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MONOMERIZATION OF AQUEOUS RHODAMINE B BY UREA

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ABSTRACT

Absorption and pH of rhodamine B in aqueous-urea solutions are examined. The obtained experimental results suggest that the monomerization of aqueous rhodamine B by urea may be explained by taking account of the change in the dissociation energy of dimeric rhodamine B molecules. Some other features of rhodamine B-urea-H_2O are also discussed briefly.

1. Introduction

Dimers of rhodamine B molecules show parallel plane configurations in water (ROHATGI 1968). The dimerization of aqueous rhodamine B is promoted by the addition of LiCl (MUTO, KUROSAWA 1977). Whereas, rhodamine B, as well as other xanthene dye molecules, tends to dissociate in aqueous solution by the addition of surfactants such as Triton X-100 and Ammonyx LO (ALFANO, SHAPIRO, YU 1973; PETERSON, TUCCIO, SNAVELY 1970; DREXHAGE 1973). Dimers of aqueous rhodamine B seem to fluoresce scarcely, although monomers show efficient fluorescence (MUTO 1972), and then the dissociation of dimers by the detergents becomes important to obtain the efficient fluorescence emission and lasing of rhodamine B in water.

In aqueous solution, organic molecules having hydrophobic groups are inclined to associate, and the structural region of low entropy, called icebergs, appears around them (NÉMETHY, SHERAGA 1962). Naturally rhodamine B in water tends to associate, since it contains hydrophobic groups of C_2H_5. There has already been established that urea weakens hydrophobic bonding of organic molecules in water, and thus

destroys the icebergs (ABU-HAMDIYYAH 1962; MUKERJEE, GHOSH 1963). The dissociation of organic molecules containing hydrophobic groups, therefore, is also promoted by the addition of urea to the solution.

The urea effect in water in relation with the above mentioned behaviours has been studied for various kinds of proteins (SHIFRIN, PARROT 1975; NOZAKI, TANFORD 1963; TANFORD 1962; WHITNEY, TANFORD 1962) and dyestuffs (MUKERJEE, GHOSH 1963; MUKERJEE, RAY 1962; MALIK, SALEEM 1969). The activity coefficients of monomeric dodecylpyridinium iodide and methyleneblue have been observed to decrease by a factor of 3.1 and 14 respectively, in 8 M urea (MUKERJEE, GHOSH 1963; MUKERJEE, RAY 1963). While the effect of urea on the aggregation number of orange G and arizanine red S has been studied by polarographic method (Malik, SALEEM 1969).

In this article, we have examined the effect of the addition of urea on the absorption and pH of rhodamine B in water. From the obtained results, the monomerization of aqueous rhodamine B is discussed.

2. Experimentals

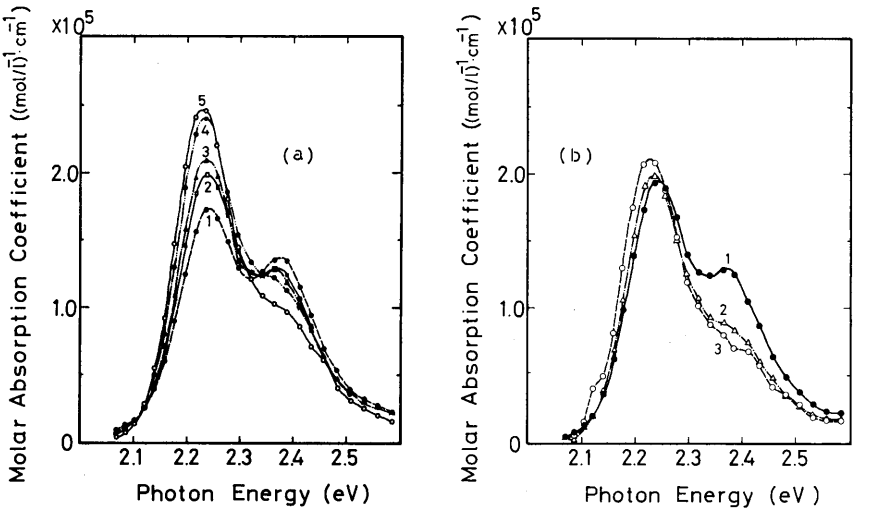
Absorption measurements were done using a Shimazu High intensity monochromator with a resolution of 4.8 nm, and the detection of light through matched quartz cells of 0.01, 0.2, and 1.0 cm path length was done with a photomultiplier (Hamamatsu-TV, R-189). A Hitach Horiba H-5 pH meter was used for the pH measurements. Rhodamine B was obtained commercially (Tokyo Kasei Industries, reagent grade). All the measurements were performed at room temperature.

