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Dimerization of Cyanine Dyes in Water Driven by Association with Hydrophobic Borate Anions

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Abstract: The titrametric addition of hydrophobic borate anions to water-soluble cationic cyanine dyes readily perturbs the dye visible absorption spectrum. The insensitivity of the spectral effect to the oxidation potential of the borate indicates that this interaction is not a charge-transfer complex. Both concentration and solvent dependencies suggest the effect is due to the formation of cyanine dye–borate complexes, which are driven primarily by the hydrophobicity of the borate. Thus, in water, the hydrophobic borate anion–dye interaction reduces the dye solubility with the concomitant formation of dimers of the cyanine dye–borate complexes that facilitate electronic interactions of the dyes. Furthermore, the addition of hydrophobic borate anions to a mixture of two water-soluble cyanine dyes results in the formation of mixed dimers. The effect of the borate in these phenomena is opposite to the more familiar effect of surfactant solubilization of a hydrophobic dye. Indeed, the hydrophobic borate anion is acting as an asurfactant, in the sense that it interacts with a water-soluble species to form a defined aggregate structure.

Introduction

Noncovalent association of two or more molecules in solution or the gas phase occurs upon diffusive encounter. A simple collision usually leads to rapid dissociation of the molecules. However, in some cases, the associated molecules are stabilized relative to the individual components, thereby retarding dissociation. The resulting molecular complexes are supramolecular species which often display chemical and physical properties which are distinct from those of the individual components.[1,2]

A complex can be stabilized by a number of different mechanisms such as electrostatic attraction, hydrogen bonding, and solvophobic forces. Charge-transfer (CT) interaction is also a common factor in the stabilization of molecular complexes.[3] In this mechanism, one molecule acts as a donor by transferring some of its electron density to an acceptor molecule.[4] As one might expect, the magnitude of this interaction depends strongly on the redox potentials of the donor and acceptor.[1,5,6]

Recently, we reported the formation of aqueous cyanine dye cation–hydrophobic borate anion complexes.[7,8] Addition of the borate to the water-soluble dye resulted in drastic perturbations on the visible absorption spectrum of the dye. This observation was consistent with an earlier report of the effect of tetraphenylborate anion on aqueous rhodamine-6G cation.[9] However, a seeming contradiction arose from another report in which cyanine dye–borate ion pairs formed in low-polarity organic solvents such as benzene exhibited absorption spectra which were indistinguishable from those of cyanine dye–inorganic ion pairs.[10,11] This indicated that intimate association with the borate has no effect on the electronic states of the cyanine dye.

In the work described here, further examination of the aqueous dye–borate complexes has revealed that they are in fact dimeric, that is, they consist of two cyanine dye and associated borate molecules per complex and the observed spectral perturbations result from the dye–dye interaction. Other studies have demonstrated similar spectral changes arising from the spontaneous dimerization in water of various dye molecules which are more hydrophobic than the ones utilized here.[12-19] The unusual effect of the borate in the present study appears to be to increase the effective hydrophobicity of the dye, thereby promoting dimerization. This effect is similar in result but opposite in direction from previous reports that hydrophobic dyes can form small aggregates (premicellar) in dilute solutions of surfactant. A recent report of premicellar prophyrin aggregates provides a detailed review of the dye–surfactant studies.[20]

Experimental Section

Materials. N,N'-Bis[3-(trimethylammonio)propyl]thiadicarbocyanine tribromide (Cy^{3+}; λ_{max} = 650 nm, ϵ_{max} = 130 000 M^{-1} cm^{-1}) and N,N'-dimethyldimethylindocarbocyanine iodide (Cy^{+}; λ_{max} = 538 nm, ϵ_{max} = 140 000 M^{-1} cm^{-1}) were purchased from Molecular Probes, Inc. (Eugene, OR), and used as received. The molar extinction coefficients, measured in methanol, matched those reported by the supplier. Sodium tetraphenylborate, triphenylboron, benzylmagnesium bromide (2.0 M in THF), n-butyllithium (1.6 M in hexanes), and tetramethylammonium bromide were purchased from Aldrich Chemical Co. (Milwaukee, WI). Sodium tetraphenylborate was purified by recrystallization from chloroform while triphenylboron was purified by vacuum sublimation. Milli-Q water (Millipore Co., Bedford, MA) was used in all experiments. Spectral grade methanol and acetonitrile (J. T. Baker Inc., Phillipsburg, NJ; Photrex grade) were used as received.

