Bull. Chem. Soc. Jpn., **72**, 1197—1202 (1999)

Dominant Factors of Preventing Rhodamine 6G from Dimer Formation in Aqueous Solutions

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(Received October 22, 1998)

Rhodamine 6G/water/alcohol or carboxylic acid systems were studied. Rhodamine 6G molecules, which tend to associate into nonfluorescent dimers in aqueous solution, were prevented from dimerization by mixing them with organic compounds. It was found that additives with smaller dielectric constants prevented the dye molecules from associating to effectively form dimers. It was found that 2-butanol and isobutyric acid were the most effective additives for dissolving Rhodamine 6G dimer and that the amount demanded to obtain the necessary concentration of monomer in aqueous solution was less than 10%.

Xanthene dyes including Rhodamine are used as a laser medium in organic solvents such as ethanol. However, since this solvent is flammable and toxic because of its high vapor pressure, it would be dangerous if large-scale laser devices were used in industrial plants or factories. Water is one of safest solvents, but it is well-known that in water dye-molecules associate to form dimers, water-soluble complexes which are not fluorescent,[1] making them inappropriate as a laser source.

Mixing of surfactants (or detergents) with aqueous dye solutions was one method employed to obtain an aqueous-solution dye laser.[2—6] Since surfactants act to prevent dye molecules from aggregating, it would have been rational to apply this idea to obtain an efficient laser power as the first stage. We have shown that an aqueous solution of Rhodamine 6G requires a volume fraction of surfactant as high as 10% to achieve almost the same efficiency of laser oscillation as a Rhodamine 6G/ethanol system.[7]

Rohatgi et al.[8] measured some thermodynamic constants of the dimerization of Rhodamine B and showed that the entropy change for its dimer formation is positive, i.e., $\Delta S > 0$, while the absolute value of the enthalpy change $|\Delta H|$ is very small. Therefore, the entropy change is dominant for the dimerization of Rhodamine B, and the association is a result of hydrophobic bonding.

Arvan, et al.[9] stated that there was a relationship between the dimerization of Rhodamine 6G and the dielectric constants of mixed solvents in aqueous solution. However, their conclusion was based on the results of a few solvents and was not quantitative.

In this paper, the dependence of a variety of additives on dissociation of Rhodamine 6G dimer in aqueous solution was investigated, and a clear linear relationship was found between the concentration of the dye monomer and the dielectric constants of the additives.

Materials and Methods

Methanol, ethanol, 1-propanol, 2-propanol, 2-propen-1-ol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-buten-1-ol, 2-butanol, formic acid, acetic acid, propionic acid, isobutyric acid, and methacrylic acid were of guaranteed grade (Kanto Chem. Co.). High-performance liquid-chromatography grade water was obtained from Kanto Chem. Co. Rhodamine 6G, referred to as Rhodamine 590 chloride, was obtained from Exciton Co.

Rhodamine 6G was dissolved in water, water/alcohol mixtures, or water/carboxylic acid mixtures. The concentration of the dye in those solutions was fixed at 2.0×10^{-4} mol dm^{-3}, which demonstrated the highest laser efficiency.[7] The solutions were prepared by dilution of stocked solutions with a concentration of 1.0×10^{-3} mol dm^{-3}. The solvents, the stocked solutions and the dye powder were all measured gravimetrically.

Absorption spectra were obtained with a spectrophotometer (Shimadzu UV-160A), in which Pyrex-glass cells with an optical path of 1 mm were used.