3. Results and Discussions

Absorption coefficients of rhodamine B at the concentration between 1.78×10^{-3} M and 1.78×10^{-5} M are examined in aqueous-urea solutions. Typical absorption results are shown in Fig. 1. In Fig. 1-(a), the lower energy peak intensifies at the expense of the higher energy peak with increasing urea concentration and, furthermore, the observed spectra pass through an isosbestic point. Similar spectral features are also seen for aqueous rhodamine B by dilution (SELWYN, STEINFELD 1972; MUTO 1972). In Fig. 1-(b), however, the observed spectral peaks shift toward lower energies slightly by the addition of urea. The spectral shift in absorption is also found in Fig. 1-(a) at higher urea concentration of 7.09 M.

In the following, we shall discuss the effect of urea on the dissociation of dimeric rhodamine B. The mass action expression for the dimeric dissociation equilibrium of aqueous rhodamine B at the concentrations of C_0 and C_c gives,

$$\frac{2C_0x_0^2}{1-x_0}=\frac{2C_cx_c^2}{1-x_c}=K\cdot\exp(-E/RT), \qquad (1)$$



(a) (b)

Fig. 1. Effect of urea on the absorption spectra of aqueous rhodamine B.
(a) Concentration of rhodamine B: 8.90×10^{-4} M. Concentration of urea: curve 1, 0 M, 2, 1.51 M, 3, 2.27 M, 4, 3.78 M and curve 5, 6.80 M.
(b) Concentration of rhodamine B: 4.37×10^{-4} M. Concentration of urea: curve 1, 0 M, 2, 3.00 M, and curve 3, 6.00 M.

where x_0 and x_c denote fraction of monomers at C_0 and C_c, respectively. E in eq. (1) shows the dissociation energy of dimers, R universal gas constant, T absolute temperature, and $K\cdot\exp(-E/RT)$ expresses the equilibrium constant of rhodamine B. The dissociation energy and equilibrium constant for aqueous rhodamine B were already determined to be 4.2 kcal/mol and 6.8×10^{-4} M, respectively (SELWYN, STEINFELD 1972).

Taking account of the previously described role of urea for the dissociation of aqueous rhodamine B molecules, we may assume that, in aqueous-urea rhodamine B containing C_0 M rhodamine B and U M urea, the dimeric dissociation energy, E_t, decreases to become

$$E_t=E-\beta U\,, \tag{2}$$

and the corresponding dimer-monomer equilibrium is shown as

$$\frac{2C_0x_c^2}{1-x_c}=K\cdot\exp(-E_t/RT)\,, \tag{3}$$

in which x_c means fraction of monomeric rhodamine B molecules in the solution. From eq. (1) and (3), we have

$$C_c/C_0=\exp(-\beta U/RT)\,. \tag{4}$$

As mentioned previously, main absorption peak around 2.23 eV increases and subsidiary peak at about 2.36 eV decreases, in aqueous rhodamine B by dilution,

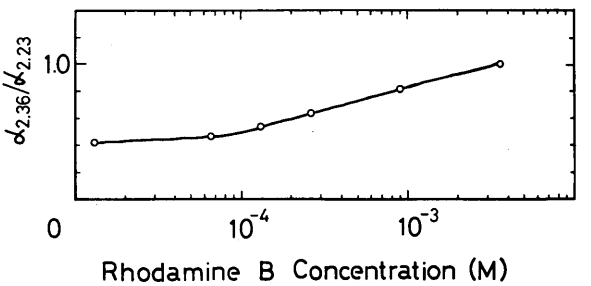


Fig. 2. Ratio of absorption coefficient, $\alpha_{2.36}/\alpha_{2.23}$, as a function of rhodamine B concentration.

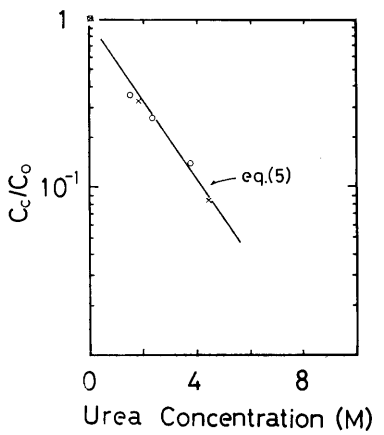


Fig. 3. Ratio of two concentrations, C_c/C_0, as a function of urea concentration. Rhodamine B concentration: circles, 8.90×10^{-4} M, and crosses, 1.87×10^{-3} M. Solid line indicates eq. (5).

and then the ratio of the absorption coefficients, $\alpha_{2.36}/\alpha_{2.23}$, increases with increasing rhodamine B concentration (see Fig. 2). We are now going to determine the values of C_c in eq. (4) by calculating the ratios of experimentally obtained two absorption peaks for rhodamine B in urea-H_2O, and by finding the corresponding rhodamine B concentrations in Fig. 2.

