

Review

The First Century of Successful Applications of Pinacyanol: Some Noteworthy Results

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Abstract: The most important results obtained during the first century of pinacyanol (PIN) application in fundamental and applied research are summarized. The main usages of PIN during the century are described. The structural, protolytic, and thermodynamic properties of the dye in different systems (aqueous and aqueous–organic solutions, pre-micellar and micellar surfactant systems, and salt-containing solutions) have been analyzed. Quantitative characteristics of intermolecular interactions are considered. Self-association and dissimilar association of PIN with the participation of other dyes, organic ions and molecules, and metal complex compounds under 5×10^{-7} – 8×10^{-5} mol/L concentrations of PIN are discussed. The analyzed data indicate that at present, as before, the scientific interest in this dye is very high.

Keywords: pinacyanol; cyanine dyes; self-association; dissimilar association; vis-spectroscopy; thermodynamics; solutions; computer simulation



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1. Introduction

The era of laboratory synthesis of dyes began in the middle of the 19th century. The first step on this path was the production of aniline as an individual substance. In 1826, the German scientist Otto Unverdorben was one of the first to try to separate a coloring substance from natural indigo. By distilling indigo with lime, an oily substance known as “crystalline” was obtained [1]. In 1843, August Wilhelm von Hofmann summarized the experiments of O. Underdorben and his followers: Friedlieb F. Runge [2], Carl J. Fritzsche [3], and Nikolay N. Zinin [4]. He set that four substances, namely “crystallin” [1], “kyanol” [2], “aniline” [3], and “benzidam” [4], are one substance, i.e., phenylamine, traditionally also called “aniline”. Aniline has become the basis for the synthesis of many dyes [5].

Perhaps the most significant year was 1856. In that year, three dyes were synthesized for the first time at once. The Polish chemist Jakub Natanson discovered that, when technical aniline is heated with dichloroethane, a bright red product is formed (“aniline red”, later called fuchsine) [6]. Eighteen-year-old English chemist William H. Perkin, on the advice of his teacher August W. Hofmann, accidentally synthesized purple dye whilst trying to synthesize quinine, an anti-malarial drug [7,8]. Experimenting with coal tar, he unexpectedly synthesized a purple pigment. This pigment was later called “mauveine” (from the French word “mauve”), because its color was similar to the forest flower mallow. Finally, Charles G. Williams (University of Glasgow) succeeded in obtaining the first “ethane” (more precisely, monomethine) dye, “cyanine blue” (1,1'-diisoamyl-4,4'-cyanine iodide) [9]. The chemical structure of monomethine was not established immediately, but only half a century later, thanks to the development of chemical bonding theory and instrumental methods of investigation.

It turned out that, from a chemical point of view, “mauveine” and other synthesized dyes were not individual substances, but mixtures of homologues. However, this was not an obstacle to the industrial production of synthetic dyes, which started already in the

middle of the 19th century. Polymethines have become a priority in scientific research. Initial interest in polymethines was related to the desire to expand the range of dyes with new light-sensitive substances. Over time, the need arose for a targeted selection of such compounds in which the spectral-luminescent, protolytic, and aggregate properties are successfully combined.

A common structural feature of polymethines is the presence of two heteroatom (often nitrogen) centers in the molecule [10]. One of them has a charge and is linked to the other heteroatom by a conjugated polyene chain. This chain is made up of an odd number of carbon atoms. The most prominent is pinacyanol (PIN), or quinaldine blue (Figure 1).

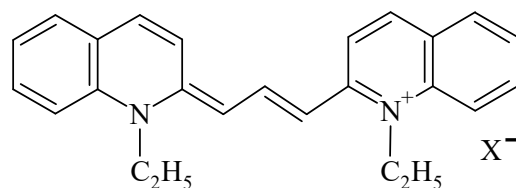


Figure 1. Structure of PIN ($X^- = \text{Cl, Br, I}$).

The IUPAC name of PIN is 1-ethyl-2-[3-(1-ethylquinolin-1-ium-2-yl)prop-2-enylidene]quinoline. More concisely, although not nomenclaturally exact, PIN is referred to in the scientific literature [11] and on the commercial market [12,13] as 1,1'-diethyl-2,2'-carbocyanine ("carbo" indicates the methyl chain of 3 carbon atoms). Less commonly, the names 1,1'-diethyl-2,2'-quinocarbocyanine or 2,2'-trimethinequinocyanine are used. Taking into account the salt-like nature, the anion (chloride, bromide, iodide, etc.) should be indicated in the name of the molecular compound. For example, "pinacyanol iodide" $\text{C}_{25}\text{H}_{25}\text{IN}_2$ (2*E*)-1-ethyl-2-[(*E*)-3-(1-ethylquinolin-1-ium-2-yl)prop-2-enylidene]quinoline iodide (CAS number 605-91-4) (all IUPAC names correspond to *Pub-Chem release 2021.05.07* [12]).

2. The Beginning of PIN Research

In contrast to the date of the beginning of the era of the synthesis of dyes, it is difficult to establish the exact date of the first mention of PIN. Despite the variety of chemical and commercial names for this dye, the generic semantic name "pinacyanol" was the first. It has been in use up until the present day since its inception and is ideographically dominant in the synonymic series. The first mentions of PIN date back to the very beginning of the twentieth century.

Researchers drew attention to the usefulness of PIN in modifying photographic plates to improve color rendering and light resolution. The use of "pinacyanol" in the construction of color photographic plates is known, dating from 1902 to 1904 [14]. Around 1902, Arthur Traube and Adolf Miethe proved the applicability of isocyanine dyes for creating panchromatic emulsions, which are sensitive to the entire range of visible light. Three years later, German researcher (of Austrian nationality) Benno Homolka synthesized PIN and modified the emulsions with dye additives. [15,16]. This improved the sensitivity of the long-wave ("red") part of the visible spectrum. However, the exact chemical structure of pinacyanol could not be set [16] (p. 972). Nevertheless, B. Gomolka's improvements made full color separation and the creation of color photographic and cinematographic films possible. At the same time, the first color (panchromatic) films appeared. However, this technique remained inaccessible to amateur filmmakers until the 1930s. A publication by Charles Edward Kenneth Mees [17] mentions the synthesis of pinacyanol as early as 1904. Moreover, W.H. Mills and F.M. Hamer note the following [18]: "One of < . . . > sensitizers is a substance patented in 1905 by the Farbwerke vorm. Meister, Lucius & Brüning (Brit. Pat. 16227, 1905; D.R.-P. 172118), and sold under the name of pinacyanol".

In 1908, the "Lowell Observatory Bulletin" published a scientific report by the American spectroscopic astronomer Vesto Melvin Slipher on the spectral study of the planets of the solar system [19] (p. 443). The report mentions experiments with "new sensitizing

dyes" (pinacyanol, pinachrom, orthochrome T, pinaverdol, blue pinachrom, homokol, and dicyanin). W.M. Slifer draws attention to the use of pinacyanol as early as 1907 or even 1906 as a suitable dye in mixtures with other dyes (pinaverdol, dicyanine), but does not refer to any publications [20]. This message has not gone unheeded. *Nature* journal published an abstract by Percival Lowell (founder of the Astronomical Observatory) with the same title, "Spectra of the Major Planets", in the same year [21] (p. 42). P. Lowell briefly summarizes the results of V.M. Slifer's observations and notes the following: "Mr. V.M. Slifer succeeded in 1907 in rendering some plates (Seed, 23) sensitive far into the red. This was performed < . . . > in a solution of pinacyanol, pinaverdol, dicyanin, alcohol, and water. With them he photographed the spectra of all the major planets". According to biographer William G. Hoyt, V.M. Slifer "< . . . > made more fundamental discoveries than any other observational astronomer of the twentieth century" [19] (p. 411). His most famous discovery was the unusual radial velocity of spiral nebulae, made in 1913/1914, based on the analysis of "red shifts" in the line spectra of emissions from spherical star clusters. In turn, this discovery was a precursor to Edwin P. Hubble's theory of an expanding universe, proposed somewhat later in the 1930s. V.M. Slifer set the existence of gas and dust in interstellar space and proved that some nebulae only glow with reflected light from nearby stars. The famous researcher of the spectra of stars and planets was born on 11 November 1875 and did not live to see his 94th birthday, which took place three days after his death. Symbolically, more than any other astronomer, he was at the forefront of the development of instrumental spectroscopy of the starry sky at the turn of two centuries and witnessed the beginning of human exploration of space, including the first landing of compatriots on the Moon.

Perhaps the reason for using pinacyanol was V.M. Slifer's acquaintance with the studies of L. Blythswood, W.A. Scoble, and R.J. Wallace [22–24] and an interesting publication by P.P. Lazareff in the *Journal of the Russian Physical and Chemical Society* (physical section) [25]. An English-language abstract of this article was published in the *Journal of the Chemical Society, Abstracts* in 1908 [26]. The Russian researcher found a correlation between the decoloration process and the optical properties of the pigments in the visible spectrum, and also set a relationship between the amount of decomposed matter and the wavelength or energy of incident light. Experiments were made with cyanin, lepidinecyanin, pinacyanol, pinaverdol, quinaldinecyanin, and pinachrome in the form of thin layers of collodion impregnated with the dye that were decolorized in the region of the absorption bands, "but in no other part of the spectrum" [26] (p. 4). P. Lazareff also proposed and described the construction of a device for photometric examination of various parts of a colored plate under the influence of rays causing discoloration of the dye. It is worth noting that the use of light-sensitive plates containing PIN has contributed to astronomical discoveries in the study of Mars [27] and comets [28–30].