Results

Absorption spectra of Rhodamine 6G/water/alcohol systems are plotted in Fig. 1; here (a) is methanol, (b) ethanol, and (c) 1-propanol. The spectra in Fig. 1(a) show the patterns at percent volumes of 0, 20, 40, 60, and 80% methanol. It is known[10] that the peak at approximately 530 nm is assigned to the monomer of the dye and that of ca. 500 nm to the dimer. The height of the 530 nm peak is approximately proportional to the concentration of dye monomers existing in solution. The absorption of the monomer increased with the fraction of methanol along with a decrease in the dimer concentration. The curves of 60 and 80% look like overlapping

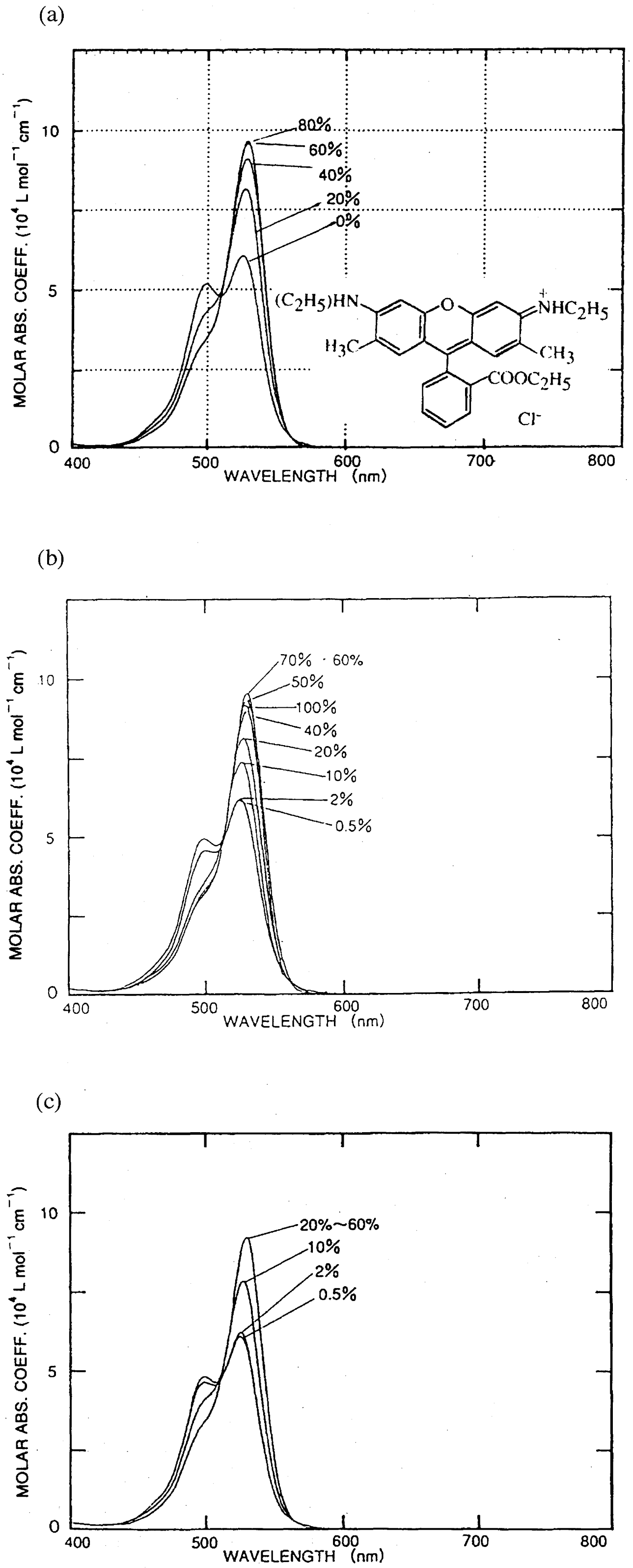

Fig. 1. Absorption spectra of Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol system. The numbers show percentage of ethanol volume fraction. Alcohols are (a) methanol, (b) ethanol, (c) 1-propanol.

in the vicinity of 500 nm.

Figure 1(b) is a series of spectra of water–solvent mixtures with several volume fractions of ethanol. Those of 0.5 and 2% showed a distinct dimer peak, and the higher was the ethanol ratio, the steeper was the monomer peak. The peak wavelengths of monomer hardly shifted with the solvent composition.

