High-Pressure Study of Rhodamine B in Solution and Adsorbed on Oriented Single-Crystal ZnO

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The effect of hydrostatic pressure to 10 kbar has been measured on the spectrum of rhodamine B in buffered aqueous solution (2×10^{-5} M) and adsorbed on the 0001 face of single-crystal ZnO in equilibrium with the solution. The dye exists as a mixture of monomer and dimer, both in solution and adsorbed. The monomer and dimer peaks shift to lower energy with increasing pressure in both environments as is characteristic of $\pi-\pi^*$ excitations. From the monomer–dimer equilibrium constant in solution one finds a decrease in volume on dimerization. At low pressure $\Delta \bar{V} = -4.2$ cm^3/g-mol, while at high pressure $\Delta \bar{V} = -5.1$ cm^3/g-mol. The monomer showed virtually no decrease in volume with adsorption. The dimer exhibited a smaller partial molar volume when adsorbed than in solution ($\Delta \bar{V} = -1.2$ cm^3/g-mol at low pressure and -0.4 cm^3/g-mol at high pressure). The volume change for the process from monomers in solution to adsorbed dimers is essentially independent of pressure.

Introduction

In this paper we present the effect of pressure to 10 kbar on the spectrum of rhodamine B, both in solution and adsorbed on the 0001 face of ZnO single crystals.

In solution xanthene dyes exhibit a tendency to aggregate that is strongly dependent on concentration. Rhodamine B exists in the monomer form at low aqueous concentrations (less than 10^{-6} M) and atmospheric pressure. As the dye concentration is increased, rhodamine B dimers appear. At concentrations greater than 5×10^{-3} M, trimers and associates of higher orders are present. It has been suggested that hydrogen bonding either between the dye molecules[1,2] or with the participation of water molecules[3] and in interaction with the accompanying anions[4,5] may be responsible for the dimerization in certain cases. Experimentally determined values of the binding energy for rhodamine B dimers range from 5 to 10 kcal/mol.[3] These values support the hypothesis that hydrogen bonding is important in dimer formation.

In this study the dye concentration was 2×10^{-5} M. One of the purposes of the work was to extract monomer–dimer equilibria. The solvent was an aqueous solution 1 M in KCl buffered by 0.1 M sodium acetate.

The monomer and dimer have distinctly different absorption spectra. The absorption band of the monomer consists of two vibrational bands. The lower energy band is more intense, and the higher energy band appears as a high-energy shoulder. The absorption band of the dimer consists of two peaks. The two possible electronic transitions of the dimer are due to the twofold splitting of the excited electronic level as two monomers are brought together to form a dimer. The high-energy dimer peak arises from the dimer form in which the transition dipole moments of the two monomers composing the dimer are parallel, whereas the low-energy dimer peak arises from the dimer form in which the transition dipole moments are not parallel. In general, the two transitions possess different transition dipole moments. Most often the low-energy transition has a negligible transition dipole moment so that only one absorption band of the dimer is observed, located on the high-energy side of the monomer band. This phenomenon is observed for rhodamine B at atmospheric pressure.[6] In the parallel plane model of the high-energy rhodamine B dimer, the angle between the transition dipole moments of the two monomers is 64°, and the distance between the monomer units is 6.43 Å.[3]

The equilibrium constant for the dimerization (K_{eq}) is given by the following expression

$$K_{eq} = X_{dimer}/X_{monomer}^2 \tag{1}$$

where X is the mole fraction. The volume change in the system ($\Delta \bar{V}$), as 2 mol of monomer react to form 1 mol of dimer, is found from the effect of pressure on the equilibrium constant:

$$\Delta \bar{V} = \bar{V}_{dimer} - 2\bar{V}_{monomer} = -RT(\partial \ln K_{eq}/\partial P)_T \tag{2}$$

Experimental Procedure

The high-pressure techniques and methods for obtaining and analyzing the spectra have been discussed in detail elsewhere.[7–9] The solution data were obtained by optical absorption while the spectra of the adsorbed molecules were obtained by photoelectrochemical techniques. The absorption of the dye was sufficiently far from the absorption edge of ZnO that deconvolution of the tail of the ZnO absorption edge was straightforward. The scatter of the points in the various figures gives the best representation of the consistency and reproducibility of the data.