The organic synthesis methods known at the time resulted in the production of PIN mixed with alternative products. Louis E. Wise et al. first tried to avoid impurities in the dye product [31]. They described a detailed procedure for the synthesis of fairly pure PIN, using ethiodides (i.e., compounds of the $R_2C(C_2H_5)I$ type) of quinaldine and quinoline as initial substances. The authors argued that, based on "< . . . > absorption data and the results of photosensitization experiments, further purification of the dye appears to be unnecessary".

The suitability of PIN as a photographic (and later "cinematographic") color sensitizer prompted an increase in production volumes and a switch from laboratory synthesis to industrial-scale production of the dye. Industrial production started in Great Britain in 1916, and in Germany somewhat earlier [31]. At the same time, PIN received the first commercial name "sensitol red" (actually "sensitive to red"; similarly, "pinaverdol" was called "sensitol green", i.e., "sensitive to green").

The ability to produce individual forms of dyes and, therefore, to adjust the chemical composition of composite bicolor and multicolor sensitizers has stimulated a number of original inventions, as well as basic and applied scientific research. In addition, scientific

laboratories and trading companies were already drawing attention to the need for standardization and the development of quality standards for light-sensitive materials by the 1920s [32,33]. In this regard, not only the devices and designs (light plates, light filters, etc.), but also the chemical composition of the gelatin media, solvents, and developer agents are being modernized [34–46]. Since the late 1910s and early 1920s, PIN has been proposed as one of the “standards” of photographic materials [31–33,47]. It is actively used as an ingredient in panchromatic light-sensitive substrates [17,40], along with naphthacyanol and acetaminocyanol [48,49]. PIN is also being tested as a highly sensitive component of silver halide media, photographic plates, and photographic and cinematographic films [50–54]. Thus, conditions have developed for a more favorable and meaningful practical application of PIN among other cyanine dyes.

3. Further Progress on the Dye

Since then, hundreds of sensitizing dyes have been synthesized and studied [10,14]. Quinoline dyes are gradually giving way to other, more effective sensitizers, due to their lack of light fastness and the short life of photographic materials. However, interest in PIN has not waned.

The properties of PIN are investigated in media of a different nature: in organic solvents [55,56], in solutions with added salts [57–61], in pre-micellar and micellar systems [62–74], and in emulsions [75,76]. Temperature effects [55,64] and kinetics of spectral changes [69,70], thermal conductivity [77], viscosity [78], and flocculation [79,80] of the dye have been studied. Pinacynol has been proposed not only as a color indicator (marker) [81] but also as an organic reagent in methods for the qualitative and quantitative determination of mercury and silver [82,83], thorium (IV) [84], tungsten (VI) [85], and rhenium (VII) [86]. The actual Rayleigh scattering of PIN in solution is up to four times higher than the intensity of the theoretically expected values in the red part of the light absorption spectrum [87]. It was found that the adsorption of dye molecules on negatively charged colloids SiO₂ or SnO₂ induces the formation of H-aggregates [88]. Excitation by a 532 nm laser pulse produces a short-lived (less than 30 ps) singlet excited H-aggregate state on the SiO₂ surface. In contrast, long-lived cation radicals are observed on the surface of SnO₂ [88].

PIN has been systematically studied as a component of laser fluid media [89–98]. The dye increases the stability of femtosecond pulses and enhances the efficiency of frequency filtering [99]. Electron paramagnetic resonance spectroscopy revealed the unusual property of PIN as a photodynamic inducer in the processes of mitochondrial and nuclear mutations in yeast cells [100]. A solution of pinacyanol chloride is used to determine the singlet oxygen released during photo-irradiation in this case.

The properties of PIN in alcohol systems (methanol, propanol, isopropanol, and glycerol) [101–103], as well as in pre-micellar and micellar surfactant media [104,105] (including binary ones [105]), are investigated. The dye has proven to be an acceptable color marker for studying the properties of DNA-like structures [106–111], biological cells and tissues [112–115], enzymes [116], and antibiotics and medications [117,118].

Similar to other carbocyanines, PIN forms associated structures, both in solutions [119] and at heterophase interfaces [88,120]. The aggregation of pinacyanol acetate leads to the formation of chromic liquid crystalline phases. They are used as templates to produce mesoporous silica nanofibers, using a template sol–gel reaction [121]. By spectral and other instrumental methods, it has been set that PIN forms molecular films upon interaction with polymers [122] and even acquires optical activity by binding to DNA [123]. Dye interaction with organized structures is accompanied by relief spectral effects [124–127], so PIN has been successfully used to determine the critical micelle concentration (CMC) of anionic surfactants [128,129].

PIN is applied in the study of polysaccharide properties [130–137], dendrimers [138–140], metal-sensitive holographic sensors [141], hydrophobically modified polymers [142], oligomeric cationic surfactants [143], complex lipids and lipopolysaccharides [144–147], electron transfer mechanisms [148], complexation reactions [149,150], and supramolecu-

lar processes [151–153]. For example, UV–Vis spectroscopy is used to monitor the phase transition from micelles to vesicles facilitated by the gradual addition of lipid (cholesterol) to micellar solutions of cetyltrimethylammonium bromide. Pinacyanol chloride acts as a solvatochrome indicator that is sensitive to changes in medium polarity [153].

The interest in PIN has further increased with the development of semi-empirical, non-empirical, and molecular dynamics methods [154–159]. The energetics and structure of pinacyanol acetate-based supramolecular polymers are studied. It was shown that, when assembled in water, the dye molecules are capable of forming polyaminated supramolecular fibers [157].

Pinacyanol is one of the leading spectroscopic studies involving polymethines. Interactions with organic counterions [160–164], anionic polyelectrolytes [165–167], and the formation of host–guest complexes [168–170] are characteristic for PIN, as well as other polymethines. Such interactions significantly change the spectral properties of the systems due to the formation of ionic associates, aggregates, and molecular ensembles in solution under 5×10^{-7} – 8×10^{-5} mol/L of PIN. For such dye contents, electron spectroscopy is an indispensable instrumental method of investigation.

Of particular interest is the association of PIN with dyes of various classes or large molecules in aqueous solutions and in systems with the addition of organic solvents or surfactants. Water is a medium in which interacting protolytic and aggregative forms of dyes exhibit unique spectral–luminescent properties [171]. Under certain conditions, a self-associate or dissimilar associate of two dyes can function as an analytical reagent, a color marker, and a bioprobe. This feature is used in solving a number of topical problems. Examples are as follows: the possibility of controlling the formation of water-soluble bilayers and vesicles [172]; incorporation of photosensitive agents into materials containing cyclodextrins [173]; determination of the mechanism and kinetics of electrically charged phospholipid membranes [174], liposomes [175], and β -amyloid peptides [176–180]; search for medical and pharmaceutical drugs, including antibiotics and antitumor drugs [181–183]; and improvement of biological cell imaging technologies in biology and medicine [184]. For these reasons, PIN is very intensively studied in the processes of self- and dissimilar association [185–190].

4. Spectral, Protolytic, and Aggregative Properties of the Dye

The widespread use of PIN in various studies is due to its unique spectral and protolytic properties. The dye is stable in organic and mixed solutions, in contrast to aqueous solutions. The absorption spectrum of PIN iodide in methanol is shown in the Figure 2 (see References [191,192]; the databases are open access), and the properties of the bands are shown in Table 1.

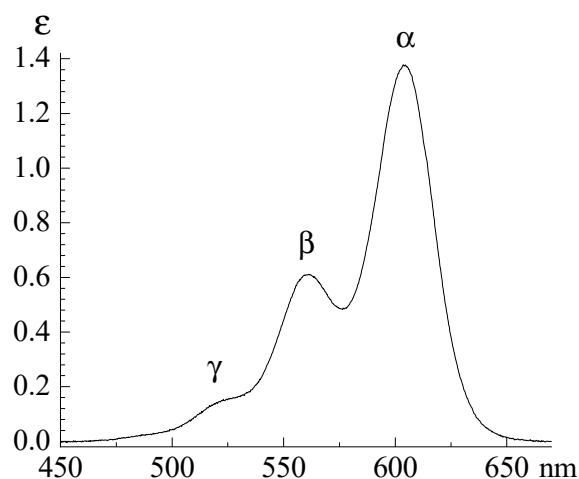


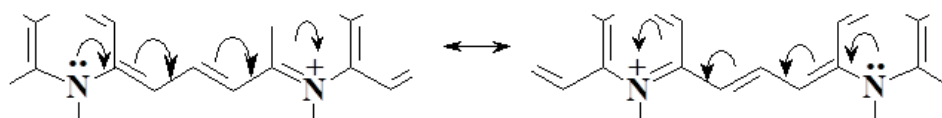
Figure 2. Absorption spectrum of PIN iodide in methanol and its constituent bands.

Table 1. Spectral properties of PIN bands.