Synthesis of Tetramethylammonium Triphenylbenzylborate (Ph$_3$BnB$^-$). All manipulations were performed under argon atmosphere. Solvents were freshly distilled and purged with argon for at least 15 min before use.

[⊛] Abstract published in *Advance ACS Abstracts*, October 15, 1993.

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Triphenylboron (0.5 g, 2.1 mmol) was dissolved in 10 mL of THF in a 50-mL two-necked, round-bottomed flask. A solution of 1.0 mL of benzylmagnesium bromide (2.0 M in THF) in 10 mL of THF was added dropwise with stirring at 0 °C. Addition was complete in 10 min; the clear, colorless solution was allowed first to stir for 30 min and then to warm to room temperature. The solvent was removed by rotary evaporator. (An argon line was connected to the pressure inlet of the evaporator to prevent exposure of the product to air which would lead to decomposition.)

The resulting colorless oil was dissolved in water. A solution of 1.0 g (6.5 mmol) of tetramethylammonium bromide in 10 mL of water was added dropwise with stirring at room temperature. A white precipitate formed immediately. The mixture was stirred for 30 min, and then the white solid was collected by gravity filtration. (This and all subsequent manipulations were done without inert atmosphere since the tetramethylammonium borate salts are stable to air.[21]) The white solid was washed with water to remove excess bromide. Recrystallization from CH_2Cl_2/methanol gave 0.1 g (0.24 mmol) of tetramethylammonium triphenylbenzylborate (11% yield). The white powder decomposed at 251–252 °C and gave the following ^{1}H NMR (DMSO-d_6): δ 7.1–7.2 (br s, 6H), 6.8–6.9 (t, 6H), 6.6–6.8 (m, 6H), 6.4–6.5 (d, 2H), 3.1 (s, 12H), 2.4 (m, 2H).

Spectroscopy of Aqueous Dye–Borate Complexes. UV–vis absorption spectra were acquired on a Varian DMS-200 (Varian Techtron Pty. Ltd., Victoria, Australia) double-beam instrument. Cy^{3+}–Ph_4B^- and Cy^+–Ph_4B^- complexes were studied; procedures for the Cy^{3+}–Ph_4B^- complex are given below. The absorption spectrum of a 3.85 μM aqueous Cy^{3+} solution (1.3 mL) was recorded before and after the addition of successive 2.0-mL aliquots of a 0.5 mM Ph_4B^- stock solution (CH_3CN).

The stoichiometry of the Cy^{3+}–Ph_4B^- complex was determined using Job's method.[1,22] Stock solutions employed were 1.0 μM Cy^{3+} in water and 1.0 μM Ph_4B^- in CH_3CN. The total volume of these solutions added to 1.3 mL of water was held constant at 12.0 μL. Initially, 12.0 μL of Cy^{3+} and 0 μL of Ph_4B^- were added, and the absorption spectrum was recorded. The procedure was repeated for 10:2, 8:4, 6:6, 4:8, 2:10, and 0:12 (μL of Cy^{3+}:μL of Ph_4B^-) mixtures of the two components. The optical density of the solution at 725 nm was used to assay for complex formation as the free dye does not absorb at this wavelength.

The empirical stoichiometry of the complex was extracted from the data by first plotting OD_{725} versus X where

$$X = \frac{\mu\text{L of Ph}_4\text{B}^-}{\mu\text{L of Cy}^{3+} + \mu\text{L of Ph}_4\text{B}^-} = \text{mole fraction of borate}$$

The plot exhibits a maximum at X_{max}; the empirical stoichiometry of the complex $(Cy^{3+})_m$–$(Ph_4B^-)_n$ is calculated from

$$\frac{n}{m} = \frac{X_{max}}{1 - X_{max}}$$

Concentration Dependence of Complex Formation. Cy^{3+} (1.0 μM) and Ph_4B^- (2.0 μM) were added to 1.2 of mL water in 1.2-mL increments up to 12.0 mL of each. Absorption spectra were recorded after each addition. In this manner, the 1:2 Cy^{3+}:Ph_4B^- stoichiometry was preserved even though the overall concentrations were varied. The ratio OD_{650}/OD_{671} was plotted versus Cy^{3+} concentration. (650 nm is the dye absorption maximum; 671 nm is the isosbestic wavelength observed during titration with Ph_4B^-.)