The obtained values of C_c/C_0 at various urea concentrations in Fig. 3 may be approximated by the empirical equation such as

$$C_c/C_0=0.93\cdot\exp(-0.54U)\,. \qquad (5)$$

Since our experiments were done at room temperature, βU in eq. (2) becomes $0.32U$ (kcal/mol), in which U denotes urea concentration in M as was already stated. Eq. (5) seems to show that the explanation that urea reduces the dimeric dissociation energy of aqueous rhodamine B, as shown in eq. (2), may be valid for the description of the effect of urea in the solution.

In the above treatment, only the dimer-monomer equilibrium is taken into account, since the higher aggregation does not exsist in aqueous rhodamine B at the concentration of our examination (SELWYN, STEINFELD 1972). Our analysis on the dissociation of rhodamine B in urea-H_2O may be a simplified one, only the ratios of the two absorption peaks being considered for the determination of C_e. Further extensive studies on the detailed spectral behaviours in absorption will be necessary to understand fully the effect of urea on the dissociation of dimeric rhodamine B in water.

Now, all the molar absorption spectra of aqueous rhodamine B in the dimer-monomer equilibrium state are found to pass through an isosbestic point (SELWYN, STEINFELD 1972; MUTO 1972). Our absorption results, however, show that the obtained spectra do not pass through an isosbestic point at $U/C_0 > 3 \sim 4 \times 10^3$ (Fig. 6). Monomeric rhodamine B molecules in water show zwitterion structure, $[R^{+-}]$, (see Fig. 4) at pH$>3\sim4$ with only one absorption peak around 2.23 eV (RAMETTE, SANDELL 1956). Whereas, the observed spectra are inclined to shift slightly at high values of U/C_0, though pH of the solution is larger than 3 (see Fig. 5). The maximum values of absorption for rhodamine dyes having carboxyphenyl substitu-

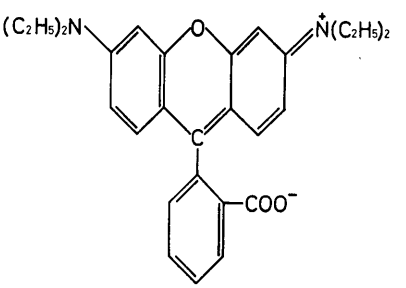


Fig. 4. Zwitterion structural formula of rhodamine B, $[R^{+-}]$.

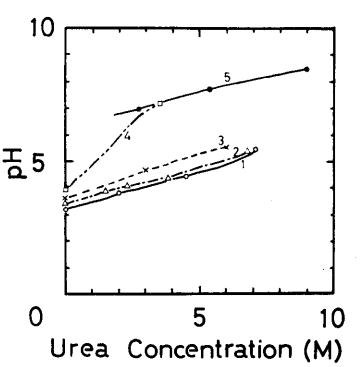


Fig. 5. Effect of urea on pH of rhodamine B-urea-H_2O. Concentration of rhodamine B: curve 1, 1.78×10^{-3} M, 2, 8.90×10^{-4} M, 3, 4.37×10^{-4} M, 4, 1.78×10^{-4} M, and curve 5, 0 M.

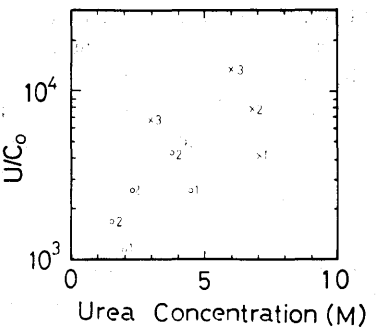


Fig. 6. Ratio of urea to rhodamine B concentrations, U/C_0, as a function of urea concentration. For results indicated by circles, dimer-monomer equilibrium seems to be realized; while for results showed by crosses, absorption spectral shift appears. Numbers 1, 2 and 3 represent results obtained for rhodamine B concentrations of 1.78×10^{-4} M, 8.90×10^{-4} M, and 4.37×10^{-4} M, respectively.

ents are affected by 3- and 6-positions of the nucleus (DREXHAGE 1972). It might be considered that urea influences on $N(C_2H_5)_2$ groups of rhodamine B molecules in water at high U/C_0 values.

The fluorescence quantum yield of aqueous rhodamine B, as described in "Introduction", is greatly reduced by dimerization. Our results seem to indicate that the dissociation of non-fluorescent dimers to fluorescent monomers by the addition of proper amount of urea may improve the apparent fluorescence yield and then the lasing efficiency of aqueous rhodamine B.

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