Medium	λ_{\max} , nm (Band)	ϵ_{\max} (α -Band)
Water [82]	600 (α)	1.2×10^5
Methanol [193]	603.5 (α)	1.28×10^5
Ethanol, 30% [85]	608 (α)	1.35×10^5
Ethanol, abs. [194]	606 (α)	1.752×10^5
	563 (β)	
	522 (γ)	

The dimension of molar absorption coefficient ϵ is $L \times \text{mol}^{-1} \times \text{cm}^{-1}$ hereinafter. The quantum yield of fluorescence is 0.001 ($\lambda_{\max} = 622$ nm, methanol, excitation wavelength is 550 nm) [193]. The λ_{\max} and ϵ_{\max} values are traditionally assigned to the more energetically favorable *cis*-isomer (PIN isomerism will be discussed later). However, relaxation energy studies (excitation of molecules by 565 nm radiation) in ethanol medium also show subbands of absorption apparently inherent to the *trans*-isomer [148]. The rather developed PIN vibrational structure is more clearly visible in the absorption spectra (three bands, Figure 2) at low temperatures [193,195].

The maxima in the absorption band correspond to transitions from the lowest vibrational level of the ground state to different vibrational levels of the excited state ($S_0 \rightarrow S_1$ for the α -band). For the coordinates I_{absorb}/ν (absorption) and I_{lumines}/ν^4 (luminescence), a mirror symmetry of the absorption and fluorescence spectra of the PIN alcohol solutions at 77 K is observed [195,196]. The long-wave absorption band is due to electronic transitions in the conjugated bond system between two nitrogen atoms (Figure 3).

**Figure 3.** Alternation of π -bonds in the electronic system of the cation.

Excitation of the PIN changes the length of the polymethine fragment [195,197]. If the intensity of the α -band maximum is taken as 1, then the second (β -band) and third (γ -band) maximums have intensities of 0.305 and 0.052 (methanol; calculated values are 0.305 and 0.047) [195].

In aqueous solutions, the single-charged PIN cation (Ct^+) dominates over a fairly wide pH range of 4.5 to 9.5 (the pK_a value of the double-charged cation is 3.5 [198] 3.48 ± 0.03 [199]). PIN is protonized at a pH that is lower than 2.5 [82] and hydrolyzes markedly at a pH that is higher than 10. These protolytic processes are accompanied by the disruption of the chromophore system and consequently lead to discoloration of the aqueous solution. Reducing the dielectric constant of the medium markedly reduces the pK_a value (down to -1.39 when the dielectric constant varies from 78.36 (water) to 9.53 (82 % 1,4-dioxane) [199]).

In contrast to alcohol and other organic systems, the light absorption of PIN in water depends significantly on the concentration. The deviation of the optical density from the basic law of light absorption becomes noticeable even at relatively low concentrations of PIN (1×10^{-6} mol/L) [200].

Numerous experiments [187,190,194,199–203] show that increasing the concentration causes an increase in light absorption throughout the spectral range (Figure 4). As can be seen from curves 1–4, the intensity of the α -band with $\nu_{\max} = 16,670 \text{ cm}^{-1}$ ($\lambda_{\max} = 600$ nm) is higher than the β -band with $\nu_{\max} = 18,180 \text{ cm}^{-1}$ ($\lambda_{\max} = 550$ nm), while the situation is reversed on curves 5 and 6. At concentrations greater than 1×10^{-4} mol/L, the γ -band $\nu_{\max} = 19,610 \text{ cm}^{-1}$ ($\lambda_{\max} = 510$ nm), which is characteristic of H-type self-aggregates, becomes noticeable [201]. Spectral changes in coordinates $A \times C^{-1} \times I^{-1}$ vs. ν (Figure 5; normalized spectra of PIN are presented) indicate a redistribution of

the intensities of the α - and β -bands [190,194,202,203]. This phenomenon has been interpreted as the conversion of the PIN monomer into a dimer (Ct_2^{2+}) [190,201]. Similar band redistribution is also observed at elevated temperatures [202], and not only in water but also in media with small additions of organic solvents (e.g., in mixtures of ethanol (7.5%) with water [194] or 5% mixtures of ethylene glycol, 2-methoxyethanol, dioxane, tetrahydrofuran, ethylamine, diethylamine, triethylamine, ethanolamine, diethanolamine, and triethanolamine with water [203]). On the contrary, lowering the temperature of the solution induces the dimerization of PIN. This fact was first brought to the attention of S. Sheppard and H. Brigham back in 1944. By using mixtures of ethanol with methanol, diethyl ether, and hexane, they were able to lower the temperature of the solutions from 298 to 202 K, and even to 108 K. Under these conditions, a relative increase in the intensity of the β -band and the manifestation of the γ -band as the temperature decreases has been observed [55].

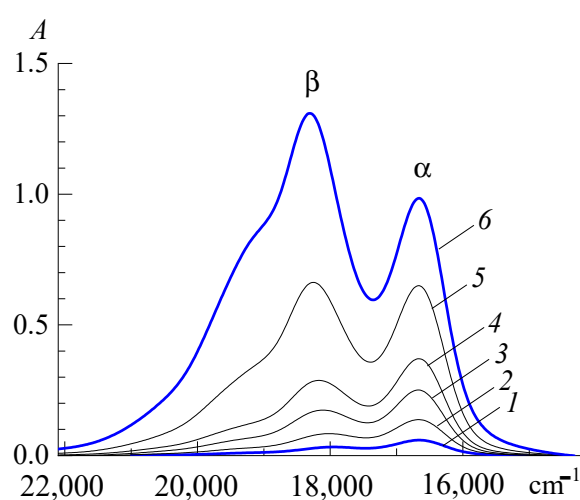


Figure 4. Redistribution of absorption band intensities of PIN in water. Concentration, mol/L: 2.1×10^{-6} (1), 4.1×10^{-6} (2), 6.2×10^{-6} (3), 8.2×10^{-6} (4), 1.9×10^{-5} (5), and 3.1×10^{-5} (6). The thickness of the absorbing layer is 1.00 cm; pH = 6.4.

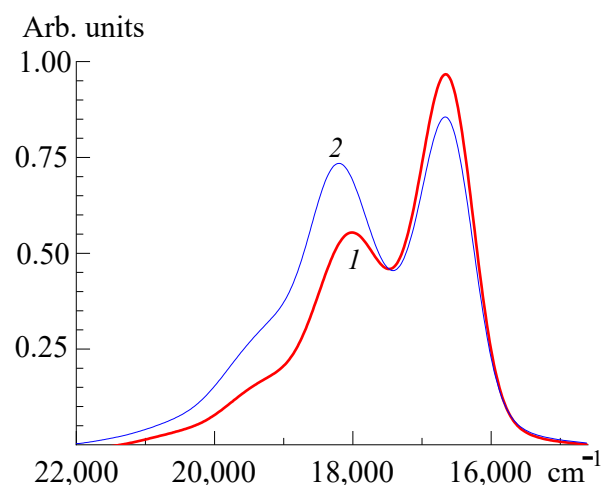


Figure 5. Normalized spectra of two concentration of PIN in water. Concentration, mol/L: 2.2×10^{-6} (1) and 8.2×10^{-6} (2); pH = 6.4.

The appreciable self-association of PIN in water is due not only to the high value of the dielectric constant but also to the manifestation of hydrophobic interactions [203]. The latter are particularly characteristic of planar structures, including cyanines [160–164,171,185–190,195,204]. As for non-aqueous or organic solvents mixed

with water, the basic law of light absorption is observed in a much wider concentration range; the absorption intensity of the α -band is greater than that of the β -band at higher concentrations of the dye. The maxima of the α - and β -bands of PIN monomer in monatomic *n*-alcohols, DMSO, acetone, and chloroform are bathochromically shifted with respect to the aqueous spectrum. The α -band shift increases with hydrocarbon radical lengthening and is 4.61 nm (methanol), 13.33 nm (1-octanol), and 17.52 nm (benzyl alcohol) [205]. The value of the bathochromic shift of the α -band is linearly dependent on the dielectric constant of the solvent for a number of the pure alcohols (from methanol to 1-octanol) [199,206].

The normalized absorption spectrum of the monomeric form of PIN in water has four overlapping bands (the deconvolution model is an equally flat Gaussian; the search for the positions of the maxima was carried out by using the second derivative) [190] (Figure 6).

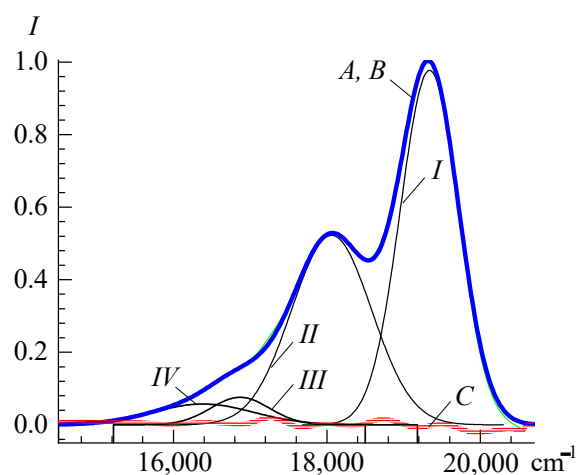


Figure 6. Normalized spectrum of PIN monomer (A); the algebraic sum (B) of bands I_M (I), II_M (II), III_M (III), and IV_M (IV); and the difference (C) of curves A and B.