The molar absorption coefficient of a 70%-ethanol solution surpasses that of a 100% ethanol solution. We assumed that this was due to a nonlinear relationship between the fraction of water/ethanol in the system and the physical properties such as viscosity, vapor pressure and index of refraction.

The vertical axis represents the molar absorption coefficient, which changes by the equilibrium between monomers (R) and dimers (R–R) of the dye;

$$\text{equilibrium} \qquad 2R \rightleftarrows R\text{–}R, \tag{1}$$

$$\text{molarity} \qquad (1-\alpha)c_{\mathrm{i}} \quad \alpha c_{\mathrm{i}}/2, \quad 0 \leq \alpha \leq 1 \tag{2}$$

where c_{i} is the initial concentration (in this case, monomer 2.0×10^{-4} mol dm^{-3}) and α is the fraction of dimerization. The α depends on solvent and the prepared (initial) dye concentration (c_{i}). The molar absorption coefficient should be called the apparent molar absorption coefficient.

Each molar absorption coefficient of monomers and dimers, ε(R) and ε(R–R), does not change. Then, the molar absorption coefficient is

$$\varepsilon = \varepsilon(\mathrm{R})(1-\alpha) + \varepsilon(\mathrm{R{-}R})\alpha/2, \tag{3}$$

at every wavelength.

All the lines pass through a point at 513 nm (isosbestic point). Since two Rhodamine 6G molecules associate to become one dimer, R–R must have a molar absorption coefficient that is twice the magnitude of R at an isosbestic point. This is because at the wavelength,

$$\varepsilon(\mathrm{R})(1-\alpha) + \varepsilon(\mathrm{R{-}R})\alpha/2 = \text{constant}, \qquad 0 \leq \alpha \leq 1 \tag{4}$$

$$\therefore\ 2\varepsilon(\mathrm{R}) + \alpha(-2\varepsilon(\mathrm{R}) + \varepsilon(\mathrm{R{-}R})) = \text{costant}, \qquad 0 \leq \alpha \leq 1 \tag{5}$$

$$\therefore\ 2\varepsilon(\mathrm{R}) = \varepsilon(\mathrm{R{-}R}), \tag{6}$$

in the case that trimers do not generate.

The molar absorption coefficients of monomer R at 530 nm ($\varepsilon_{\mathrm{MAX}}$'s) are shown in Fig. 2 as a function of the volume fraction of alcohol (methanol, ethanol, and 1-propanol). Within the range of 20 volume percent, $\varepsilon_{\mathrm{MAX}}$ increases steeply with the volume percent of alcohol, and it was found that alcohols having a larger alkyl chain show a larger $\varepsilon_{\mathrm{MAX}}$ at low alcohol concentrations. In the range of ca. 50%, the order of the $\varepsilon_{\mathrm{MAX}}$'s of ethanol and 1-propanol was reversed. The value of methanol increased continuously from zero to 80%, meanwhile, ethanol had a maximum at about 70% and 1-propanol at 20%.

Series of the absorption spectra of Rhodamine 6G (2.0×10^{-4} mol dm^{-3}) in water/2-propanol mixtures and water/2-propen-1-ol ones for various fraction of alcohols were measured. The wavelengths of their peaks were barely different from those in the case of the water/ethanol solvent,

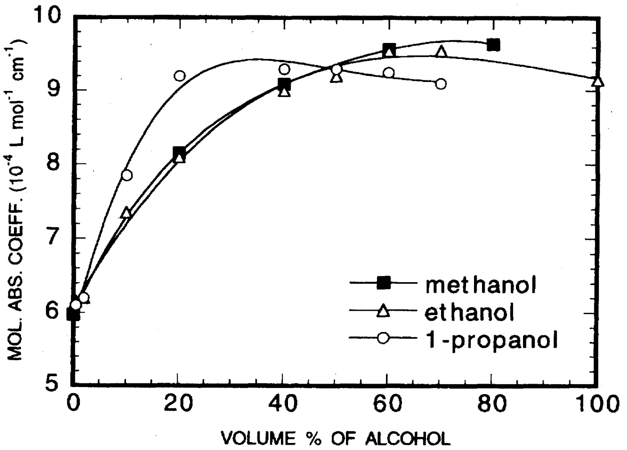

Fig. 2. Molar absorption coefficient as a function of alcohol fraction in the Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol systems.