Typical absorption spectra for rhodamine B in solution at 1 atm and 10 kbar are shown in Figure 1a,b. The low- and high-energy peaks correspond to monomer and dimer, respectively. Figure 2a,b presents the same data for adsorbed molecules. In both cases the data are corrected for lamp, filter, and detector response.[8,9] In addition, the adsorbed spectra are corrected for absorption of the dye in solution and for the tail of the absorption edge of ZnO.[8,9]

Discussion

We first discuss the peak shifts briefly; then we present a discussion of the various equilibria involved.

The effect of pressure on the shifts of the monomer and dimer peaks of rhodamine B, both in solution and adsorbed onto the surface of zinc oxide, is shown in Figures 3 and 4, respectively. In order to obtain a first-order evaluation of the effect of pressure, the shift in peak location was approximated by a straight line, calculated by using a least-squares analysis. There is in fact a small curvature, but the linear fit provides the best quantitative comparison of the results. In the case of the dye in solution, both the monomer and dimer peaks shift red (toward lower energies) with increasing pressure. The monomer peak is longated at $\bar{\nu}_0 = 17\,950$ cm^{-1} and shifts red by -28 cm^{-1}/kbar. The dimer peak is located at $\bar{\nu}_0 = 18\,990$ cm^{-1} and shifts red by -37 cm^{-1}/kbar. The red shift is a common feature of $\pi \rightarrow \pi^*$ excitations. The shift toward lower energies occurs because the excited state (π^*) is more polarizable than the ground state (π); thus, the attractive

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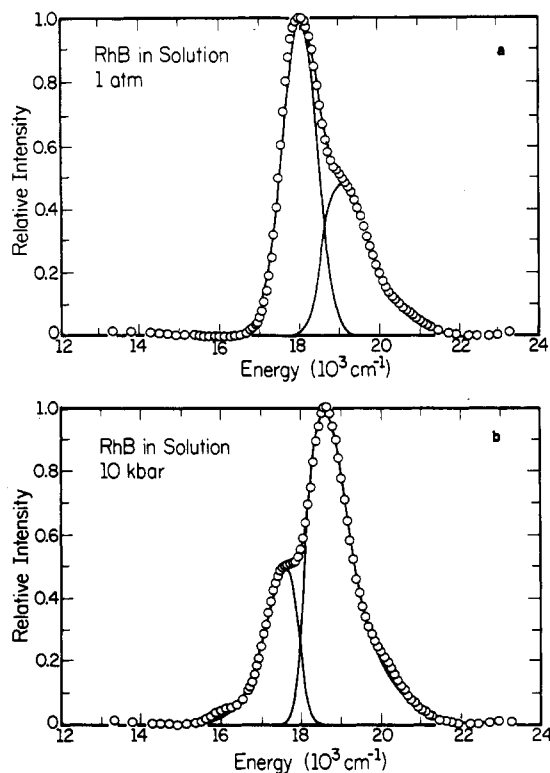(9) F. T. Clark and H. G. Drickamer, *J. Chem. Phys.*, **81**, 1024 (1984).

