Pressure Effects on Aminonaphthalene Dye Fluorescence in H₂O and D₂O

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The pressure dependence of excited-state proton transfer equilibria has been examined for aqueous solutions of several substituted naphthalene dyes, in particular 1-dimethylaminonaphthalene-5-sulfonic acid (DANS). The pressure-induced shift in equilibrium is characterized by volume changes spanning the range $ΔV^* = -18 \text{ cm}^3 \text{ mole}^{-1}$ to $ΔV^* = +4 \text{ cm}^3 \text{ mole}^{-1}$. A deuterium oxide solvent isotope effect is evident in the pressure response of DANS, leading to a 35% smaller $|ΔV^*|$ in $D_2O$ relative to $H_2O$.

KEY WORDS: High pressures; fluorescence; aqueous solution; dyes; excited-state proton transfer; solvent isotope effects.

The protonation equilibria of weak electrolytes undergo large shifts upon electronic excitation. The aminonaphthalene dye molecules in aqueous solutions are preeminent examples of a class of compounds in which fluorescence and excited-state proton transfer occur at competitive rates and the luminescence of both the parent dye molecules and the corresponding protonated species is observed simultaneously.¹⁻³ The principal evidence for the establishment of excited-state equilibrium in these systems derives from the fluorescence titration curves (as a function of pH).¹⁻² Solvent isotope effects have also been noted.⁴⁻⁶ Substitution of deuterium oxide for water invariably reduces both ground state and excited state dissociation constants, the isotope influence being larger the weaker the acid. Herein, we report the effects of high pressure on this class of luminescent probes in light and heavy water.

The molecules subjected to pressure studies were 1-dimethylaminonaphthalene-5-sulfonic acid (DANS), its sulfonyl chloride called dansyl

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chloride (DNS), 2-ethylaminonaphthalene-6-sulfonic acid (ENAS), and 2-octadecylaminonaphthalene-6-sulfonic acid (ONS). Concentrations of 1.0 \times 10^{-5} \text{ M} were used, except for DNS which forms a saturated solution of ca. 2 \times 10^{-5} \text{ M}. Air-saturated water was twice glass-distilled, and 99.8\% D_{2}O was used as received from Stohler Isotope Chemicals.

Luminescence measurements were performed at room temperature with a three-window optical high-pressure cell situated in the sample compartment of a Perkin-Elmer MPF-3 spectrophotometer. The fluorescence spectra are recorded as a function of increasing pressure at ca. 1 kbar intervals up to 5 kbar and found to be reversible. Most of the work concentrated on DANS and DNS for which sample excitation occurred at \lambda 298 nm (10 nm slit width). This wavelength was determined to be the isosbestic point in the absorption spectrum of the acid–base pair. These aromatic amines are also photochemically stable and insensitive to oxygen quenching; in fact, DANS has been proposed as a quantum yield standard\(^{(7)}\). Also, concentration quenching was found to be unimportant at concentrations used in these experiments.

Evidence for the excited state proteolysis reaction

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\begin{align*}
N(CH_3)_2 & \quad * \\
\text{SO}_2\text{Cl} & \\
+ H_2O & \xrightleftharpoons{K^*} \\
& \rightarrow N(CH_3)_2 \quad * \\
\text{SO}_2\text{Cl} & + OH^- \\
\end{align*}
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is derived from the two well-separated peaks in the fluorescence spectrum, where the green band (ca. \lambda 500 nm) is assigned to the parent dye and the

![Fig. 1. Fluorescence spectra of dansyl chloride (DNS) in water at pressures of 1 atm (---), 1 kbar (--), and 5 kbar (----).]