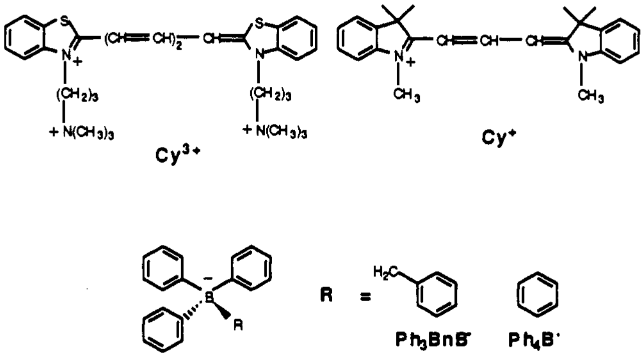
Solvent Effects. The absorption spectra of Cy^{3+}:Ph_4B^- (1:2, 7.69 μM Cy^{3+}) were measured in a series of water–acetonitrile mixtures. The full width at half-maximum (fwhm) was plotted versus the percent water in the solvent.

Titration of the Cy^+–Cy^{3+} Mixture. An aqueous solution containing an equimolar mixture of Cy^+ and Cy^{3+} (3.08 μM for each dye) was titrated with Ph_4B^- and added in 0.75-molar equiv increments up to 3.0 equiv (relative to total dye). Absorption spectra were recorded after each addition. Spectra for separate solutions of Cy^+ and Cy^{3+} were added together and then subtracted from the spectrum of an equimolar mixture of the two.

Results

The hydrophilic cyanine dye cations and hydrophobic borate anions used in these experiments are shown in Chart I. Both cyanine dyes absorb intensely in the visible with the pentamethine Cy^{3+} exhibiting a longer wavelength absorption band than the trimethine Cy^+. Within the range of concentrations studied (<10.0 μM), the dyes dissolve in water without aggregation as indicated by their adherence to the Beer–Lambert law and the lack of broadening of their absorption bands.

Chart I



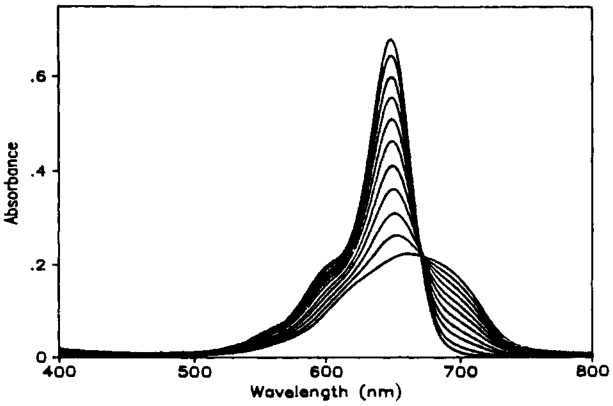


Figure 1. Absorption spectra of 3.85 μM aqueous Cy^{3+} (λ_{max} 650 nm) titrated with successive additions of 0.2 molar equiv of Ph_4B^-.

Figure 1 shows the results of the titration of Cy^{3+} with Ph_4B^-. The progressive broadening and red shifting of the absorption spectrum with concomitant depression of the molar extinction coefficient as the borate concentration increases are indicative of molecular complex formation. Similar spectral changes were observed by Hirano and Takagi for the addition of Ph_4B^- to rhodamine 6-G cation in water.[9] Isosbestic behavior is observed up to the addition of 2.0 molar equiv of Ph_4B^-; further addition causes the isosbestic point to shift to the red. The association phenomenon illustrated in Figure 1 is quite strong: spectra were recorded after sequential additions of just 0.2 molar equiv of the borate.

The stoichiometry of the complex was determined from a Job plot,[22] which gives a maximum at $X = 0.67$ (Figure 2), i.e., a ratio of 1 Cy^{3+}:2 Ph_4B^- (designated as the Cy^{3+}–$(Ph_4B^-)_2$ complex). The sharp maximum provides further evidence of strong binding.