and the shapes of their spectra were almost the same. The system was also isosbestic. The heights of the absorption peaks (ε's) were plotted as a function of the fraction of alcohols in Fig. 3. Here, alcohols with saturated and unsaturated hydrocarbon chains were compared, and it was found that the $\varepsilon_{\mathrm{MAX}}$ values were nearly the same for each fraction. In Figs. 2 and 3, the absorptions in 1- and 2-propanols are compared; in the range of the fraction of 0 to 20%, the $\varepsilon_{\mathrm{MAX}}$'s of both systems showed almost the same behavior.

Figure 4 shows the absorption spectra of dye (2.0×10^{-4} mol dm^{-3}) in water–butyl alcohol mixtures. As shown in Fig. 4(a), the absorption for 2-methyl-2-propanol (*t*-butyl alcohol) increased simply and rapidly. The wavelengths of these peaks were almost the same compared with the case of the water/ethanol solvent, and were also almost constant upon changing the 2-methyl-2-propanol/water ratio.

In the case of 40% 2-buten-1-ol in Fig. 4(b), the curve exhibits absorption throughout the visible region. This is because the solvent mixture was biphasic, and the probe light was scattered by the interface of phases at all wavelengths. The 2-methyl-1-propanol/water mixture had a two-phase region between 10 and 100%, 2-butanol had one between 20 and 80%.

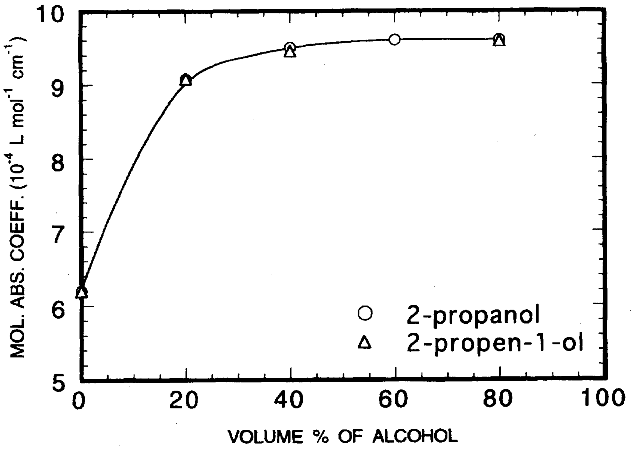

Fig. 3. Molar absorption coefficient as a function of alcohol fraction in Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol systems.

Alcohols are 2-propanol $CH_3CH(OH)CH_3$, 2-propen-1-ol $CH_2{=}CHCH_2OH$.

