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Prototropic studies in vitreous and in solid phases: Pyranine and 2-naphthol excited state proton transfer

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ABSTRACT

Excited state proton transfer processes in vitreous glasses and in solid mixtures are investigated by steady state fluorimetry and laser flash photolysis kinetic studies with the photoacids pyranine and 2-naphthol. Glasses were derived from TEOS by the sol–gel condensation process and hydrated solid mixtures from NaCl or $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ crystals. The extent of the water content necessary for the reaction is determined. Shrinkage of TEOS derived monoliths from water loss leads to an increase in proton transfer extent due to the increase in local concentrations of accepting and donor buffer species, but the concomitant increase in the ionic strength actuates in an opposite direction. Furthermore, water losses by aging of air-exposed gel goes to a critical 20% weight fraction, beyond it proton transfer reactions are hindered. Similar studies with solid NaCl or solid phosphate buffer mixtures demonstrated the same critical water level indicating that free water molecules are crucial for the proton to escape from the original cage where the geminate ion pair $[-\text{RO}^- \cdot \text{H}^+ -]$ is formed and can undergo coupled proton transfer reactions.

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1. Introduction

Proton transfer reactions are a cornerstone of modern chemistry and biochemistry. Among the systems suited for accompanying the H^+ transfer reactions, photoacids in general and 8-hydroxy-1,3,6-trisulphonatepyrene (pyranine) and 2-naphthol (NOH) more specifically, are very attractive mostly because of the convenient colors of the acid base pairs and the possibilities to follow either stationary state or time resolved measurements. Studies using pyranine and related compounds on excited state proton transfer (ESPT) started with the work by Förster and by Weller in the late fifties and sixties [1,2].

Previous studies on ESPT is sol–gel derived from tetraethyl (TEOS) and tetramethyl (TMOS) orthosilicates having pyranine as the H^+ sensor arrived to the conclusion that after some days of aging exposed to air, water is adsorbed back into the gel as seen by the extent ESPT [3–6]. However, the effects of: (i) increase in the concentration of H^+ donor and accepting species, (ii) increase in the local ionic strength (μ), and (iii) the water content were not

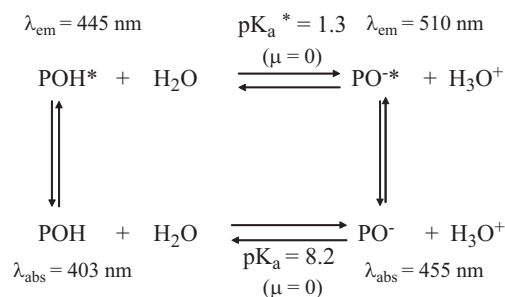
considered in detail. In the present study these effects are addressed. The effect of increased ionic strength due to shrinkage (decrease in the water mole fraction) of the gel by aging in the prototropic process and the decrease in the water mole fraction are highlighted. Studies of H^+ transfer in crushed solid salts as a function of the water content are also presented. The study shows that the understanding of the participation of water concentration added to the increase in the ionic strength and in the approximation of donor and accepting proton species must be taken in account for exploitation of H^+ reactions.

2. Background

2.1. Photoacids

Pyranine and 2-naphthol properties can be reviewed elsewhere [1–5], for the sake of clarity pyranine's more important features are included here (relevant properties of 2-naphthol will be included in the results section). Pyranine is a weak acid in the ground state ($\text{pK}_a=8.2$ at limiting ionic strength ($\mu=0$) [5] whereas it is a strong one in the excited state ($\text{pK}_{a(\mu=0)}=1.3$ [5]). In aqueous medium the lifetime of both excited species (acid

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Scheme 1. Prototropic properties of Pyranine acid (POH) and basic (PO^-) species. (symbols have their usual meanings).

and conjugate base) are long enough (~ 6 ns [1–3]) to ensure a quasi equilibrium condition, that is, ESPT occurs before excited state deactivation. These properties are thus very suitable to monitor the surroundings proticity conditions. Scheme 1 depicts the most relevant properties of pyranine as absorption and emission wavelengths of ground and excited states species and $\text{p}K_{\text{a}}$'s.

3. Materials and methods

Pyranine (Eastman, Kodak) was dissolved in bidistilled Milli-Q water, stock solutions were prepared routinely and kept cold (~ 8 °C) and in dark. 2-Naphthol solutions were prepared daily in ethanol and kept in dark. The dye pH indicators Bromophenol Blue (BPB), Bromocresol Green (BCG), Bromocresol Purple (BCP), Cresol Red (CR) and Bromothymol Blue (BTB) (Sigma-Aldrich) were solubilized in ethanol and few microliters were added to the sols for spectrophotometric monitoring the eventual changes in pH's. Buffer solutions were prepared from KH_2PO_4 and NaOH. Tetraethylorthosilanes 98% (TEOS) were from Acros Organics. The liquid stock jar was kept under N_2 atmosphere in a freezer. Polystyrene plastic 1 cm path length cuvettes having all faces polished were used thoroughly. In experiments with solid $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$, samples were weighed from vacuum desiccated solids and mixed in the proper amounts into a homemade quartz chamber. Following, the photoacids probes and water (microliters fractions) were added. Water molar fractions (X_{w}) are mass (weight) based calculated. All reagents were from the best analytical grade available and used without further purifications.