Figure 1. (a) Spectrum of rhodamine B (2 × 10⁻⁵ M) in buffered aqueous solution at 1 atm. (b) Spectrum of rhodamine B (2 × 10⁻⁵ M) in buffered aqueous solution at 10 kbar.
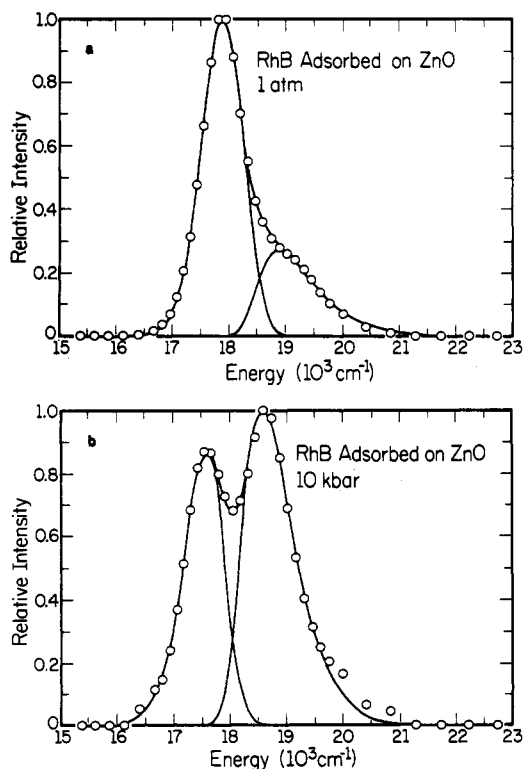

Figure 2. (a) Spectrum of rhodamine B adsorbed on ZnO at 1 atm. (b) Spectrum of rhodamine B adsorbed on ZnO at 10 kbar.

(van der Waals) forces are larger and the system volume is smaller.

A similar red shift occurs for the monomer and dimer of rhodamine B adsorbed on the surface of zinc oxide. The monomer peak is located at $\bar{\nu}_0 = 17\,840$ cm⁻¹ and shifts red by −29 cm⁻¹/kbar. The dimer peak is located at $\bar{\nu}_0 = 18\,860$ cm⁻¹ and shifts red by −28 cm⁻¹/kbar. For both the monomer and dimer, the peak corresponding to the adsorbed dye is located at lower energies than the peak corresponding to the dye in solution. In
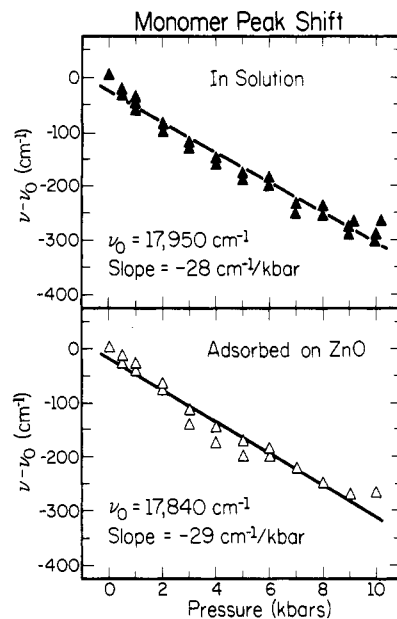

Figure 3. Peak shift vs. pressure for rhodamine B monomer both in solution and adsorbed.
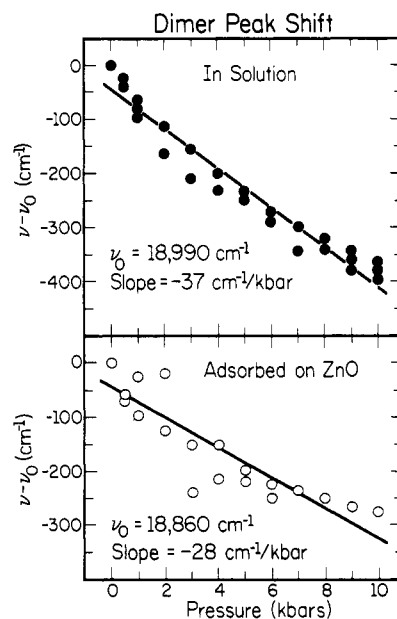

Figure 4. Peak shift vs. pressure for rhodamine B dimer both in solution and adsorbed on ZnO.

the case of the dimer, the shift in peak location with pressure is less for the adsorbed dye than for the dye in solution, whereas in the case of the monomer, the shifts in peak location for the adsorbed dye for the dye in solution are the same. These results are probably real, however, in view of the uncertainties involved in deconvolution, and it is best not to overinterpret them at present.