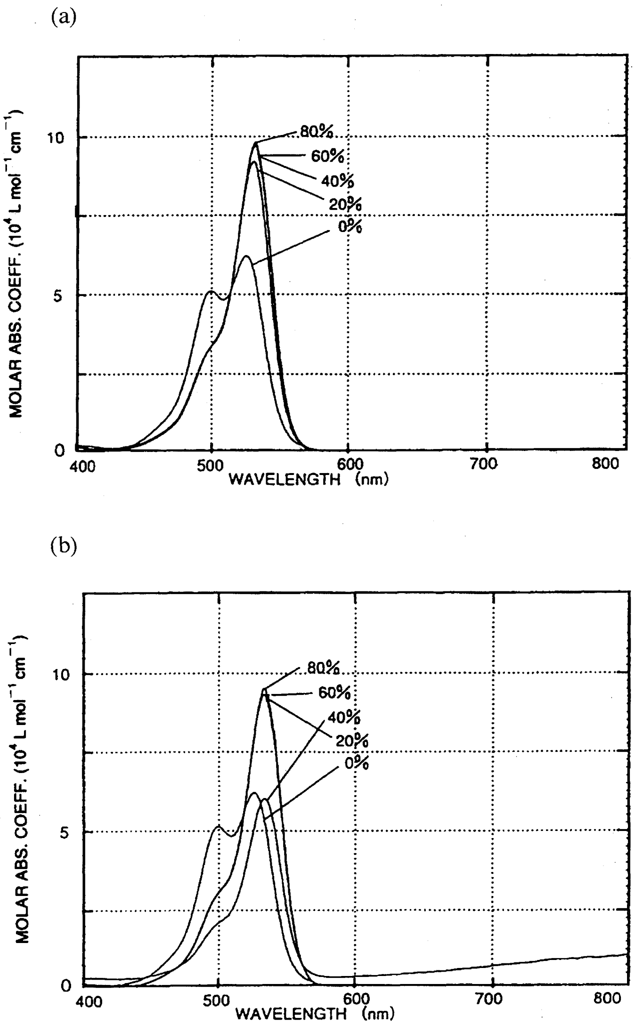

Fig. 4. Absorption spectra of Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol systems. The numbers show volume percentage of alcohol.

Alcohols are (a) 2-buten-1-ol $CH_3CH{=}CHCH_2OH$, (b) 2-methyl-2-propanol $CH_3CH(OH)(CH_3)CH_2$.

Figure 5 shows the relationship between the alcohol fraction and the maximum molar absorption coefficient for 2-buten-1-ol, 2-methyl-1-propanol, 2-butanol, and 2-methyl-2-propanol. All of these alcohols have four carbon atoms. The dissociability of two types of unsaturated alcohols was compared, and it was found that the order of effectiveness is 2-buten-1-ol > 2-propen-1-ol at 20%. In the case of 2-butanol and 2-methyl-2-propanol at 20%, the order of the effect is secondary alcohol > tertiary alcohol. Comparing the curves, the effect of secondary alcohols in Figs. 3 and 5, 2-butanol was slightly better than 2-propanol.

Figure 6 shows absorption spectra of a Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/formic acid system. The wavelengths of the peaks were almost the same as those of the alcohol solutions. The peak of 60%-acid was higher than

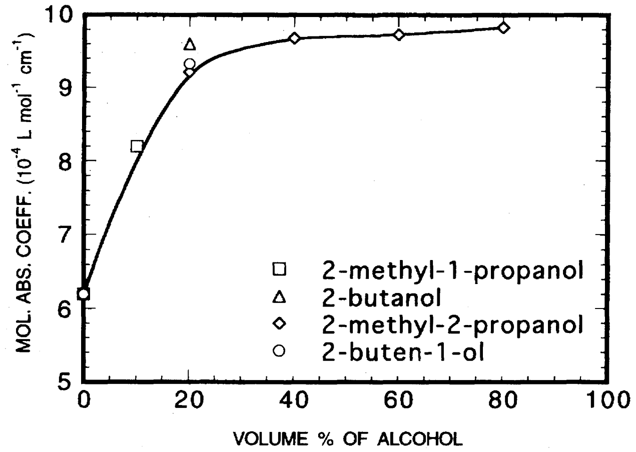

Fig. 5. Molar absorption coefficient as a function of alcohol fraction in the Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol systems.

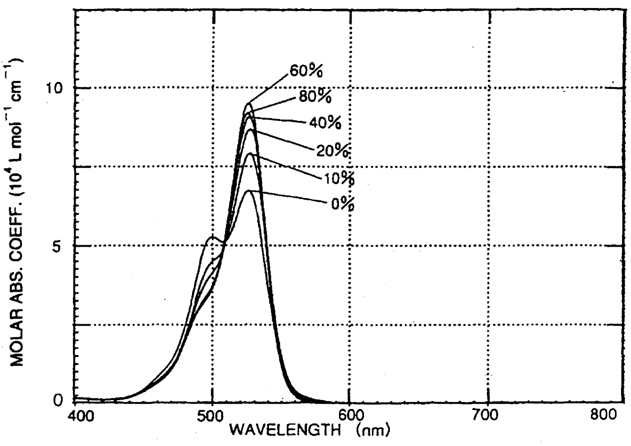

Fig. 6. Absorption spectra of Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/formic acid HCOOH system. The numbers show volume percentage of acid.

that of 80%.