The spectral changes observed upon formation of the Cy^{3+}–$(Ph_4B^-)_2$ complex (broadened, attenuated, red-shifted absorption band) are typically ascribed to charge-transfer (CT) interaction.[6] However, observation of CT complexes usually requires one of the components to be present in large excess since this type of association is generally weak with association constants less than 10^3. The titration data indicate that the association between Cy^{3+} and Ph_4B^- is much stronger than this. To investigate the possible contribution of CT interaction to the stabilization of the Cy^{3+}–$(Ph_4B^-)_2$ complex, similar experiments were performed with Ph_3BnB^- which is more easily oxidized than Ph_4B^- by 360 mV.[10,11] Thus, a complex formed between Cy^{3+} and Ph_3BnB^- should be even stronger than the Cy^{3+}–$(Ph_4B^-)_2$ complex.

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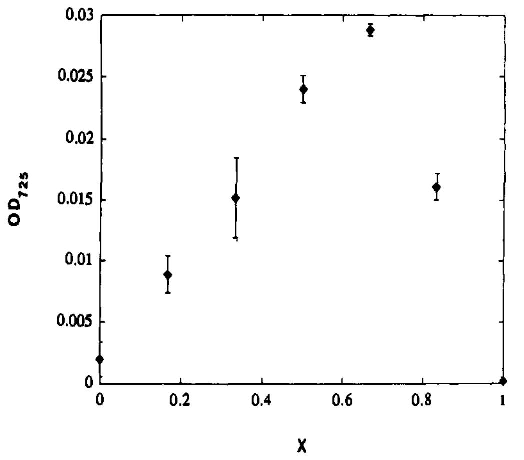

Figure 2. Job plot for formation of the aqueous Cy^{3+}–Ph_4B^- complex, where X is the mole fraction of borate. Each data point and set of error bars represent the mean and standard deviation, respectively, for three separate measurements.

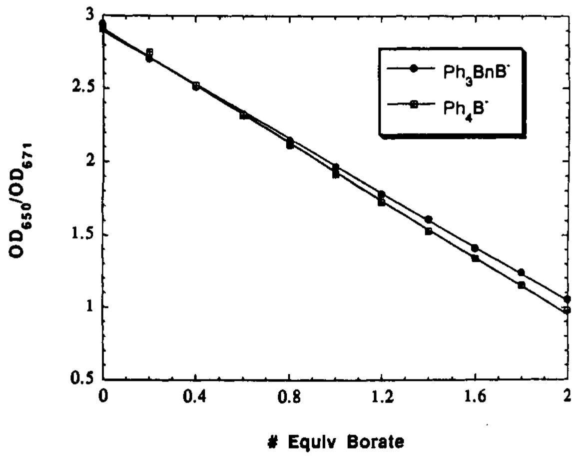

Figure 3. Plot of the ratio OD_{650}/OD_{671} versus added borate for titration of Cy^{3+} with Ph_3BnB^- and Ph_4B^-.

Titration of Cy^{3+} with Ph_3BnB^- yields similar spectral perturbations to those exhibited by Cy^{3+} with Ph_4B^- in Figure 1. The absorption band is broadened, attenuated, and bathochromically shifted as borate is added. Isosbestic behavior is maintained at 671 nm until the amount of added borate exceeds 2.0 molar equiv. Job analysis reveals that this complex also has 1:2 (dye:borate) stoichiometry. Figure 3 shows how the ratio OD_{650}/OD_{671} varies with added borate for the two complexes. The similar dependencies indicate that the two complexes have comparable association constants.

The optical properties of the Cy^{3+}–$(Ph_3BnB^-)_2$ and Cy^{3+}–$(Ph_4B^-)_2$ complexes are summarized in Table I. The Cy^{3+}–$(Ph_4B^-)_2$ complex exhibits a somewhat longer wavelength absorption, more attenuated extinction coefficient, and broader absorption band. These relatively minor differences due to the respective oxidation potentials of the two borates are inconsistent with the size of the effect usually associated with charge-transfer phenomena.[5,6]. Thus, CT interaction does not appear to be the driving force for complex formation.