The equilibrium characteristics of the monomer and dimer are extracted from the effect of pressure on the relative areas under the monomer and dimer peaks. The analysis assumed that the area fractions of the monomer and dimer peaks are equal to the mole fractions of the monomer and dimer, respectively, both in solution and in the adsorbed state (see below). The relationship for the dimer is given by

$$\mathrm{AF}_{\mathrm{dimer}} = \frac{E_{\mathrm{d}}c_{\mathrm{d}}l}{E_{\mathrm{m}}c_{\mathrm{m}}l + E_{\mathrm{d}}c_{\mathrm{d}}l} =$$

$$\frac{\text{moles of dimer}}{k(\text{moles of monomer} + \text{moles of dimer})} \quad (3)$$

where $\mathrm{AF}_{\mathrm{dimer}}$ is the area fraction of the dimer and the cross-sectional area is constant and $E_{\mathrm{m}} = kE_{\mathrm{d}}$. ($E$ is the integrated
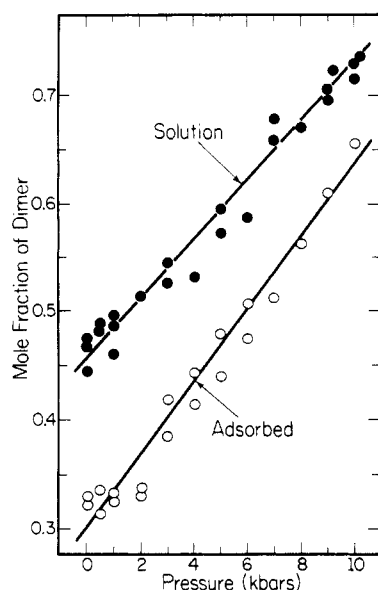
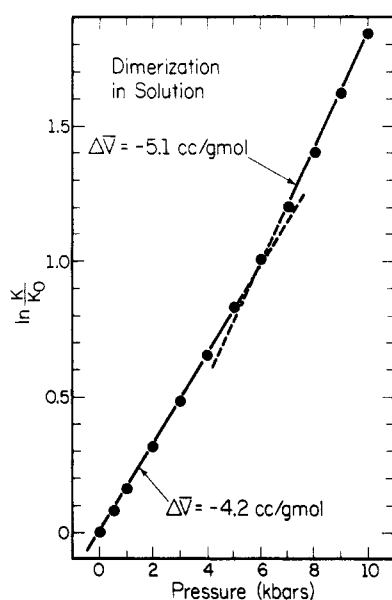**Figure 5.** Mole fraction rhodamine B dimer vs. pressure for rhodamine B dimer both in solution and adsorbed on ZnO.

Figure 6. ln K/K_0 vs. pressure for monomer–dimer equilibrium in solution.

Figure 7. ln K/K_0 for adsorption of monomer and dimer.

the change in partial molar volume on dimerization. Figure 6 shows that the partial molar volume of the dimer is less than the sum of the partial molar volumes of the monomers. Thus as pressure is applied, the system acts to relieve the stress by decreasing its volume and forming one dimer from two monomers. The formation of a bond between the monomers produces the decrease in volume; in addition, a change in the interactions of the molecules with the environment (e.g., degree of solvation) cannot be ruled out. The curve through the data in Figure 6 was approximated by straight lines between 1 atm and 5 kbar and between 6 and 10 kbar. In the low-pressure region, the change is partial molar volume on dimerization is -4.2 cm^3/g-mol, whereas in the high-pressure region, the change is -5.1 cm^3/g-mol. Therefore, the volume occupied by the dimer decreases more rapidly with increasing pressure than the volume occupied by the monomers; the local compressibility around the dimer is larger than the local compressibility around the monomers.

In order to analyze the effect of pressure on the mole fraction of dimer adsorbed on the zinc oxide surface, either of two viewpoints can be taken. Either equilibrium exists between the monomers and dimers adsorbed on the surface or equilibrium exists separately between the monomers in solution and the adsorbed dimers. The second alternative is more reasonable and has been adopted in the following analysis.

