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Pressure Effects on Equilibrium between Lactone and Zwitterion Forms of Rhodamine B in Primary Alcohols

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Synopsis. The equilibrium between lactone and zwitterion forms of Rhodamine B was studied in primary alcohols and at high pressures. The effects of solvent polarity and pressure on the equilibrium constant were examined by using a Kirkwood-type equation.

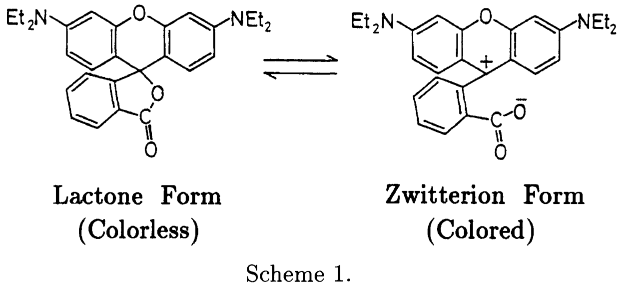
Rhodamines are extensively used in applications to dye laser and fluorescence studies.[1)] It is well-known that Rhodamine B (RB) exists as an equilibrium mixture of a colored zwitterion (Z) and a colorless lactone (L) form.[2)] In 1988, Hinckley and Seybold[3)] estimated the equilibrium constants in various kinds of alcohols, and suggested that the position of the $L \rightleftharpoons Z$ equilibrium depends on solvent-dye hydrogen bonding and solvent dielectric/polarizability properties (Scheme 1). However, they did not give a clear-cut explanation of the electrostatic factors affecting the position of the equilibrium.

In this work, we used six kinds of primary alcohols to avoid the large difference in the steric hindrance about the hydroxyl group of alcohol. To obtain further information about the electrostatic factors affecting the position of the $L \rightleftharpoons Z$ equilibrium, we have investigated the solvent and pressure effects on the equilibrium.

Experimental

Rhodamine B·HCl (9-(2-carboxyphenyl)-3,6-bis(diethylamino)xanthylium chloride) was purchased from Tokyo Chemical Industry Co. The lcatone of RB was prepared by the method of Klein and Hafner.[4)] The reagent grade primary alcohols were purified and distilled in the usual manner.

The high-pressure apparatus and procedure for spectral measurements were almost the same as those described elsewhere.[5)] To avoid the possible formation of the RB dimer, the concentrations were chosen as low as 1×10^{-6} mol dm^{-3}. A Hitachi 100-50 double beam spectrophotometer was used for spectral measurements.



Lactone Form (Colorless)

Zwitterion Form (Colored)

Scheme 1.

Results

The equilibrium constant K between the L- and Z-forms is expressed by

$$K = [\mathrm{Z}]/[\mathrm{L}] = [\mathrm{Z}]/([\mathrm{R}]_0 - [\mathrm{Z}]), \qquad (1)$$

where [L] and [Z] are the concentrations of the L- and Z-forms at equilibrium, respectively, and $[\mathrm{R}]_0$ denotes the initial concentration of RB. Since the spectral shapes in the visible region in primary alcohols are almost the same, we estimated the K-values by using the molar absorptivity for the Z-form (1.30×10^5 dm^3 mol^{-1} cm^{-1}) reported by Hinckley and Seybold.[3)]

For the measurements of the pressure effects, four primary alcohols (methanol, ethanol, 1-propanol, and 1-pentanol) were chosen so we could use available ε–p data together with compressibility data. The reaction volumes were estimated by the following equations.

$$\ln K = ap + b \qquad (2)$$

$$\Delta V = -RT(\partial \ln K/\partial p)_T \qquad (3)$$

The K and ΔV values are given in Table 1, with relevant data.

Discussion

In an aprotic solvent such as acetonitrile, the absorption band of the colored Z-form in the visible region could not be observed, while in alcohols we can observe the absorption band of the Z-form at $\lambda_{\max}$=about 545 nm. Rosenthal and Peretz[2)] have reported the similar observations, and suggested that the protic character of the solvent is an important factor for the formation of the Z-form. In the L-form, the oxygen atom on lactone ring is probably too hindered to form an effective hydrogen bond with alcohol solvents. However, in the Z-form the strong hydrogen bonding may occur at the charged $-\mathrm{COO}^-$ group, resulting in increased stabilization of the Z-form relative to the L-form. Therefore, the equilibrium of RB in alcohols can be expressed as follows:[3)]

$$\mathrm{L} + \mathrm{S} \rightleftharpoons \mathrm{Z}\cdots\mathrm{S}$$

in which S represents the solvent. Moreover, Hinckley and Seybold[3)] have proposed that the factors determining the position of the equilibrium in alcohols are the dielectric constant of the solvent (ε), the number of carbon atoms in the alcohol, the number of carbons