The very narrow corridor of the optical density difference curve (not more than ± 0.018 units, $C = A - B$) indicates the coincidence of the experimental (A) and total (B) light absorption curves and, therefore, the eligibility of the light absorption curve contour as a sum of four bands (Table 2). Spectrum B (Figure 6) has the following features: ν_{\max} , cm^{-1} , 17,920 (558.0 nm) and 16,680 (599.5 nm); and the surface area is 1762.2 cm^{-1} . Deconvolution calculation procedures may vary and the number of bands may be different. For example, the authors of Reference [202] point out that five bands are possible, but conclude that only three of them are significant. However, it must be considered whether there is a statistical difference between the parameters of each band and the error in the experimental determination of the light absorption intensity values (as a rule, not more than 3%), as well as the error in the calculation of the band area [207,208]. Furthermore, it makes sense to relate deconvolution results to the existence of one or another particle type (monomer, dimer, or self-aggregate) at specific dye concentrations. The consideration of these circumstances leads to the conclusion that four bands [190] are valid in the aqueous spectrum of PIN monomer. The ratio of the intensities of the maximums for the bands is as follows: $I_M:II_M:III_M:IV_M = 1:0.53:0.078:0.058$. Meanwhile, the IV_M band ($\nu_{\max} = 19,614 \text{ cm}^{-1}$, $\lambda_{\max} = 509.7 \text{ nm}$) indicates the existence of more aggregated forms of PIN, that is, H-aggregates (with $\nu_{\max} = 19,610 \text{ cm}^{-1}$, $\lambda_{\max} = 510 \text{ nm}$, and γ -band [201]). Note that the closely spaced bands III_M and IV_M have similar intensities. When the temperature rises from room temperature to 325 K [202], these bands practically merge into one, and the I_M and II_M bands change insignificantly. A similar situation is observed for somewhat higher concentrations of PIN, even at normal temperatures (e.g., for $4.32 \times 10^{-6} \text{ mol/L}$ according to [176]); their ratio of band intensities was found to be 1:0.49:0.21. In the methanol medium [193], three bands of the general absorption spectrum contour were also identified. The ratios obtained from the experimentally measured spectrum of 1:0.305:0.052 (calculated as 1:0.305:0.047) are known. The normal-logarithmic

deconvolution of the PIN spectrum (5×10^{-5} mol/L) also demonstrates three bands in the micelles of *n*-tetradecyltrimethylammonium bromide $C_{14}H_{38}NBr$ [205].

Table 2. Features of normalized PIN monomer bands.

Feature	Band			
	I _M	II _M	III _M	IV _M
ν_{\max} , cm^{-1}	16,661	17,939	19,132	19,614
λ_{\max} , nm	600.2	557.4	522.3	509.7
<i>I</i> , relative units	0.977	0.522	0.076	0.057
Half-width, cm^{-1}	892	1205	916	1543
Surface area, cm^{-1}	925.0	669.3	73.8	94.1

An experimental study of the self-association of $n\text{Ct}_2^{2+} \rightarrow \text{Ct}_n^{n+}$ requires the creation of higher concentrations of the dye. However, this is hindered by the limited solubility of PIN in water. This can create an additional error in the measurement of the light absorption of concentrated PIN solutions.

The equilibrium dimerization constant $2\text{Ct}^+ \rightleftharpoons \text{Ct}_2^{2+}$ is determined on a combination of the basic law of light absorption, the law of acting masses, the conditions of material balance, and the principle of additivity of optical density [202,203,209]:

$$A(\lambda) = \varepsilon_D(\lambda) \times \left(\frac{C}{2} - \frac{-1 \pm \sqrt{1 + 8K_D \times C}}{8K_D} \right) + \varepsilon_M(\lambda) \times \left(\frac{C}{2} - \frac{-1 \pm \sqrt{1 + 8K_D \times C}}{4K_D} \right),$$

where *A* is the optical density at a wavelength of λ , $\varepsilon_M(\lambda)$ and $\varepsilon_D(\lambda)$ are the coefficients of molar light absorption of the monomer and dimer at a wavelength of λ , *C* is the initial molar concentration of PIN, and K_D is the equilibrium dimerization constant. This ratio ignores the presence of higher-order self-associates. The nonlinear approximation of the least squares method gave the values $K_D = 35,002$ L/mol (294.16 K; the calculated spectra of the monomer and dimer were used, and the presence of particles of higher orders of dye aggregation in the solution was taken into account) and $K_D = (350 \pm 5) \times 10^2$ L/mol [202,209]. Spectrophotometrically, the value $\log \beta_{20} = 4.59 \pm 0.06$ has been obtained for the thermodynamic (ionic strength $I \rightarrow 0$) dimerization constant $\beta_{20} = a_D \times a_M^{-2}$, $\beta_{20} = (A_\lambda - \varepsilon_M \times C \times l) \times (\varepsilon_D \times l - 2\varepsilon_M \times l) \times (C \times \varepsilon_D \times l - 2A_\lambda)^{-2}$, where a_M and a_D are monomer and dimer activities, and *l* is the thickness of the absorbing layer [190]. An increase in temperature to 325.16 K lowers K_D by about five times, and the dimerization process is exothermic (the standard Gibbs energy is -25.59 kJ/mol at 294.16 K [202]).

The formation of higher-order aggregated particles under certain conditions can be observed in non-aqueous or mixed systems. One example is a mixture of “ethanol (7.5%)–water (92.5%)” at a PIN concentration of 7.5×10^{-5} mol/L. Deconvolution of the two-band spectrum (601 and 546 nm), using the PeakFit program, reveals seven constituent bands with maxima at 601, 572, 557, 546, 522, 507, and 486 nm (the deconvolution model uses the fourth derivative of the light absorption curve) [194]. The calculated values of the molar absorption coefficient are 1.92×10^5 , 1.56×10^5 , 2.82×10^5 , and 3.765×10^5 for the maxima of the monomer (601 nm), dimer (546 nm), trimer (522 nm), and tetramer (507 nm) bands respectively. It is noteworthy that the data obtained are in satisfactory agreement with the value $\varepsilon_{\max} = 1.42 \times 10^5$ for the PIN dimer located in the cavity of γ -cyclodextrin [210].

The properties of PIN in mixed aqueous–organic solutions (with 5% of organic component under 303.15 K) [203] demonstrate the importance of hydrophobic interactions as a driving force of self-association. Dye aggregates are better stabilized in a more hydrophobic environment (alkylamines), despite the lower dielectric constant of mixed solvents with respect to water. In the ethylamine–diethylamine–triethylamine series, the dielectric constant changes insignificantly (76.51 ... 76.37 ... 76.31), but the dimerization constant of PIN increases appreciably (1.873×10^4 ... 2.089×10^4 ... 2.424×10^4) [203].

The values given for the dimerization constant of PIN in water are quite similar, despite the different approaches in the calculations used. However, it should be noted that different methods often produce statistically different results. For example, it has been noted [190] that, for rhodamine B, the $\log \beta_{20}$ value takes from 2.98 ± 0.03 [211] to 3.24 ± 0.02 [212,213]. PIN is inferior to only a few carbocyanines (e.g., 3,3'-diethylthiatricarbocyanine with a constant of 2.4×10^5 [214]) in dimerization ability, surpassing safranin T (the $\log \beta_{20}$ value is 2.41 ± 0.01), methylene violet (2.66 ± 0.01), rhodamine 6G (3.35 ± 0.01), and methylene blue (3.70 ± 0.01) [215]).

The normalized absorption spectrum of the PIN dimer in water is interpreted as consisting of three bands (Figure 7 and Table 3) [190,202].

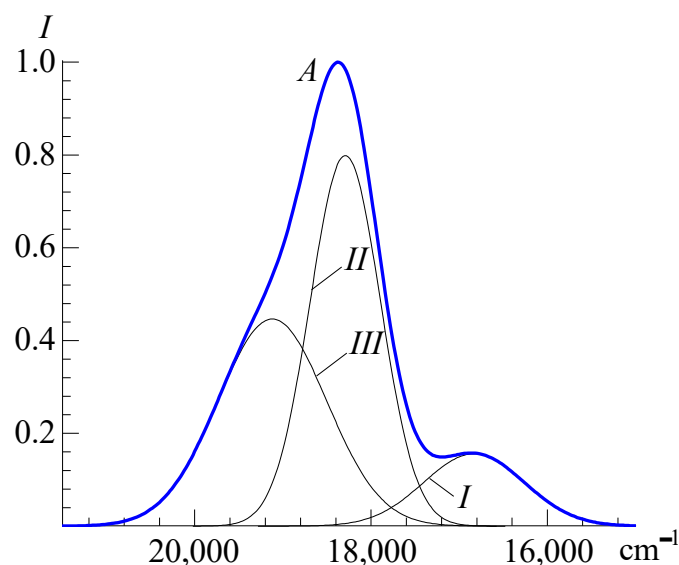


Figure 7. Normalized spectrum of PIN dimer in water (A). Bands: I_D (I), II_D (II), and III_D (III).

Table 3. Features of normalized PIN dimer bands.