From the pressure derivative of the equilibrium constants so defined, the difference in partial molar volumes of the species in equilibrium can be extracted. For the monomers and the dimers, the change in volume on adsorption is negative as shown in Figure 7. In the case of the monomers, the data have been approximated by a straight line which gives a small decrease in volume on adsorption of -0.1 cm^3/g-mol. For the dimers, the partial molar volume of the dimer in solution is -1.2 cm^3/g-mol less than the partial molar volume of the dimer adsorbed on the solid in the low-pressure region, and the difference is 0.4 cm^3/g-mol in the high-pressure region. Therefore, either due to steric factors or to differences in the degree of solvation, the adsorbed dimer has a smaller partial molar volume. In addition, the local compressibility around the dimer in solution is larger than the local compressibility around the adsorbed dimer.

It is difficult to put a precise number on the accuracy of $\Delta \bar{V}$. The peak fits show excellent precision, but there is not quantitative way to establish possible errors in the various deconvolutions involved. It is reasonable to say that the trends shown are certainly correct but that absolute errors of 5–10% in $\Delta \bar{V}$ are not impossible.

Suzuki and Tsuchiya[11] measured monomer–dimer equilibrium for RhB in aqueous solution to 4.5 kbar. They quote a $\Delta \bar{V}$ of -10.4

extinction coefficient.) For $k = 1$, the area fraction is equal to the mole fraction. An analogous equation exists for the monomer. Our analysis is based on the assumptions that $k = 1$ at 1 atm and that the ratios of the integrated transition dipole moments for the monomer and dimer transitions are pressure independent. If one uses $k = 1.25$, obtained by Obermueller and Bojarski,[3] rather than $k = 1$, the volume changes discussed below differ by less than 5%. The second assumption is reasonable based on past experience in this laboratory and on work done by others:[10] no significant effect of pressure on the absolute magnitudes of the extinction coefficients for $\pi \rightarrow \pi^*$ transitions over the 1 atm to 10 kbar range was found.

The mole fraction of dimer was found to increase with increasing pressure both in solution and on the solid as shown in Figure 5. The increase, however, was less rapid for the dye in solution than for the adsorbed dye.

For the dye in solution, equilibrium exists between the monomer and the dimer present. The equilibrium constant is defined in eq 1. As developed in eq 2, the pressure derivative of K_{eq} gives
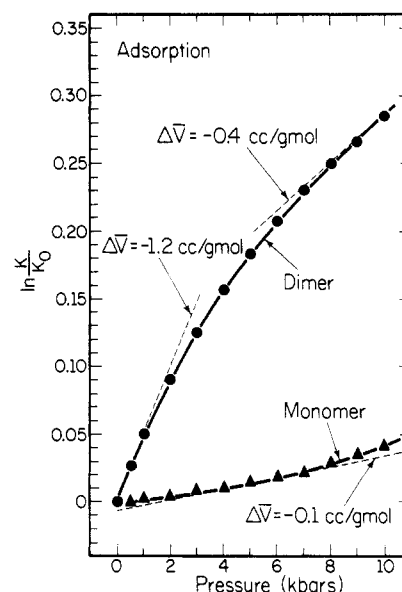
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cm³/g-mol. A replot of their equilibrium constants shows a curvature increasing with pressure such as appears in Figure 6, with $\Delta \bar{V}$ = -7.5 in the range 0–2 kbar and -11.5 in the range 2.5–4.5 kbar. It is difficult to account for the factor of approximately 2 between their results and ours, unless it is associated with the fact that we used a buffered aqueous solution 1 M in KCl while they apparently used pure water, the pH of which decreases by ~0.25 unit per kbar.[12]

Studies involving the effect of pressure on crystal violet, a triphenylmethane dye, dissolved in solution and adsorbed on the surface of zinc oxide were conducted by Clark.[9] Crystal violet existed as a multiequilibrium among isomeric monomers and dimers. As in the present study, Clark found a decrease in volume upon dimerization. However, for the dimers, there was an increase in volume on adsorption for crystal violet while we observed a decrease in volume on adsorption for rhodamine B. From a comparison of Clark's results to the results of the present work, it is evident that the mode of attachment and/or the degree of solvation for crystal violet differs from that of rhodamine B.