Their maximum molar absorption coefficients in Fig. 6 are plotted in Fig. 7 as a function of the volume fraction of acid. Up to 20%, the absorptions increase rapidly. The order of molar absorption coefficients among these three normal-chain acids is propionic acid, acetic acid, and formic acid over the region of measured fractions.

Figure 8 shows the maximum molar absorption coefficient of Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water with methacrylic acid and with isobutyric acid. The water/isobutyric acid system had a region in which the water phase and the oil phase coexist in the concentration range of ca. 10 to 60% acid by volume, and the absorptions could not be observed.

With an increase of the acid percentage up to 10% the absorption of the dye in isobutyric acid increased quite rapidly, and its value at 10% exceeded that in ethanol, a typical laser medium. This means that the amount of this additive required to obtain the necessary concentration of monomer in aqueous dye solution was less than 10%.

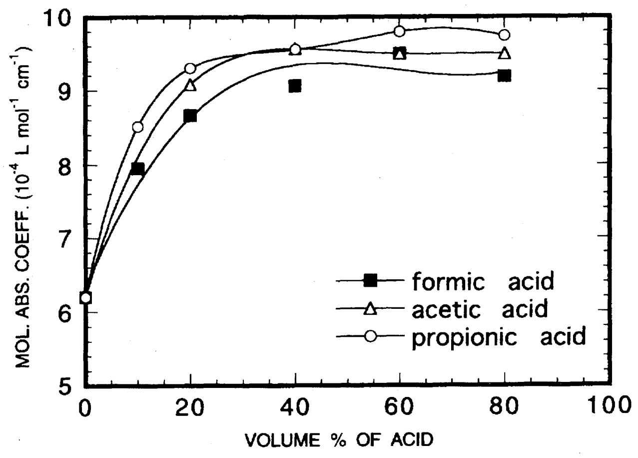

Fig. 7. Molar absorption coefficient as a function of acid fraction in Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/carboxylic acid systems.

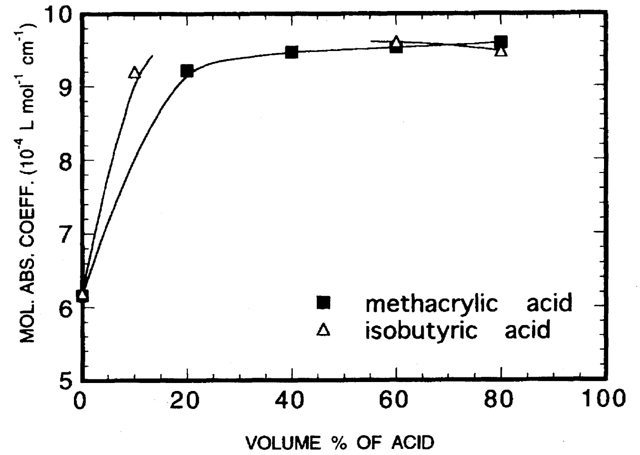

Fig. 8. Absorption spectra of the Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/acid systems. Acids are isobutyric acid $CH_3CH(CH_3)COOH$, methacrylic acid $CH_2{=}C(CH_3)$-$COOH$.

Discussion

Organic additives prevented Rhodamine 6G molecules from associating in water, in which the effectiveness is estimated from the maximum absorption, which is approximately proportional to the number of dye-monomer species present in solution at a given concentration of the dye reagent (2.0×10^{-4} mol dm^{-3}). Ethanol is a standard solvent for Rhodamine 6G, and generates very low dimer concentrations. Additives with equal or better dissociative power to ethanol were sought after. Several alcohols and carboxylic acids were examined to determine their ability to prevent dimer formation; it was found that all the organic compounds used in this experiment satisfied these requirements, and comparing monomer concentrations, some modified aqueous solvents exceeded that of 100%-ethanol.