Feature	Band		
	I_D	II_D	III_D
$\nu_{\max}, \text{cm}^{-1}$	16,840	18,300	19,120
$\lambda_{\max}, \text{nm}$	593.8	546.5	523.0
I , relative units	0.156	0.798	0.446
Half-width, cm^{-1}	1340	950	1444
Surface area, cm^{-1}	223.5	800.1	688.4

Spectrum A (Figure 7) has the following features: $\nu_{\max}, \text{cm}^{-1} = 18,380$ (544.1 nm) and 16,840 (593.8 nm); and the surface area is 1712.0 cm^{-1} . A comparison of the data in Tables 2 and 3 shows that the α -band intensity in dimer (I_D) is significantly lower than in monomer (I_M), and the course of spectral changes in Figure 4 is explained by the increasing intensity of band II_D and decreasing intensity of band I_D . An analysis of the spectra of the monomer and dimer leads to an unobvious conclusion: even in the “monomer” PIN, the bands inherent to the dimer and H-aggregates (γ -band) are recognized [190]. This is indicated by the almost identical arrangement of the III_M and III_D absorption bands, as well as the IV_M band and the H-aggregate spectrum given in S. Sheppard’s publication [201]. The two-band spectrum of the dimer can be explained by Davydov’s splitting effect [216]. This is observed when two neighboring molecules are arranged at some (less than 90°) angle to each other [164,217]. The first of the bands is hypsochromic with respect to the monomer and is related to H-type self-aggregation (coplanar arrangement of chromophores,

“one above the other”), while the bathochromic band is related to J-type self-aggregation (arrangement of chromophores in one plane, “adjacent to each other”).

5. Structural and Thermodynamic Features of the Dye

The PIN cation has a planar structure; only the ethyl groups of are not in the plane of the heterocyclic system due to the sp^3 -hybridization of the carbon atoms of the alkyl groups. Assuming that the aromaticity is distributed over all π -electron fragments of the cation, the rotation angle in relation to axis 1 (see Figure 8) ranges from 4.6° to 6.7° (vacuum, semi-empirical methods AM1, PM3, PM7; MOPAC, GAMESS packages [190]).

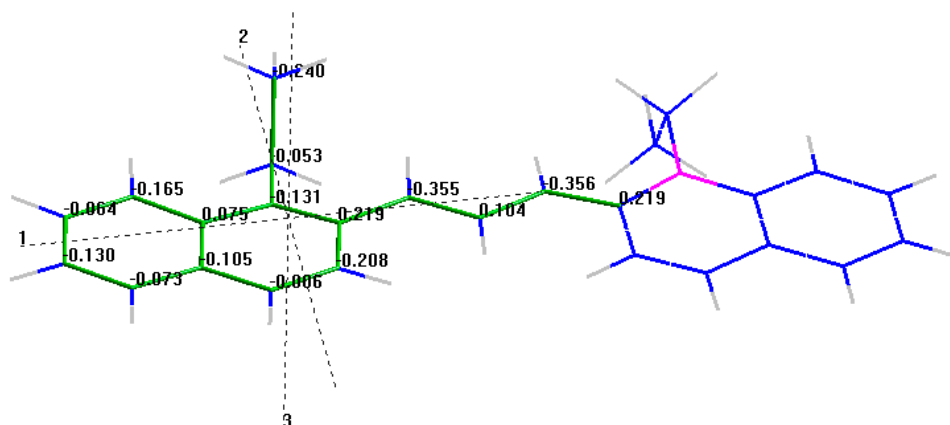


Figure 8. Electron density in PIN cation (AM1 semi-empirical method; hydrogen is gray, nitrogen is violet, and some carbon atoms show electron density or are marked in blue).

A slightly larger angle of rotation along the polymethine chain is given by calculations for the boundary resonance positions (alternating single and double bond) and calculations using non-empirical methods. For example, the rotation angle is 23.4° (the GIAO-HF/DFT method using the B3LYP/6-31G (d) basis [218]), or 8° (DFT/B3LYB, 6-31G basis [219]) and even $\sim 36^\circ$ (MM2 method and molecular orbitals calculation [202]). The transition of the cation to an excited state also entails disruption of the planar conformation [95,98,220].

The discrepancy in the semi-empirical calculations of the standard enthalpy of formation of PIN ($\Delta_f H^\circ$) is not more than 11%. The AM1 method gives values of 1070.9 kJ/mol (MOPAC) and 1110.6 kJ/mol (GAMESS), the PM3 method gives 965.9 and 974.2 kJ/mol respectively, and the MNDO method gives 1121.7 and 1125.2 kJ/mol [190]. Taking into account the systematic error of semi-empirical calculations, we see that these $\Delta_f H^\circ$ values are very close to each other. However, there is no unambiguity with regard to the electron density distribution on heteroatoms. The AM1, MNDO, and CNDO methods on nitrogen atoms give $-0.13 \dots -0.25$ (see “ -0.131 ” in Figure 8, AM1 method), the Hartree–Fock method (HF, 6-31G basis) gives -1.13 , whereas the PM3 method gives $+0.31$ (MOPAC, GAUSSIAN, GAMESS) [190]. Obviously, significant differences in electron densities are due to the particular parameterization of one or the other method. One must also take into account the fact that the electron density at the atom is not a measurable quantity, in contrast to, for example, the dipole moment of a molecule [218]. In addition, differences in the geometry of the molecular system may be the cause of the ambiguity of the electron density on the atoms.

The isomerization of *cis*- and *trans*-positions is possible for the PIN cation. A uniform distribution of the electron density is observed at the lowest angle of rotation of the polyene hydrocarbon chain. The electron density symmetry is broken when the heterocyclic fragments are mutually rotated. The calculation of the electron oscillation forces for a number of different conformers leads to the conclusion [190] that the *cis*-conformation of the PIN is more energetically stable. However, under certain conditions (changes in the dielectric constant of the medium) a *trans*-isomer is also possible (e.g., in ethanol [148]).

Isomerization is also possible for a dimer. In a *cis*-dimer, the ethyl radicals of the two cations point in the same direction. A *trans*-dimer is characterized by an opposite arrangement of ethyl radicals. Its cation planes are nearly coplanar, while for the *cis*-dimer, no predominant arrangement can be calculated. In the latter case, the total energy values of the two cations are found to be approximately the same for several different mutual arrangements of the two cations. For this reason, the *trans*-dimer is more energetically advantageous. The self-association of the PIN *trans*-dimer (Figure 9; stereo image; distance between the planes of the structure is equal to 3.7 ... 3.8 Å; the energy is 79.1 kcal/mol, and MM+ method) leads to the experimentally observed H-aggregates [201,221].

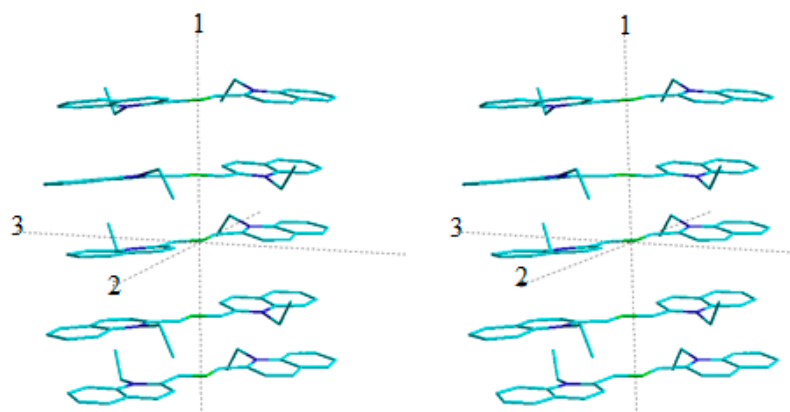


Figure 9. Optimized construction of PIN pentamer (no hydrogen atoms are shown).

6. Intermolecular Interactions Involving PIN

The processes of interactions involving PIN are accompanied by a rather complex combination of different forces, including non-Coulomb, π -electronic, and solvophobic effects. Below we focus on some of them, including multi-atomic organic molecules (dyes), metal complex particles, and surfactants.

A spectral feature of cation–anion interactions in solutions involving dyes is the significant change in the intensity of the PIN absorption bands. A typical example is the aqueous system of “PIN + bromocresol purple (BCP)”. The light absorption bands of HAn^- and An^{2-} forms of BCP have $\lambda_{\text{max}}(\text{HAn}^-) = 430 \text{ nm}$ and $\lambda_{\text{max}}(\text{An}^{2-}) = 588 \text{ nm}$ with $\epsilon_{\text{max}}(\text{HAn}^-) = 24,900$ and $\epsilon_{\text{max}}(\text{An}^{2-}) = 67,200$. For this reason, the absorption bands of BCP^- and Ct^+ are well spectrally spaced.

As the initial concentration of BCP increases (Figure 10, curves 2–7), the intensity of the short-wave part of the spectrum increases, which is related to the light absorption of the single-charged sulphonephthalein anion (hereafter, arrows indicate the direction of the spectral shift). At the same time, a decrease in the intensity of the light absorption of the α -band of PIN is noticeable. The absorption bands of BCP^{2-} and Ct^+ are mutually superimposed. However, also in this case, a decrease of the α - and β -bands intensity of PIN for the mixture “ $\text{Ct}^+ + \text{BCP}^{2-}$ ” is detected if the absorption spectra of the system are measured not against water but against a solution with the same concentration of sulphonephthalein (Figure 11).