Table I. Optical Properties of the Cy^{3+}–$(Ph_3BnB^-)_2$ and Cy^{3+}–$(Ph_4B^-)_2$ Complexes

borate	E_{ox} (V)[a]	λ_{max} (nm)	ϵ_{max} (M^{-1} cm^{-1})	fwhm (nm)
Ph_3BnB^-	1.09	657	66 000	100
Ph_4B^-	1.45	663	59 000	110

[a] References 10 and 11.

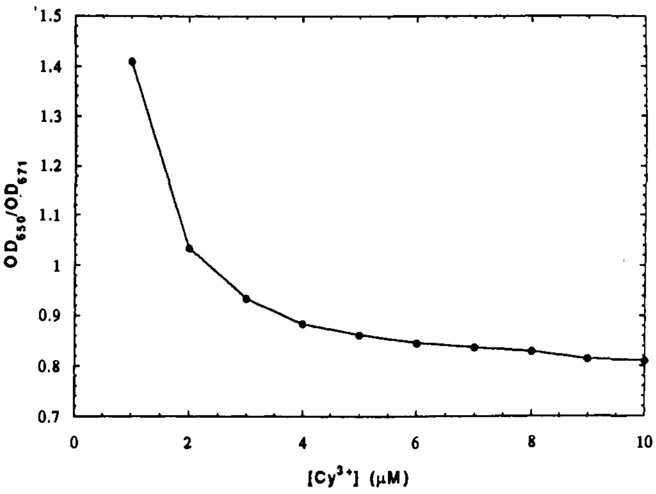

Figure 4. Plot of the ratio OD_{650}/OD_{671} versus $[Cy^{3+}]$ in the presence of 2.0 molar equiv of Ph_4B^-.

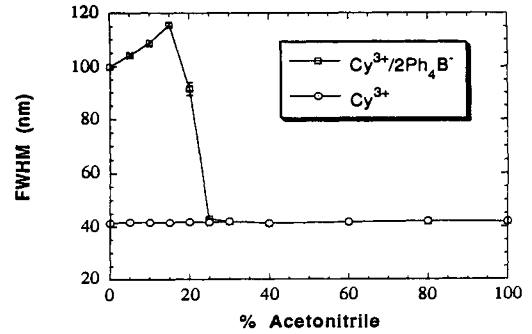

Figure 5. Plot of the fwhm of the absorption band due to 7.63 μM Cy^{3+} in water–acetonitrile mixtures with and without 2.0 molar equiv of Ph_4B^-.

The tendency for a 1:2 Cy^{3+}:Ph_4B^- mixture in water to form complexes depends on the concentration of the dye and borate (Figure 4). The low value of OD_{650}/OD_{671} when the $[Cy^{3+}]$ exceeds 4.0 μM shows that complex formation is essentially complete in this concentration range. However, at lower concentrations, the OD_{650}/OD_{671} values rapidly increase, indicating that complex formation becomes progressively diminished upon dilution.

Complex formation is also solvent-dependent. In acetonitrile, a complex is not observed between Cy^{3+} and Ph_4B^-, presumably because the borate is freely soluble in this solvent. For water–acetonitrile mixtures, complex formation (as detected by a broadening of the fwhm of the cyanine absorption band) does not occur until the water content exceeds 75% (Figure 5).

The singly-charged indocarbocyanine Cy^+ also forms an aqueous complex with Ph_4B^- (Figure 6) which Job analysis reveals to have 1:1 stoichiometry (data not shown). The isosbestic point at 554 nm is preserved until the amount of borate exceeds 1.0 molar equiv, in a manner indicative of quantitative complex formation. It is tempting to attribute the spectral perturbations evident in Figures 1 and 6 to overlap of the orbitals of the cyanine dyes with those of one or more bound borate molecules. However, Schuster and co-workers reported that the contact ion pairs Cy^+–Ph_4B^- and Cy^+–PF_6^- formed in benzene have identical absorption spectra, indicating that intimate association of the borate does not perturb the low-lying electronic states of the cyanine dye.[10,11]

The electronic interactions which give rise to the spectral effects illustrated in Figures 1 and 6 could also be due to overlap of the orbitals of one cyanine dye with those of another dye molecule. Indeed, aqueous cyanine dye dimers are known to exhibit significantly altered absorption spectra relative to those of the solvated monomers.[19] In the present study, *this would require the formation of dimers of the cyanine–borate complexes.* Since