The maximum molar absorption coefficient of Rhodamine 6G in ethanol was 9.1×10^4 dm^3 mol^{-1} cm^{-1} (Fig. 1). Isobutyric acid, followed by 2-butanol, was found to demand the minimum amount as an additive to achieve the same level of absorption as the ethanol solution. In the case of carboxylic acids, propionic acid, acetic acid, and formic acid were followed in this order of effectiveness from high to low, and in the case of alcohols, the order was butyl, propyl, ethyl, and methyl alcohols.

Figure 9 shows the relationship between the maximum molar absorption coefficients of aqueous dye solutions containing 20% organic additives by volume and their relative dielectric constants.[11] There was clearly a linear correlation; this is the most important result of our study. Isobutyric acid can not be plotted here, because its solubility in water is less than 20%. Its dielectric constant is 2.5 and the molar absorption coefficient can be expected from the curve of Fig. 8 to be plotted higher than propionic acid (number 3) at 20%. This is, therefore, a substance which confirms the correlation.

In order to explain this correlation, we would offer the model shown in Fig. 10(a). The illustrated situation is as follows: While the concentration of organic solvent is small, water molecules behave as a continuous medium, in which added organic molecules surround a dye molecule. The organic molecules would be oriented around the dye monomer with the alkyl chain onto the molecule.

While nothing was added, Rhodamine 6G molecules tend to associate to form dimers in water. This means that the monomer is not sufficiently hydrophilic to completely disperse in water, and its dimerization is due to hydrophobic bonding, which follows from the analogy of Rhodamine B mentioned in the introduction.

However, once alcohol or carboxylic acid is mixed with the aqueous dye solution, the dye molecules are thought to be solvated with those organic molecules even in water. The reason is that the number of dye-dimers decreases as the concentration of organic additive increases. Organic molecules are less polar than water, and could solvate hydrophobic molecules such as Rhodamine. Then, if organic molecules with a small polarity or a small dielectric constant are added, they would surround the dye molecules rather than disperse in water. The smaller is the dielectric constant, the more this occurs.

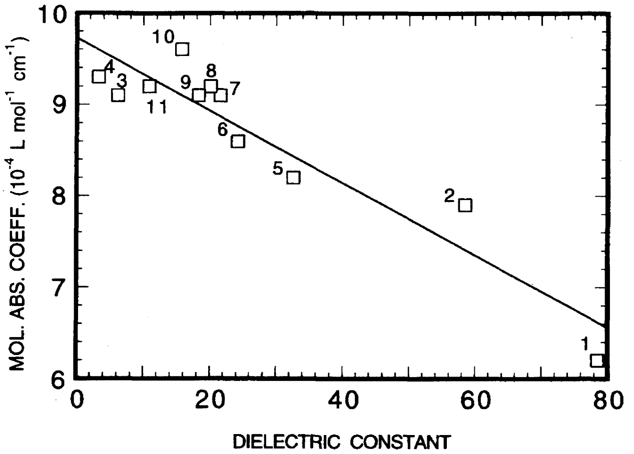

Fig. 9. Correlation between the maximum molar absorption coefficients and the dielectric constants of solvents that were mixed by 20% to Rhodamine 6G (2.0×10^{-4} mol dm^{-3}) aqueous solution **1** water H_2O, **2** formic acid $HCOOH$, **3** acetic acid CH_3COOH, **4** propionic acid CH_3CH_2COOH, **5** methanol CH_3OH, **6** ethanol CH_3CH_2OH, **7** 2-propen-1-ol $CH_2=CHCH_2OH$, **8** 1-propanol $CH_3CH_2CH_2OH$, **9** 2-propanol $CH_3CH(OH)CH_3$, **10** 2-butanol $CH_3CH_2CH(OH)CH_3$, and **11** 2-methyl-2-propanol $CH_3CH(OH)(CH_3)$-CH_2.