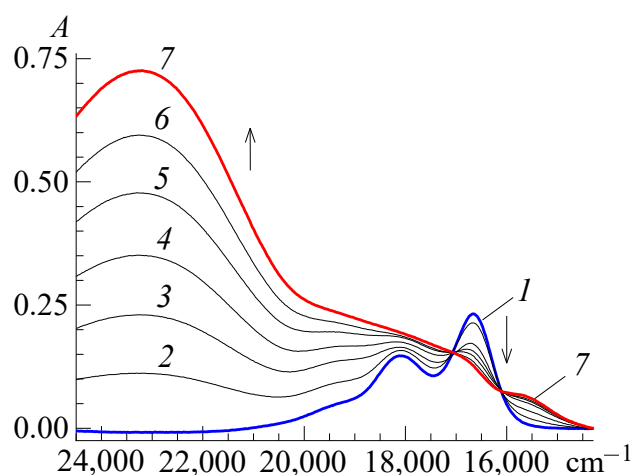


Figure 10. Absorption spectra in the system “Ct⁺ + BCP⁻”. Concentrations, mol/L; PIN, 4.4×10^{-6} (1–7); BCP, 0 (1), 3.1×10^{-6} (2), 5.0×10^{-6} (2), 1.0×10^{-5} (3), 1.5×10^{-5} (4), 2.0×10^{-5} (5), 2.6×10^{-5} (6), and 3.0×10^{-5} (7). The thickness of the absorbing layer is 1.0 cm; pH = 4.7. Comparison solutions are water.

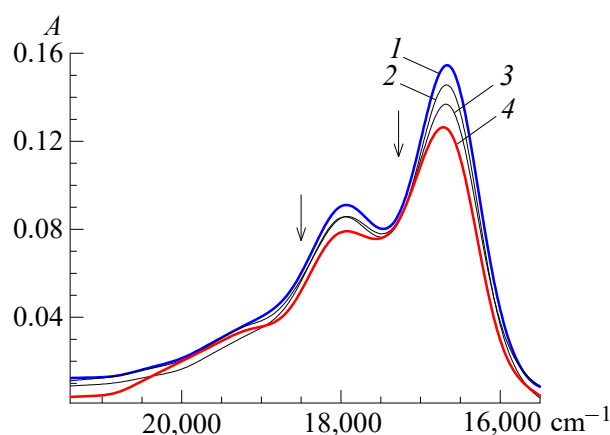


Figure 11. Absorption spectra in the system “Ct⁺ + BCP²⁻”. Concentrations, mol/L; PIN, 5.4×10^{-7} (1–4); BCP, 0 (1), 1.2×10^{-6} (2), 2.6×10^{-5} (3), and 5×10^{-5} (4). The thickness of the absorbing layer is 5.0 cm; pH = 9.1. Comparison solutions are water (1) and BCP solution at the appropriate concentration (2–4).

Similar effects have been observed for systems involving not only PIN [171,186–188,190,200] but also other polymethine dyes [162,171,185]. In all cases, the analysis of the electronic absorption spectra of mixtures of dyes reveals a violation of the additivity principle of light absorption. The optical density of the mixture is systematically lower than the total absorbance of the individual ions. This phenomenon is observed over a fairly wide range of initial concentrations of both PIN (4.9×10^{-7} – 4.8×10^{-5} mol/L) and other dyes. Similar cases are observed in the interaction of PIN with phenolsulfonephthalein [190,222,223], its alkyl [223–225] and halogen derivatives [187,226,227], oxyxanthenes [187,228], alizarines [229,230], xylenol orange [231], arsenazo II [232], and anionic rhodamine 200C [233], as well as with colorless bulky organic anions (tetraphenylborate [200]), polyelectrolytes (humic acids [232,234]). Spectral shifts in the absence of new or splitting of existing bands indicate a solvate-separated type of associative structure (in accordance with the general features of spectral shifts for associative dye systems [161,163,171]). The results of numerous studies give us reason to consider PIN as a kind of “colored” cation standard in the spectral study of supramolecular cation–anion interactions.

Both the Ct⁺ monomer and the Ct₂²⁺ dimer interact with organic bulk anions. However, the association of Ct⁺ under the influence of excess anion is not accompanied by

dimerization of the Ct^+ (in contrast, for example, to some cyanines, bisindocarbocyanines, which induce the formation of dimeric particles upon interaction with borate anions [235]) or H-aggregation (in contrast to the interaction of cyanines with DNA duplexes [236]). PIN interactions have also been experimentally detected with dissimilar associates [171,187,200]. The PIN cation is involved in the formation of more complex particles: $(Ct^+)_j \cdot An^{j-} + kAn^{j-} \rightleftharpoons (Ct^+)_j \cdot (An^{j-})_{k+1}$. However, the nature of these interactions cannot be studied in more detail due to the aggregative instability of such systems. Nevertheless, a similar mechanism has been established by 1H NMR spectroscopy in the systems “daunomycin + ethidium bromide” [237] and “acridine orange + caffeine” [238]. Inorganic ions at the same low concentrations do not cause noticeable spectral changes.

The association of the PIN with various counterions is characterized by common spectral signatures. This includes the presence of an isosbestic point (similar to Figure 10) and areas of “saturated” optical density. The interactions of PIN or other cationic polymethines with anions are considered according to the equilibrium model: $jCt^+ + An^{j-} \rightleftharpoons (Ct^+)_j \cdot An^{j-}$ [171,185,187,190,230,232,239]. The equilibrium association constant (K_{as}) can be calculated on the basis of the mass action law:

$$K_{as} = [(Ct^+)_j \cdot An^{j-}] \times (C_{An^{j-}} - [(Ct^+)_j \cdot An^{j-}])^{-1} \times (C_{Ct^+} - j \times [(Ct^+)_j \cdot An^{j-}])^{-j},$$

where $[(Ct^+)_j \cdot An^{j-}] = (\epsilon_{Ct^+} \times C_{Ct^+} \times l - A) \times (j \times \epsilon_{Ct^+} - \epsilon_{as})^{-1} \times l^{-1}$, and the equilibrium molar concentration of particles are in brackets; $C_{An^{j-}}$ is the initial molar concentration of the anion; C_{Ct^+} is the initial molar concentration of PIN; l is the thickness of the absorbing layer, cm; A is the optical density of the solution; and ϵ_{Ct^+} and ϵ_{as} are the molar extinction coefficients of cation and an associate, respectively.

When the ionic strength of the solutions is low, the concentration value of K_{as} practically does not differ from the thermodynamic value (Table 4; the data are given according to References [187,190,222–228,230]). Note that the ratio of stoichiometric coefficients in dissimilar associates is determined not only by the electrostatic factor, but also by the effect of π -electron fragments of counterions. An example is the associate of the monomeric form of the PIN with the single-charged spherical tetraphenylborate-anion (TfB^-). Interaction occurs according to the scheme: $2Ct^+ + TfB^- \rightleftharpoons (Ct^+)_2 \cdot TfB^-$ with $\log K_{as} = 13.4 \pm 0.1$ [200]. An indirect confirmation of this association is the fact that the calculations result in meaningless negative K_{as} values for 1:1 stoichiometry. Other examples are the interactions of PIN with multiply charged anions of humic acids. The $\log K_{as}$ values are from 1.74 ± 0.12 to 3.09 ± 0.03 depending on the composition of the polyelectrolyte [234]. Moreover, the stoichiometry is not directly related to the charges of anionic particles in PIN associates with arsenazo II [232].

Table 4. Dissimilar associates of Ct^+ with dyes.

A Dye	$\log K_{as}$	
	$Ct^+ \cdot An^-$	$(Ct^+)_2 \cdot An^{2-}$
Alizarin red C	6.12 ± 0.10	10.92 ± 0.10
Bengal Rose B	6.91 ± 0.12	13.46 ± 0.11
Bromocresol green	6.74 ± 0.04	12.09 ± 0.09
Bromocresol purple	6.67 ± 0.05	11.07 ± 0.10
Bromophenol blue	6.88 ± 0.05	13.73 ± 0.10
Bromothymol blue	5.95 ± 0.11	10.89 ± 0.09
Cresol red	4.59 ± 0.03	10.96 ± 0.10
Eosin	5.15 ± 0.09	11.25 ± 0.10
Erythrosin	6.60 ± 0.12	11.84 ± 0.10
Ethyleosin	5.45 ± 0.09	–
Fluorescein	4.58 ± 0.11	9.75 ± 0.10
Phenol red	5.83 ± 0.10	11.81 ± 0.10
Tetrabromophenylfluoron	6.38 ± 0.11	–
Thymol blue	5.29 ± 0.05	11.0 ± 0.1

The K_{as} values for the dye associates (Table 4) are comparable with the known values of similar values for the complexation process [161,163,171].

The rather high K_{as} values may indicate the formation of contact ionic associates in the solution. The dye association process is characterized by some deformation of the flattened π -electron system of the PIN (Figure 12; AM1 method; stereo image; the distance between neighboring marked in green ions is 4.6 ... 5.0 Å, and the inner central angle with the vertex on the central carbon atom of the PIN polymethine chain equals 144°).

