorption spectra for $K_4[Fe(CN)_6]$ and PNC^+ mixture (see spectrum *2* in Fig. 4) changes considerably with increasing NaDS concentrations (see curves *3*–*5*) and, finally (see curve *6*), it resembles PNC light absorbance in the NaDS micelles (see curve *7*).

Similar changes occur in the system "$K_4Fe(CN)_6$ + PNC + CPBr" (see Fig. 5). A characteristic feature of PNC is that the dye has greater color intensity in micelles of ionic surfactant than in pure water. At the same time absorption bands undergo batohromic shifts (*e.g.*, in NaDS micelles they are equal to about 7 nm).

At CPBr adding spectral changes are manifested at lower content of surfactant than at NaDS adding. Thus, NaDS concentrations are systematically higher (curves *3–6* in Fig. 4) than CPBr concentrations (curves *3–6* in Fig. 5). Obviously, different influence of these surfactants on associates is explained by the fact that the above mentioned CMC value for CPBr is less than CMC value for NaDS. Ferrumcyanide anions do not form heterogeneous associates with cation of dye in ionic surfactant micelles. Ions are practically isolated from each other and are solubilized by the corresponding surfactant micelles.

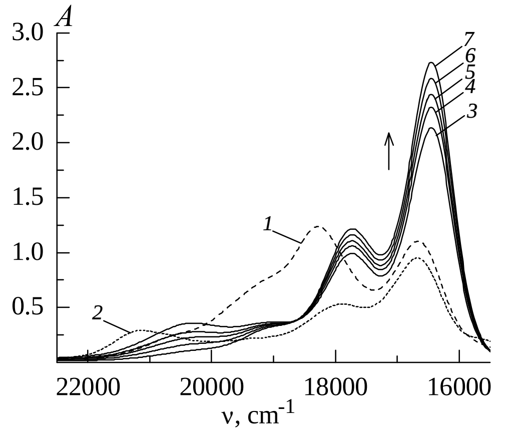

Fig. 4. Change of light absorbance in the: "$K_4Fe(CN)_6$ + PNC + NaDS" system. Concentrations of $K_4[Fe(CN)_6]$ (mol/l): 0 (*1, 7*); $1.2\cdot10^{-5}$ (*2–6*); of PNC: $1.9\cdot10^{-5}$ (*1–7*); of NaDS: 0 (*1, 2*); $1.2\cdot10^{-4}$ (*3*); $2.4\cdot10^{-4}$ (*4*); $5.9\cdot10^{-4}$ (*5*); $3.0\cdot10^{-3}$ (*6*); $8.5\cdot10^{-3}$ (*7*). The thickness of absorbing layer is 1 cm, pH 6.2. Blank solutions are water

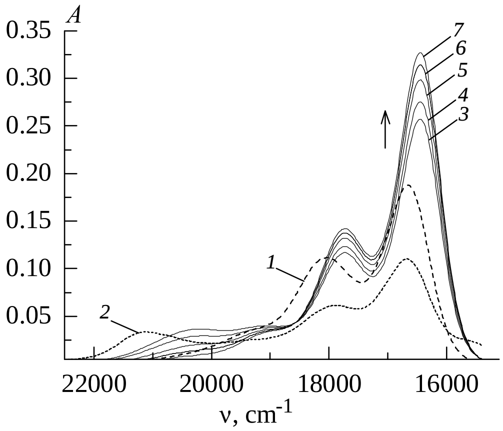

Fig. 5. Change of light absorbance in the «$K_4Fe(CN)_6$ + PNC + CPBr» system. Concentrations of $K_4[Fe(CN)_6]$ (mol/l): 0 (*1, 7*); $1.2\cdot10^{-5}$ (2–6); of PNC: $1.8\cdot10^{-6}$ (*1–7*); of CPBr: 0 (*1, 2*); $4.2\cdot10^{-5}$ (*3*); $8.5\cdot10^{-5}$ (*4*); $1.9\cdot10^{-4}$ (*5*); $3.0\cdot10^{-4}$ (*6*); $6.0\cdot10^{-4}$ (*7*). The thickness of absorbing layer is 1 cm, pH 6.2. Blank solutions are water

Equilibrium between Ct^+ and An^{i-} may be represented by the following scheme:

$$n\,\mathrm{Ct}^+ + \mathrm{An}^{i-} \rightleftarrows (\mathrm{Ct}^+)_n\cdot\mathrm{An}^{i-} \overset{\substack{\text{surfactant}\\\text{(micelles)}}}{\rightleftarrows} n\,(\mathrm{Ct}^+)_{\text{surfactant}} + (\mathrm{An}^{i-})_{\text{surfactant}}\,.$$

It should be noted that similar effects were found earlier for associates of different classes of dyes, such as oxyxanthenes [30], rhodamines [12], sulfonephthaleins [31], and alizarins [32].

The feature of "$Ct^+ + An^{i-}$ + NaDS" and "$Ct^+ + An^{i-}$ + CPBr" systems is kinetic nature of associates destruction of. Light absorbance of solutions increases not immediately after adding surfactant but continues for some time. It is noteworthy that formation of associate, *e.g.* the association of a cyanine cation and the dodecylsulfate anion (DS^-) is also kinetically controlled. However, there is a fundamental difference between these two processes. Connection of Ct^+ with DS^- occurs within a fraction of a second and at a high speed (constant reaction rate reaches 30 s^{-1} [33]). In contrast, destruction of associate may last for tens or hundreds of seconds, depending on the initial concentration of the components, composition of associate and especially at concentrations of ionic surfactants which are significantly lower than CMC.

4. Conclusions

On the basis of the results of spectrophotometric measurements and quantum chemical simulations the cation-anionic interactions which lead to the formation of associates between the $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ anions and single-charged cation of pinacyanol as a polymethine dye in aqueous solution have been analyzed. Destructive influence of anionic or cationic surfactant on associates has been considered. The kinetics of associates interaction with ionic surfactants should be explored in more detail. However, it becomes apparent that non-Coulomb interactions make an important contribution to association. The obtained results confirm the equilibrium character of the formation of these compounds and are consistent with the existing viewpoint about the nature of heterogeneous associates of dyes.

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АСОЦІАЦІЯ КОМПЛЕКСНИХ ФЕРУМЦІАНІДНИХ АНІОНІВ З КАТІОНОМ ПІНАЦІАНОЛА У ВОДНОМУ РОЗЧИНІ

Анотація. *Встановлена можливість утворення асоціатів між ферумціанідними металокомплексними аніонами* $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$ *і катіонним поліметиновим барвником пінаціанолом у водному розчині. Визначено енергетичні характеристики і будову асоціатів, розглянуто вплив на асоціати йонних ПАР.*

Ключові слова: *асоціація, водний розчин, ферумціанідний металокомплекс, ПАР, спектри поглинання, пінаціанол.*