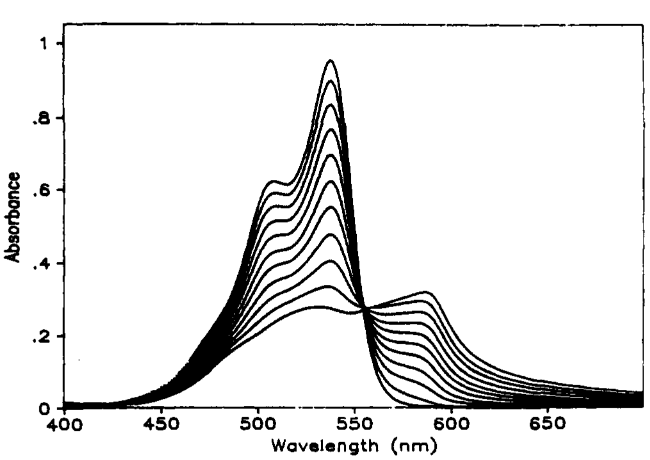

Figure 6. Absorption spectra of 7.63 μM aqueous Cy^+ titrated with successive additions of 0.1 molar equiv of Ph_4B^-.

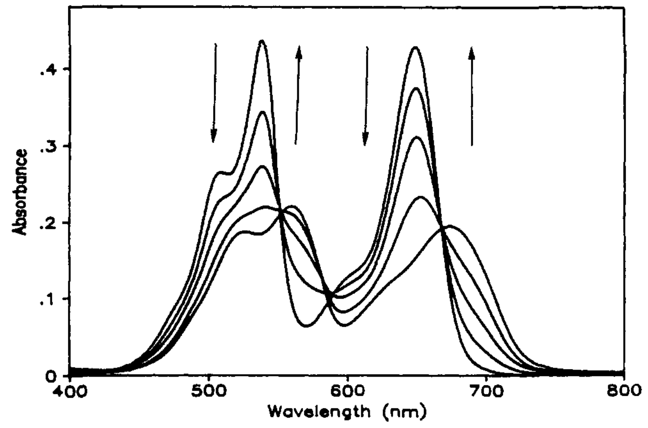

Figure 7. Absorption spectra of aqueous Cy^+–Cy^{3+} (3.08 μM for each dye) titrated with successive additions of 0.75 molar equiv of Ph_4B^- (relative to total dye concentration). The arrows indicate the effect of increasing Ph_4B^- concentration on the spectra.

the Job analysis gives the empirical stoichiometry only, it cannot be used to distinguish between 1:1 and 2:2 complexes of dye and borate.

A procedure to resolve this uncertainty is provided by West and Pearce's investigation of the dimerization of cyanine dyes in water.[19] They demonstrated the formation of mixed dimers by comparing the absorption spectrum of an equimolar mixture of a carbocyanine and a dicarbocyanine dye with the sum of spectra of the individual dyes.[19] Subtracting the latter, calculated spectrum from that of the mixture yielded a nonzero difference spectrum. This result was interpreted as due to the formation of mixed dimers consisting of one carbocyanine dye and one dicarbocyanine dye. Absorbance due to mixed dimers does not appear in the spectrum calculated by simply adding together the spectra of the individual dyes.

We performed similar experiments for the aqueous cyanine–borate complexes. Titration of an equimolar mixture of Cy^+ and Cy^{3+} with 0.75 molar equiv of Ph_4B^- is illustrated in Figure 7. Borate was added to the dye mixture up to 3.0 molar equiv (relative to either dye), which is the amount required in order to completely complex all of the dye in solution. Isosbestic points are observed at 551 and 668 nm, both of which are hypsochromically shifted by 3 nm relative to titration of the individual dyes (Figures 1 and 6).

Difference spectra are shown in Figure 8 for the equimolar mixture of Cy^+ and Cy^{3+}, with and without 3.0 molar equiv of Ph_4B^-. In the absence of Ph_4B^-, the lack of deviation from zero indicates that the dyes alone do not interact in water to an appreciable extent. However, addition of Ph_4B^- causes significant deviations from zero with enhanced absorptions between 500 and 570 nm and 650 and 720 nm but depleted absorption between 570 and 650 nm. This bears a striking resemblance to the difference spectrum reported by West and Pearce.[19] The nonzero difference spectrum indicates the formation of mixed dimeric cyanine dye–borate complexes in water.