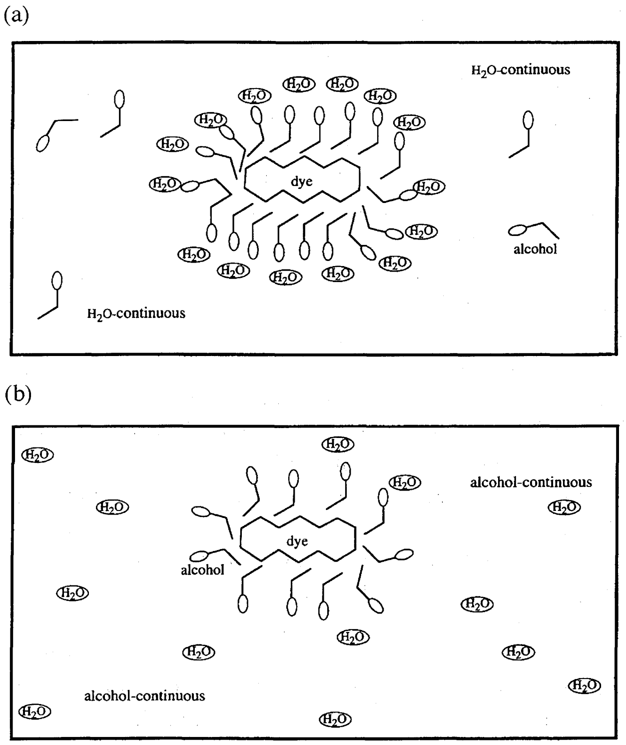

Fig. 10. Models of solvated dye monomer. (a) Fraction of organic solvent is low, and the system is water-continuous, in which added organic molecules surround a dye molecule. (b) Fraction of organic solvent is high. Dye molecules are solvated with organic molecules. In this case, water disperses in organic phase as continuous medium.

On the other hand, that correlation does not hold in the region of high fractions of organic solvent to water. As illustrated in Fig. 10(b), dye molecules are solvated with organic molecules, and water disperses in the organic solvent. Then, hydrophobic dye molecules do not need to interact with water molecules. Hence, the monomer concentration of dye barely changes with the amount of water.

As shown in Fig. 1, the molar absorption coefficient for a pure ethanol solution was smaller than that for a water-mixed solution with 60 or 70% of ethanol. This might be interpreted with the model, as illustrated in Fig. 10. In a water–ethanol mixture, ethanol molecules surround a dye molecule with their ethyl group oriented toward the dye molecule and the hydroxyl group oriented toward the surrounding water. In this situation the degree of orientation of ethanol molecules toward dye molecules would be greater than in the case of pure ethanol solvent. Then, dimer formation of the dye will be more prevented.

Conclusion

Rhodamine 6G (2.0×10^{-4} mol dm^{-3})/water/alcohol or carboxylic acid systems were studied. Rhodamine 6G molecules, which tend to associate into nonfluorescent dimers in water, were prevented from dimerizing by addition of organic compounds. The degree of dimer restraint was examined by a measurement of the monomer absorption.

It was found that additives with smaller dielectric constants prevented Rhodamine 6G molecules from becoming dimers to a higher degree in aqueous solutions. A linear correlation between the additives' dielectric constants and the dye monomer concentrations was obtained.

It was found that 2-butanol and isobutyric acid are the most effective additives for dissolving Rhodamine 6G dimers, and that the amount required to obtain the necessary concentration of monomer in aqueous solution is less than 10%.

The amount of monomer in a water/ethanol ($>$ 50%) mixture was larger than in ethanol.

The authors gratefully acknowledge Professor Kazuyoshi Ogino for helpful discussion. One of the authors thanks Joseph Baxter for his correction of the English.

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