

Abstract

H^+ transfer processes in SiO_2 glasses, from photoacids as piranine (POH), were assigned to the presence of residual water in the gel. In these experiments the effects due to the buffer basic species ($HPO_4^{=}$) were however not investigated. The understanding on how prototropic reactions are mediated in solid media and how the activity of Brønsted acid and base pairs participates in the transfer is the subject of the present study. Questions as: Does the H^+ diffuse freely through the gel? Do the buffer species interacts directly with the H^+ donors, or water is needed to intermedate the transfer? Is there a threshold in the water content? are here discussed.

H^+ transfer from POH was studied in monoliths derived from the acid hydrolysis of TEOS having varying concentrations of phosphate buffer (initial conditions Si : H_2O 1:16.5). The extent of H^+ transfer is determined by monitoring the fluorescence intensity due to the excited base ($\%PO^{*-}$) once this emission arises from the H^+ transfer reaction. In these experiments gels were prepared in the absence and presence of phosphate buffer. Up to ~ 12 days an increase in H^+ transfer is observed for all conditions. It is also found the increase in buffer concentration parallels the extent of reaction. At very short time the relatively low H^+ transfer activity is due to the presence of ETOH (hydrolysis of TEOS), which as the systems age are lixiviated together with water from the gel. After this initial aging, those gels having high buffer concentrations (50 and 250 mM) show a leveled activity, the other gels show a decrease in H^+ transfer. At the final stages ~ 50 days the gels lost around 80% of its mass, but in the final gel residual water still amounts to Si: H_2O 1:7.

In order to further exploit the buffer activity, “dry” mixtures of KH_2PO_4 and K_2HPO_4 in proportions to $pH_{app} = 6.0$ were grinded and dried and the photoacidity of 2-naphtol (NOH) were investigated. Clearly at low water contents no reaction is observed and only the emission due to the NOH^* appears ($\lambda_{em} = 345$ nm), addition step by step of H_2O is followed by an increase in the emission at 413 nm, due to the basic form (NO^{*-}). In this situation the threshold water concentration is around $X_w = 0.44$. By other hand for

POH the threshold water for H^+ transfer is $X_w = 0.13$. POH and NOH have excited state pK_a 's (pK_a^*) of 0.5 and 3.0, respectively.

In this study the activity of photoacids in solid media is shown to be dependent on pK_a^* , on the concentration of basic species and of a threshold water content.