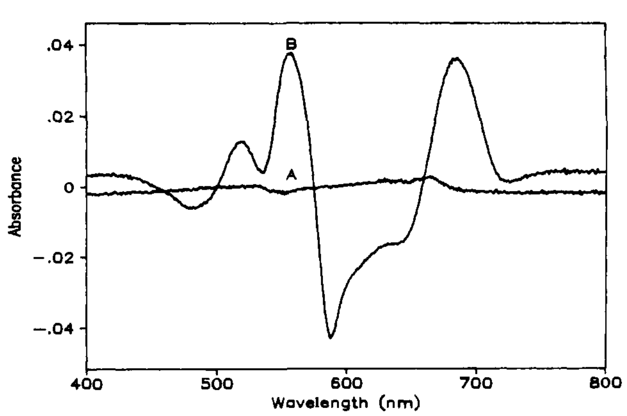

Figure 8. Difference spectra for the equimolar mixture of Cy^+ and Cy^{3+} (A) alone and (B) with 3.0 molar equiv of Ph_4B^- (relative to total dye concentration).

Discussion

Cyanine dye–borate complex formation proceeds readily in water. While the types of spectral effects demonstrated in Figures 1, 6, and 7 are typical of charge-transfer complexes, other data rule out CT interaction as the primary mode of stabilization of the complexes. The observation that the more easily oxidized borate (Ph_3BnB^-) forms a complex with shorter absorption λ_{max} is contrary to what is normally observed for CT complexes, where λ_{max} increases with decreasing oxidation potential of the electron donor.[5,6] Additionally, the association phenomena appear to be orders of magnitude stronger than those usually found for CT complexes. Unfortunately, the standard Benesi–Hildebrand treatment[23] cannot be employed to analyze the data because the approximations inherent in that method restrict its applicability to weak associations. Hirano and Takagi[9] analyzed their titration data for the rhodamine-6G–Ph_4B^- complex using a modified Rose–Drago equation.[24] However, in their analysis, they assumed the stoichiometry was strictly 1:1. The results obtained here suggest that the complexes formed in their study may actually have a 2:2 stoichiometry with the spectral perturbations arising from rhodamine dimerization. If this is true, the association constant (ca. 10^5) would be significantly underestimated. In the present study, the observations that (a) the empirical stoichiometry of the complex is 1:2 (Cy^{3+}:Ph_4B^-) and (b) the isosbestic point is lost as soon as more than 2.0 molar equiv of borate is added suggest that complex formation is quantitative. Similar arguments can be made for quantitative Cy^+:Ph_4B^- complex formation. Rather than being in equilibrium with the dissociated components, the cyanine dye–borate complexes appear to be discrete, supramolecular species.

The concentration and solvent dependencies illustrated in Figures 4 and 5 suggest that the formation of the cyanine–borate complexes is driven primarily by the hydrophobicity of the borate. At sufficiently low concentrations in water or high acetonitrile content, the solubility of the borate in the solvent competes with complex formation. In earlier studies, we have also found that complex formation can be inhibited by the use of surfactant lipid vesicles.[7,8] In those cases, the borate partitioned out of the aqueous phase into the hydrophobic interior of the lipid bilayer, preventing its complexation with the cyanine dye. Thus, in water, the

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hydrophobic anion–dye interaction reduces the dye solubility. This is opposite to the more familiar effect of surfactant solubilization of a hydrophobic dye. Indeed, the hydrophobic borate anion is acting as an *asurfactant*, in the sense that an *asurfactant* interacts with a water-soluble species to yield an aggregate structure. The small aggregates formed here can tentatively be considered as new members of the growing class of premicellar aggregates. Premicellar association of surfactants and dyes has been previously described for several systems (see ref 20 and references therein).

The addition of 3.0 molar equiv of Ph_4B^- to the equimolar mixture of Cy^+ and Cy^{3+} (sufficient Ph_4B^- to completely complex both dyes) yields an absorption spectrum which deviates markedly from the sum of the absorption spectra of the individual cyanine dye–borate complexes (Figure 8). This could be due to preferential association of the borate with one of the dyes. However, the isosbestic points at 551 and 668 nm are well-maintained during successive additions of the borate (Figure 7), a feature that would not be expected if there were any bias in the system. If, for example, more than 2.0 equiv of borate associated with Cy^{3+}, then the latter isosbestic point would most likely be lost, based on the results from titration of this dye alone.