3.1. TEOS sol–gel monoliths preparation.

Hydrolysis of a TEOS: H_2O (mole ratio 1:4) in 2 mM HCl was accomplished with a tip sonifier (Braun Sonic 1510 and 150 mW). This pre-hydrolysis step was continued until a homogeneous and translucent one-phase mixture was obtained. The mixtures were kept in ice to avoid a too fast gelation processes [6–8]. Following, buffer, pH dyes (typically 40 μL) or pyranine (20 μL) totalizing 1.5 mL were added to 1.5 mL of the TEOS hydrolyzate onto the plastic cells in a Branson water bath sonifier to ensure good mixing. Given the pre-hydrolysis condition and the fact that high buffer (electrolytes in general) concentrations (> 0.5 M) lead to a powdery gel, buffer concentrations were kept below 250 mM. In these conditions there is an inherent change in the pH as will be presented below. For this reason pH dyes were used with the gels to spectrophotometrically monitor the H^+ concentration as a function of aging (see below). All samples were kept exposed to air in dark and with a temperature of ~ 25 °C. Mole ratio of TEOS: H_2O was 1:18. The pH dye and pyranine concentrations in the assays were 10 μM and 50 μM respectively.

Solid mixtures were prepared by weighing the appropriate amounts of KH_2PO_4 and K_2HPO_4 for a nominal pH as presented in the figure captions. The mixtures were grinded in a mortar, doped with either pyranine or 2-naphthol and dried in vacuum for about 1 h at ~ 150 °C. NaCl samples were doped with pyranine and dried for the phosphate samples.

UV–vis and fluorescence spectra were obtained in a Cary 300 spectrophotometer and a Hitachi F-200, respectively. For the fluorescence measurements a work tension of 400 V was applied to the PM tube and fixed slits of 10 mm were used (bandwidth=26 nm, according to the fabricant). Pyranine emission spectra were collected from 420 nm to 600 nm keeping the excitation at 350 nm. With these conditions, scattering and Raman contributions were minimized. For the solid mixtures after drying, the samples were deposited on a quartz slide and another slide mounted on top of it. Solid samples were prepared by grinding the solids in a mortar. Powders were kept dry in vacuum desiccators. Appropriate aliquots of the solutions were mixed with the powders before pressing them with another quartz slide for frontal angle measurements in the fluorometer.

Laser flash photolysis measurements were conducted with an Applied Photophysics system composed of a Nd:YAG laser delivering light pulses width of ~ 50 ns (FWHM), using the 3rd harmonic (355 nm) and a working power of 20 mJ/pulse. In this condition photo-oxidation of pyranine was almost none (complete recovery of the o'scope traces to the pre pulse level were observed). Transients were monitored by a Xenon pulsed lamp either in a parallel or perpendicular configurations and presented the same results. Data were stored in a digital o'scope (HP 54510C) and transferred to a PC like computer for data handling and treatment.

Overall typical instrumental and experimental errors are within 4–7%.

4. Results and discussions

4.1. pH's in TEOS monoliths

In the TEOS derived glasses prepared in this study, besides the photoacid species, other acid and bases included in the gel are the phosphate buffer and the pH sensitive dyes. Previous studies showed that pH indicators (HIn and In^-) can satisfactorily monitor the pH inside the monoliths [8–11]. In general HIn's present distinct bands for the acid and base pairs, in Supplementary material Table 1, properties of the dyes used in this work are revised for the sake of clarity.

The prototropic equilibria of the pH dyes (HIn's) were monitored during 55 days after the preparation of the monoliths. In Supplementary material Fig. 1(A–E), dyes typical UV–vis absorption spectra as a function of the buffer concentration after the first day of monolith preparation is presented. The data shows that the contribution of the forms HIn and In^- are in accordance with the nominal starting pH presented in Table 1. Spectra of the dyes did not change with the aging and also with the shrinkage showing a “constancy” of pH at least from the viewpoint of the dyes equilibria. Only small variations in the absorption wavelength

Table 1
Calculated pH's inside the TEOS monoliths.

[Buffer] in monoliths (mM)	pH _{calc.}
50	5.81
40	5.75
30	5.63
20	5.17
5	3.15

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