Table 1. Equilibrium Constants at Various Pressures and Reaction Volumes at 298 K

		$K^{a)}$				ΔV	ΔV_{sol}	$10^{11}q_P$
Solvent	ε	$p^{b)}=1$	300	600	900	$cm^3\,mol^{-1}$	$cm^3\,mol^{-1}$	Pa^{-1}
Methanol	30.2	6.31	6.67	7.02	7.37	−4.2±0.1	−13.2	2.88
Ethanol	24.6	2.88	3.08	3.23	3.43	−4.7±0.2	−13.7	2.99
1-Propanol	20.0	2.10	2.26	2.46	2.66	−6.1±0.1	−15.1	3.31
1-Butanol	16.5	1.49						
1-Pentanol	14.7	0.918	1.09	1.27	1.45	−12.2±0.4	−21.2	4.62
1-Hexanol	12.4	0.674						

a) Precision within 5%. b) p in kgf cm^{-2} (1 kgf cm^{-2}=0.981×10^5 Pa).

bonded to the α-carbon (C_α), and the number of terminal methyl groups of the alcohol. In conclusion, they have pointed out that C_α and ε, which describe a measure of the steric hindrance about the alcohol hydroxyl group and the ability of solvent to stabilize a solute dipole, are important.

In the case of six kinds of primary alcohols used in our study, the environmental situation of the alcohol hydroxyl group will not change. It is therefore necessary to discuss stabilization of a solute dipole in solution. Indeed, the equilibrium constant increases with increasing dielectric constant as a criterion for solvent polarity, as can be seen in Table 1. It is instructive to discuss the capacity of solvent to stabilize solute dipoles by using an electrostatic model introduced by Kirkwood.[6)] According to the Kirkwood treatment, the dielectric influence of solvents on equilibrium constants is given by

$$\ln K = \ln K_0 + (N/RT)[(\mu_Z^2/r_Z^3) - (\mu_L^2/r_L^3)][(\varepsilon-1)/(2\varepsilon+1)] \qquad (4)$$

where μ_Z and μ_L are the dipole moments of the Z- and L-forms, respectively. K_0 is the equilibrium constant in a hypothetical condensed medium of $\varepsilon=1$ and the other symbols have their usual meanings. The second term represents the contribution from the electrostatic solute–solvent interaction. Equation 4 predicts a linear relation between $\ln K$ and $(\varepsilon-1)/(2\varepsilon+1)$ with a slope of $(N/RT)[(\mu_Z^2/r_Z^3)-(\mu_L^2/r_L^3)]$. In Fig. 1, $\ln K$ is plotted against $(\varepsilon-1)/(2\varepsilon+1)$. As can be seen in Fig. 1, a linear relation holds between them.

The equilibrium constant increases with increasing pressure, and the estimated reaction volumes are in the range of −4—−13 cm^3 mol^{-1} (Table 1). One finds that the absolute values of the reaction volumes increase with decreasing the dielectric constant of alcohol solvent. It is generally accepted that the volume change accompanied by chemical reactions consists of two components: an intrinsic part (ΔV_{int}) and a solvational part (ΔV_{sol}).

$$\Delta V = \Delta V_{int} + \Delta V_{sol} \qquad (5)$$

Differentiating Eq. 4 with respect to pressure, the solvational part (ΔV_{sol}), which describes the volume change due to changes in solvation between the L- and Z-forms, can be expressed by

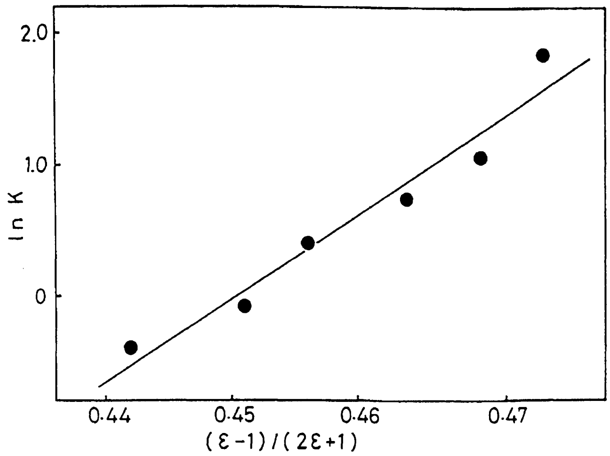


Fig. 1. Plots of $\ln K$ against $(\varepsilon-1)/(2\varepsilon+1)$ for the equilibrium of Rhodamine B at 298 K.