A more plausible interpretation for the nonzero difference spectrum is the formation of mixed dimeric complexes. As pointed out earlier, spectroscopic evidence from contact ion pairs indicates that close association of cyanine dye cations with Ph_4B^- does not perturb the low-lying electronic states of the dye since no change in the absorption spectrum of the dye is observed whether the counterion is PF_6^- or Ph_4B^-.[10,11] Therefore, the large perturbations observed on titrating the cyanine dyes in water with Ph_4B^- are attributed to the formation of dimeric complexes in which two dye molecules interact electronically. Higher order complexes such as trimers and tetramers are not considered to be present in significant amounts because of the well-preserved isosbestic points observed in the titrations as well as the single maximum observed in each of the Job plots. The similarity between the difference spectra resulting from borate-induced dimerization and from spontaneous dimerization of cyanine dyes indicates that in each case, the dye chromophores are cofacially aligned. The enhanced absorptivity occurring to the red of the absorption maximum as the borate concentration increases (Figures 1 and 6) suggests that the dye molecules do not possess a head-to-head or H-type alignment, which is characterized by enhanced absorptivity to the blue of the monomer absorption band, but rather the dye molecules are offset giving rise to a J-like dimer.[25] H- and J-aggregate formation has been reported for a variety of cyanine and other dyes.[26] The red shift attributed to the formation of a J-aggregate is generally considered due to the formation of an assembly structure where the angle between the transition dipoles and the axis of the aggregate is less than 54°.[27] Cyanine dye J-aggregates are notable for their narrow, intense absorption spectra. The fact that the absorption of the dimeric cyanine dye–borate complex reported here is neither intense nor narrow suggests that although the borate anion brings the dyes together, its location in the aggregate structure precludes the formation of a true J-aggregate.

Addition of Ph_4B^- to an equimolar mixture of Cy^+ and Cy^{3+} can lead to the formation of three different complexes: $[Cy^+–Ph_4B^-]_2$, $[Cy^{3+}–(Ph_4B^-)_2]_2$, and $[Cy^+–Ph_4B^-]$-$[Cy^{3+}–(Ph_4B^-)_2]$. The nonzero difference spectrum shown in Figure 8 provides evidence that the mixed or heterodimeric complex is formed in addition to the two homodimeric complexes. This is a likely consequence of the similarity in the structures of the two dyes. Complex formation presumably occurs by a two-step process consisting of initial association of the borate with a cyanine dye, driven by hydrophobic and electrostatic interactions, yielding an isolated cyanine dye–borate complex containing a single dye molecule. The effect of the borate on the cyanine dye is to increase its effective hydrophobicity. These monomeric complexes subsequently dimerize, which is analogous to the spontaneous dimerization previously reported for more hydrophobic cyanine dyes.[19] Apparently the individual $Cy^+–Ph_4B^-$ and $Cy^{3+}–(Ph_4B^-)_2$ complexes are sufficiently similar that mixed dimeric complexes may be formed. The formation of mixed dimers from two cyanine dyes which do not associate with one another in the absence of hydrophobic borate is an interesting and potentially useful effect. The generality of these observations remains to be tested in other systems, e.g., the addition of Ph_4B^- to a mixture of two dyes which have significant structural differences, such as rhodamine 6G and Cy^{3+}, could lead to the formation of only homodimers.

In conclusion, the addition of hydrophobic borate anions to water-soluble, cationic cyanine dyes results in quantitative formation of dimeric cyanine dye–borate complexes which are stabilized primarily by hydrophobic and electrostatic forces rather than by charge-transfer interactions. In other words, these water-soluble premicellar aggregates are formed as a result of desolubilization of the dyes by interaction with an *asurfactant*, the hydrophobic borate anion. Viewed in this manner, this unusual dimeric dye–borate assembly is likely to open the way to more complex asurfactant assemblies in the future. Careful control of concentration, electrostatics, and solubilities should permit the formation of larger aggregates of dye(s) and hydrophobic counterion(s).

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