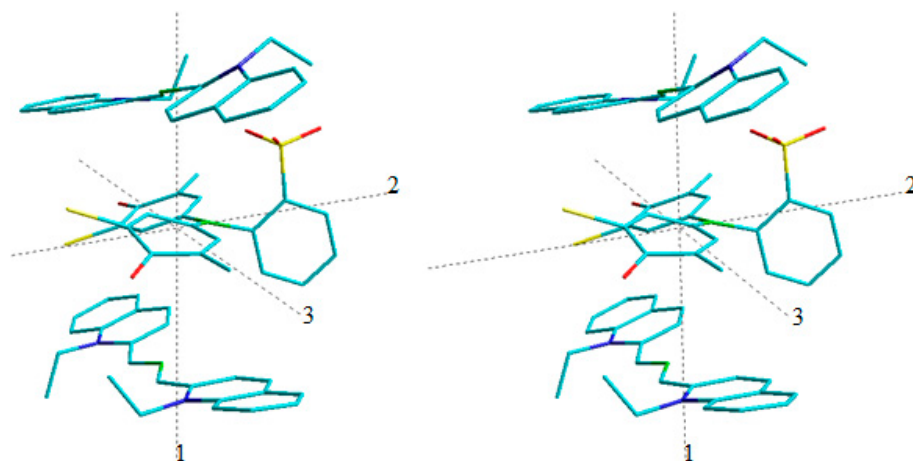


Figure 12. Dissimilar Ct^+ associate with BCP^{2-} (anion is located in the middle; no hydrogen atoms are shown).

The equilibrium nature of dissimilar associates is experimentally confirmed by the fact of their destruction under the influence of ionic surfactant additives: in micellar systems, the absorption band contours of each dye are practically restored [171,186,233,240].

The interaction of the PIN cation, not only with anions but also with cationic dyes, was found experimentally. The effect of flattened cations of neutral red (NR) and astrafloxin (AF) on PIN is not obvious [241]. AF and NC form singly charged cationic forms in aqueous solution (λ_{max} are 540 and 535 nm, respectively). AF predominates in the cationic form at pH 3.0–9.5, and NR at pH 1–5 (according to various estimates pK_a is 6.5–7.4 of the NR cationic form; see the discussion of these values in Reference [241]). Our analysis of the spectral changes leads to the conclusion that, in addition to the disturbance of the additivity of light absorption, hyper or hypochromic effects are observed depending on the concentration of PIN. Increasing the concentration of the indocarbocyanine dye AF ambiguously alters the initial absorption of PIN. At 3.0×10^{-6} mol/L, and by increasing the AF concentration from 3.0×10^{-6} to 9.0×10^{-6} mol/L, the light absorption of PIN increases throughout the spectral range, while the position of the α - and β -bands of PIN does not change. The situation is different if the initial concentration of PIN is about 10 times higher. Increasing the AF concentration from 1.0×10^{-5} to 7.0×10^{-5} mol/L first increases the light absorption and then (at more than equimolar concentration) significantly weakens it. The dimeric form of PIN, interacting with AF, tends to form an additional absorption band with a maximum of 519 nm ($19,250 \text{ cm}^{-1}$).

Thus, the spectral changes observed during “cation + cation” association depend on the structure of the dyes. The appearance of a new absorption band could be due to the rather close arrangement of the flattened chromophore systems in the “contact” associate of PIN with AF. The electrostatic repulsion of the cations of the two dyes is compensated by the affinity of their developed π -electronic systems. The stronger the induced electrostatic field and the more similar the chromophores are in the nature of π -electronic systems (e.g., PIN and AF have the same polymethine fragments), the stronger the resonance interactions appear; they lead to the appearance of new absorption bands. The formation of new bands has been observed in the interaction of identically charged dye ions in non-aqueous and

mixed media (e.g., for cyanine dyes in non-polar solvents [162]) and even for oppositely charged ions (interaction of rhodamine 6G with bromothymol blue [242]).

This conclusion is supported by the study of the interactions of PIN with the multi-charged anions (Figure 13) of organic reagents (arsenazo II), with polyelectrolytes [232], and with the metal complex ions $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$, which have a high negative charge [243,244].

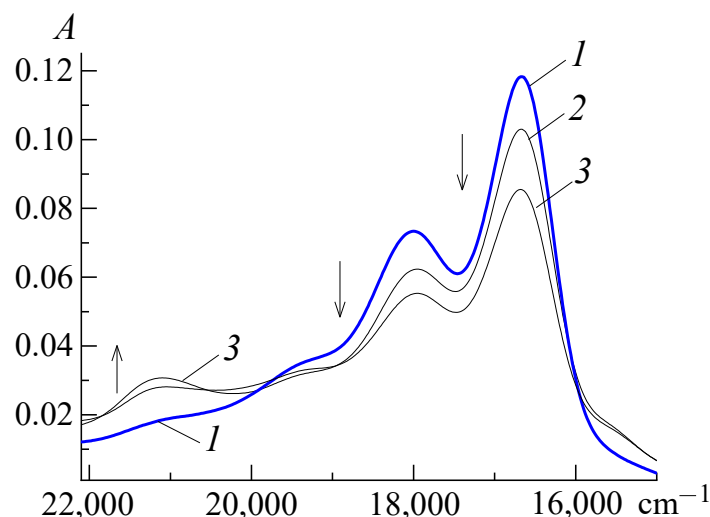


Figure 13. Absorption spectra in the system “ $\text{Ct}^+ + \text{K}_4[\text{Fe}(\text{CN})_6]$ ”. Concentration, mol/L; PIN, 1.4×10^{-6} (1–3); $\text{K}_4[\text{Fe}(\text{CN})_6]$, 0 (1), 4.1×10^{-6} (2), and 1.7×10^{-5} (3); pH = 6.8. The thickness of the absorbing layer is 1.00 cm. Comparison solutions are water.

It was experimentally found that, as increasing amounts of anion are added to the unchanged content of pinacyanol in aqueous solution, the α - and β -bands of PIN decrease in light absorption, similar to the cation–anion dye interactions discussed above. However, in addition, a new short-wavelength band appears (Figure 13) with $\lambda_{\text{max}} = 475 \text{ nm}$ ($21,050 \text{ cm}^{-1}$). Remarkably, the spectral changes occur at low initial concentrations of the dye (1.0×10^{-6} – 4.0×10^{-6} mol/L), at which its monomeric form dominates. Changes in optical density occur at anion concentrations that are even lower than the PIN concentration.

The manifestation of the short-wave band is induced not only by interaction with multi-charged inorganic ions, but also by an increase in the ionic strength of the aqueous solution. In this case, high concentrations of electrolyte salts favor a change in the hydrate environment of the PIN cation. As the ionic strength (I) of the solution increases by increasing the concentration of potassium chloride, the intensity of the α - and β -bands decreases markedly. A new short-wave absorption band appears, as evidenced by the deconvolution of the light absorption curve (Figure 14; the deconvolution model is similar to Figure 6, $I = 0.2$). Table 5 details the characteristics of the normalized spectrum components.

The experimental spectrum (curve A) is characterized by absorption bands with maxima of $18,140 \text{ cm}^{-1}$ (551.21 nm), $I = 0.6910$; and $16,660 \text{ cm}^{-1}$ (600.24 nm), $I = 1.000$ un. The total (spectrum B of five bands) has $18,140 \text{ cm}^{-1}$ (551.27 nm), $I = 0.6924$ un.; and $16,680 \text{ cm}^{-1}$ (599.62 nm), $I = 0.9863$ un. There is practically no difference between the experimentally measured light absorption (A) and the calculated sum (B) of the components of the five bands, 1–5. Bands 1–4 belong to the PIN cation (as indicated above), while the new band (5) indicates the tendency of the cation to self-association due to decreasing in the distance between neighboring dye cations, and some enhancement of the resonance interactions.

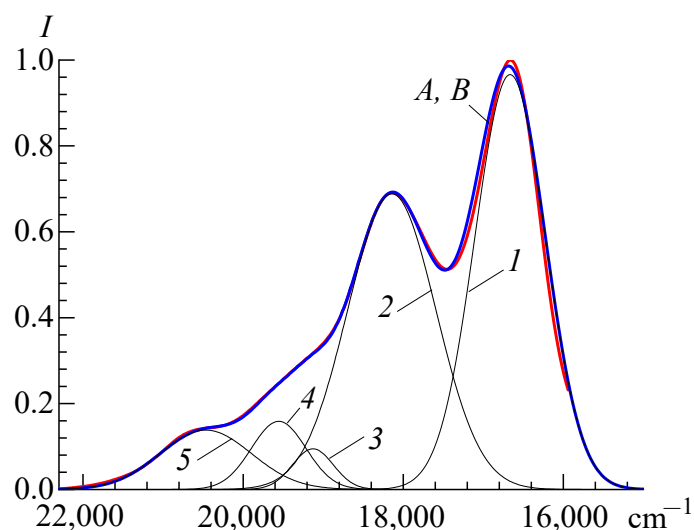


Figure 14. Normalized absorption spectrum of Ct^+ with potassium chloride at $I = 0.2$ and its constituent bands.

Table 5. Absorption bands of the normalized absorption spectrum (Figure 14) of PIN.