$$\Delta V_{sol} = -N[(\mu_Z^2/r_Z^3) - (\mu_L^2/r_L^3)]q_P$$
$$q_P = (\partial/\partial p)[(\varepsilon-1)/(2\varepsilon+1)]. \qquad (6)$$

The q_P-values were estimated by using available ε–p data.[7)] The ΔV_{int}-value for the equilibrium of RB in alcohols is considered to be the sum of the difference in volume between the Z- and L-forms without electrostriction (ΔV_{st}) and the volume change arising from the hydrogen-bond formation in the Z-form (ΔV_H).

$$\Delta V_{int} = \Delta V_{st} + \Delta V_H \qquad (7)$$

Weale[8)] estimated the change in volume for the 5-membered-ring closure from the differences between the molar volumes of a reactant and product. The reported reaction volumes are −13 cm^3 mol^{-1} for ethyl vinyl ether→tetrahydrofuran and −15 cm^3 mol^{-1} for 1-pentene→cyclopentane. Therefore, for the 5-membered-ring opening process of RB, ΔV_{st} may be about 14 cm^3 mol^{-1}. On the other hand, there has been a vast number of reports concerning the pressure effects on the hydrogen-bond formation. The volume changes for the hydrogen-bond formation vary depending on the type of bonding, but ΔV_H is generally about −5 cm^3 mol^{-1}.[8)] Accordingly, ΔV_{int} for the equilibrium of RB can be calculated to be 9 cm^3 mol^{-1}. As given in Table 1, the ΔV_{sol}-values can be estimated to be −13—−22 cm^3 mol^{-1} from Eq. 5.

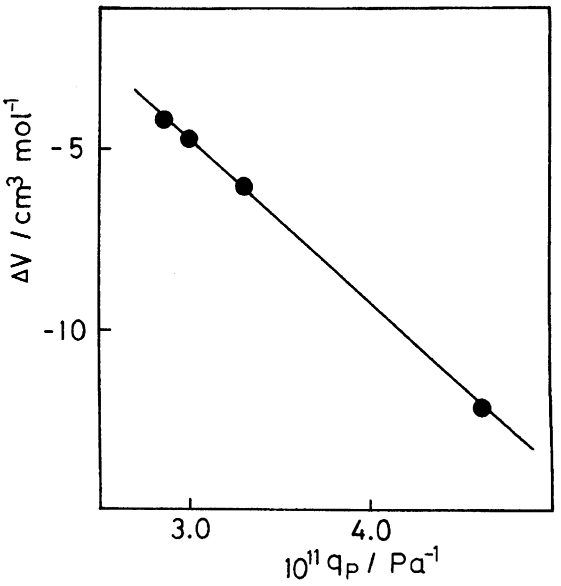


Fig. 2. Plots of ΔV against q_P in alcohols.

To estimate the volume change due to electrostriction, the hydrodynamically equivalent approximate radii of RB were estimated to be $r_Z=r_L=0.3$ nm with the aid of the Corey–Pauling–Koltun model. Further, we assumed that the dipole moment of the L-form is $\mu_L=2.0$ Debye (1 Debye$=3.3\times10^{-30}$ m C) and that the ΔV_H-value is independent of the kinds of alcohols. By substituting the above values and the estimated ΔV_{sol}-values into Eq. 6, the μ_Z-value can be calculated to be on the average 14.5 Debye. This may be an acceptable magnitude, since the dipole of 1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] has been reported to be $\mu=12.7$ Debye.[9] In Fig. 2, the reaction volumes, observed in alcohols, are plotted against q_P-values. The reaction volumes decrease linearly with increasing q_P-values, as predicted from Eqs. 5 and 6. The solid line in Fig. 2 shows the reaction volume calculated by using $\mu_Z=14.5$ Debye and the above values. The calculated reaction volumes for each solvent well reproduce the observed ones. Incidentally, substituting the above values into Eq. 4, the slope of the Kirkwood plot can be calculated to be 185. The actual slope is 63. As suggested by Whalley,[10] the volume is easier to understand on an elementary level than by thermodynamic quantities since the nuclear positions tell one a good deal about the volume. The Kirkwood treatment is a simplified model, and could provide a convenient basis for a semiquantitative comparison of solvent effects on the equilibrium. The difference between the calculated and actual slopes perhaps comes from the approximate nature of the above treatment and the numerical choices for μ and r.

All the above findings show that the position of the $L\rightleftharpoons Z$ equilibrium in primary alcohols can be explained in terms of the electrostatic interaction between the solute and the solvent dipoles, although hydrogen bonding is necessary for the formation of the Z -form.

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