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In the present study of rhodamine B, by considering equilibrium between the monomers and dimers in solution and between the dimers in solution and the adsorbed dimers, the change in partial molar volume between the monomers in solution and the adsorbed dimers can be analyzed. In the low-pressure region, the volume change is -5.4 cm³/g-mol (-4.2 cm³/g-mol + -1.2 cm³/g-mol), and in the high-pressure region, the volume change is -5.5 cm³/g-mol (-5.1 cm³/g-mol + -0.4 cm³/g-mol). The volume change for the process between monomers in solution and dimers adsorbed on a solid surface, then, is relatively constant. As pressure is increased, the dimers in solution more closely resemble the adsorbed dimers. The change may be due to steric factors or to differences in the degree of solvation, but the latter seem more likely.

Registry No. Rhodamine B, 81-88-9; ZnO, 1314-13-2.

An ESR Study of the Dissociation of Hydroxyl Protons in Hydroxycyclohexadienyl Radicals

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The hydroxylic protons of a number of carboxylated hydroxycyclohexadienyl radicals are shown by ESR methods to undergo acid dissociation with pK_a values in the range 13.5–15.3. For these radicals ionization of the hydroxylic proton has very little effect on the g factor and appreciably affects the hyperfine constants only of the protons at the methylenic position. For radicals carboxylated at positions adjacent to the OH group these latter constants ($a(H_6)$) decrease by as much as 4 G on ionization, in contrast to increases of 2–4 G observed for hydroxycyclohexadienyl and the more remotely carboxylated radicals. The acid–base equilibria can, in each case, be monitored by examining the basicity dependence of $a(H_6)$. Comparison of the pK_a values of the three radicals derived from benzoic acid shows that hydrogen bonding between OH and an adjacent carboxyl group increases the pK_a by ~0.7 unit. For the more highly carboxylated radicals the effects are shown to be nearly additive if one includes an additional term representing charge stabilization of the anionic form of the radical. These interactions have, however, only a negligible effect on electron distribution in the π system of the radical, as is indicated by the lack of dependence of the other hyperfine constants on ionization.

Introduction

α-Hydroxy radicals have been shown in optical pulse radiolysis[1,2] and steady-state radiolysis–ESR[3] experiments to have pK_a values for dissociation of the hydroxylic proton in the range of 10–12, i.e., 4–5 units lower than for the parent alcohols. The acid–base equilibria of most β-hydroxy radicals cannot be examined readily by optical methods because dissociation occurs only at high pH where side reactions usually complicate absorption spectroscopic studies. However, ESR methods can be used to advantage in this case since the hyperfine data, which represent the weighted average of the acidic and basic forms, provide direct information on their relative concentrations at equilibrium, even though the radical may be present only as a minor component in the system. Kirino[4] has discussed this approach in some detail and has examined the acid–base equilibrium of a number of β-hydroxyalkyl radicals, showing that their pK_a values are in the range 13–15, several

units higher than for α-hydroxy radicals but somewhat lower than for the corresponding alcohols. Kirino and Taniguchi[5,6] have also carried out additional studies of this type on β radicals derived from peptides. In conjunction with other observations on the ESR spectroscopy of substituted 6-hydroxycyclohexadienyl radicals,[7,8] where the OH group is β to the conjugated cyclohexadienyl π system, we have found that proton dissociation occurs in the region of 1 M base. In the case of hydroxycyclohexadienyl radical this dissociation is manifest by a 4.0-G increase in the methylenic proton hyperfine constant on increasing the pH from 13 to 16.[9] We report here results of similar studies on the ionization of the OH proton in a number of carboxylated hydroxycyclohexadienyl

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