Feature	Band				
	1	2	3	4	5
ν_{\max} , cm^{-1}	16,665	18,140	19,120	19,560	20,460
λ_{\max} , nm	600.24	551.27	523.01	511.25	488.76
I , relative units	0.966	0.6887	0.0947	0.1587	0.1382
Half-width, cm^{-1}	1011	1297	596	804	1349
Surface area, cm^{-1}	1039.120	947.033	60.144	135.700	198.255

7. PIN in Surfactant-Containing Systems

“Dye + surfactant” systems occupy a special place among supramolecular interactions. In fact, there is no class of dyes that has not been studied in the context of interactions with surfactants. In practical terms, these systems are widely used for the quantitative determination of pharmaceutical components, in the chemical analysis of surfactants, in the creation of polyintercalated and aggregated structures, in medical and biological research (study and modification of DNA and polypeptide structure), and in other areas. Pinacyanol is no exception in this aspect [186,199,205,230,240,245,246].

Surfactants have a significant influence on the spectral and protolytic properties of dyes in the premicellar and micellar concentration ranges. In the premicellar concentration range, compounds (cation–anionic associates) with different stoichiometry are formed between dyes and surfactants. In the micellar region, surfactants act as a microenvironment in which the dielectric constant is lower than that of water.

For electrostatic reasons, the interaction between the Ct^+ and the cationic surfactant is not sufficiently appreciable. Indeed, premicellar and even micellar contents of cetylpyridinium bromide (CPB) do not change the shape of the absorption bands of PIN over a wide range of own concentrations from 1×10^{-6} to 5×10^{-5} mol/L (Figure 15); some bathochromic shift of the absorption bands [186] relative to pure water is noticeable in the micelles.

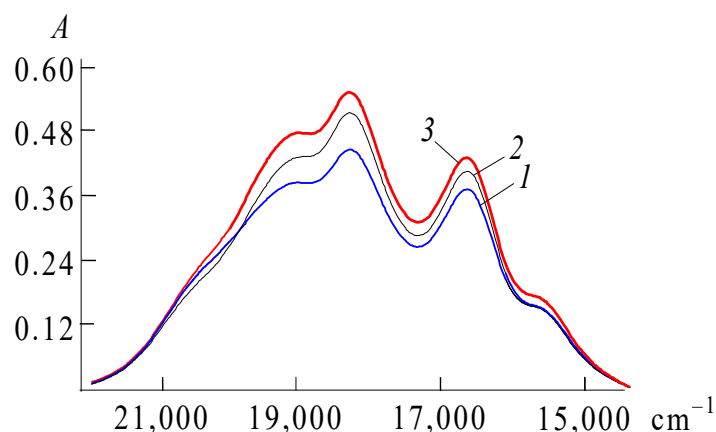


Figure 15. Light absorption of PIN at different content of CPB. Concentration, mol/L; PIN, 4.7×10^{-5} (1–3); CPB, 0 (1), 4×10^{-6} (2), and 2×10^{-3} (3); pH = 6.9. The thickness of the absorbing layer is 0.20 cm.

Only high concentrations (0.9 mol/L) of branched bromide *n*-tetradecyltrimethylammonium $C_{17}H_{38}NBr$ restore the absorption band contour characteristic of PIN monomer in water [205]. Micelles of other cationic surfactants also cause bathochromic band shifts. The shift value increases with hydrocarbon radical lengthening: 12.4 nm for $C_{15}H_{34}NBr$, 13.4 nm for $C_{17}H_{38}NBr$, and 14.6 nm for $C_{19}H_{42}NBr$ [199].

The effect of anionic surfactants on PIN is quite different (Figure 16). When a cation interacts with sodium dodecyl sulfate (SDS), the formation of compounds between Ct^+ and the SDS^- anion is observed [245], and even the formation of salts ($Ct^+_m \cdot SDS^-_n$, where $m > n$ [129]) is detected. If the dye content is unchanged and the concentration of SDS increases, the light absorption of the dye decreases. For a dye concentration of 2×10^{-6} mol/L, this is already noticed at an equimolar concentration of SDS. At higher surfactant concentrations (1.1×10^{-3} – 3.2×10^{-3} mol/L), even H-aggregates of PIN are induced, absorbing at 510 nm. However, in micellar systems with an anionic surfactant (8.5×10^{-3} mol/L or more), all compounds and aggregates are destroyed by solubilization of the dye on the surface of the homomycells. The spectrum of micellar solutions is similar to that of the PIN cation in water, but the absorption α - and β -bands are slightly bathochromically shifted ($\lambda_{max} = 610.5$ nm ($16,380$ cm^{-1}), α -band; and $\lambda_{max} = 669$ – 570 nm ($17,560$ cm^{-1}), β -band [246]).

In micellar systems of cationic surfactants, the apparent dissociation constants of PIN were determined (pK values: 3.09 ± 0.01 (*n*-dodecyltrimethylammonium bromide $C_{15}H_{34}NBr$), 3.11 ± 0.01 (*n*-tetradecyltrimethylammonium bromide $C_{17}H_{38}NBr$), 3.17 ± 0.01 (*n*-hexadecyltrimethylammonium bromide $C_{19}H_{42}NBr$), 1.82 ± 0.01 (Triton TX-100)) [199]. These values of constants are somewhat lower compared to the aqueous environment. PIN interacts most strongly with anionic surfactants (the constant of association with SDS under standard conditions is 1117.45×10^3 L/mol), and associations with cationic ones are much weaker (for example, 10.77×10^3 L/mol with cetyltrimethylammonium bromide); the non-ionic surfactant Triton TX-100 naturally occupies an intermediate position (with a constant of 418.99×10^3 L/mol) [205]. Such spectral effects are not only characteristic of PIN; they are manifested in micellar [247–251], pre-micellar [252,253], and mixed systems of ionic and nonionic surfactants [254–256] and often have a kinetic character [71,126,240,249,252].

Similar spectral shifts are manifested in the interaction of PIN with heparin [257], calixarenes [258], and cyclodextrins [210]; in “dye + alginates” systems [259]; and in dye binding by nucleic acids [260]. These and several other publications show that PIN is used in spectroscopic studies not only in homogeneous, microheterogeneous, and ultramicroheterogeneous systems, but also in studies of supramolecular schemes and mechanisms, or as a marker. For example, the interaction of PIN with nucleic acids [260] is characterized

by noticeable hypochromic effects and frequency shifts of the dye absorption bands. The analysis of spectra, DNA melting point, and electrophoresis indicated that the binding of PIN to nucleic acids occurs via an external stack in which nucleic acids serve as matrices. The use of PIN has made it possible to define a non-intercalating mechanism of dye binding to DNA and also to determine that the interaction between PIN and DNA is not only electrostatic.

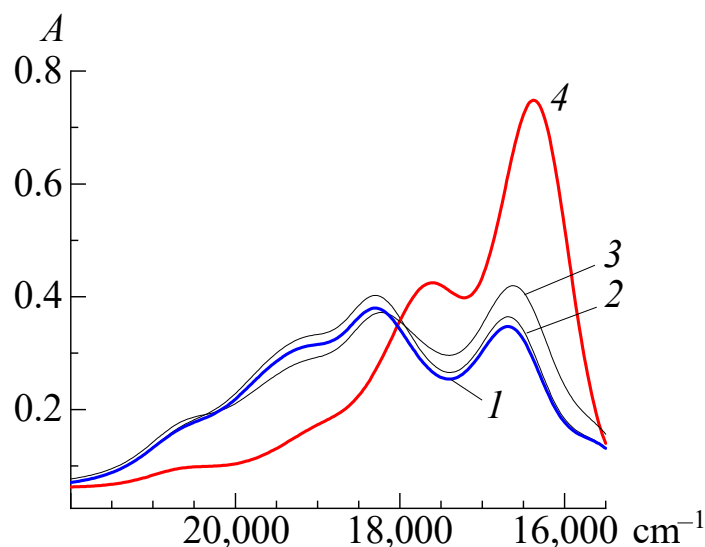


Figure 16. Light absorption in the “PIN + SDS” system. Concentration, mol/L; PIN, 2×10^{-5} (1–4); SDS, 0 (1), 4×10^{-4} (2), 1×10^{-3} (3), and 2×10^{-2} (4); pH = 6.2. The thickness of the absorbing layer is 0.20 cm.

8. Conclusions

As follows from what was discussed above, the use of PIN is effective both in respect to the identification of spectral, equilibrium, thermodynamic regularities, taking into account specific or non-specific interactions in homogeneous or heterogeneous systems, and in connection with the promising practical use of these systems. The unique spectral, thermodynamic, aggregative properties of polymethine dyes are fully attributed to PIN. That is why the use of this dye in scientific and technical research has received continuous attention for many years.

PIN was initially the standard in a range of sensitizing materials, but now the results of numerous studies give us reason to consider PIN as a kind of “colored” cation standard in the spectral study of supramolecular interactions.

For more than a century, only in sources indexed by leading services (WebSci, Science Direct, PubMed, Google Scholar, eLIBRARY, and Index Copernicus, Scopus), more than 1000 scientific works have been published on “pinacyanol” (or “quinaldine blue”), including 93.3% of original articles, 2.9% of reviews, 2.0% of monographs, brief reviews, messages, and abstracts. Furthermore, more than 900 patents for inventions have also been issued. It is noteworthy that a leading number of studies are in the fields of physical, colloidal, supramolecular chemistry, and molecular spectroscopy. The increasing percentage of publications in recent years is related to biology, pharmacy, medicine, and biochemical engineering. All of this suggests that pinacyanol is successfully entering the second century of fundamental research and applications.

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