

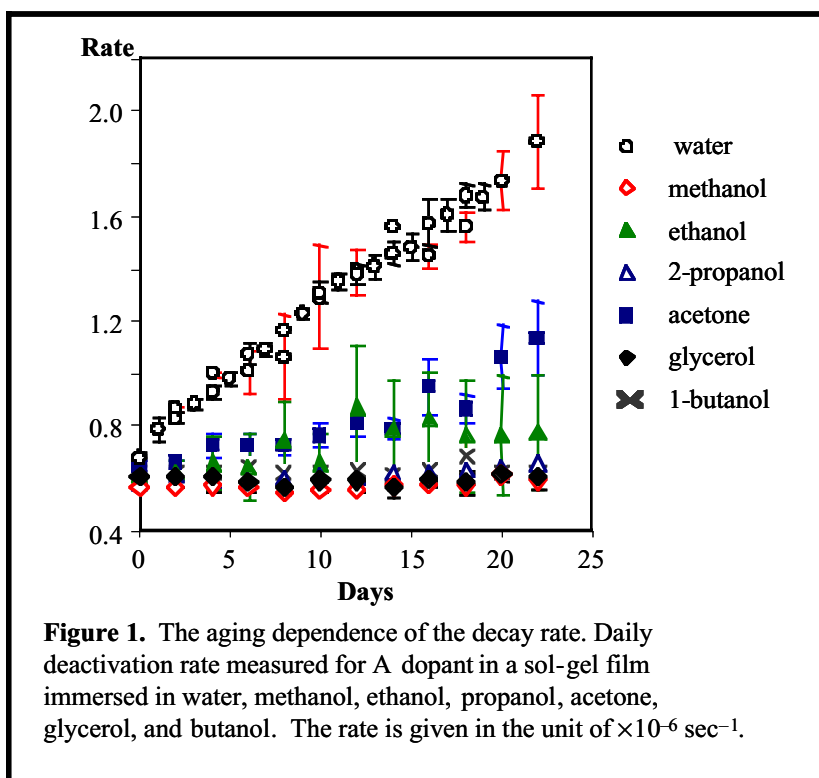
THE PROBING OF SOLVENT INTRUSION INTO A $[\text{Ru}(\text{bpy})_3]^{2+}$ Ion ENCAPSULATED SOL-GEL THIN FILM

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A transparent sol-gel host matrix is highly regarded compared to the many existent carrier materials due to its high thermo-resistance, transparency, and relatively robust photostability.^[1-5] However, a sol-gel matrix is a challenging material among host carriers studied, forming inhomogeneous amorphous-like cavities, and minor variations in preparation of a matrix can easily exhibit inconsistent physical properties. A $[\text{Ru}(\text{bpy})_3]^{2+}$ ion encapsulated in silica sol-gel material has been receiving increasing attention due to its ease of fabrication, while its photo-physical properties have been a great focus of improving designs for practical applications such as a light emitting diode and photovoltaic device.^[6, 7]



Prior to bio-medical or industrial technology development (e.g., kidney dialysis, catalysis, and membrane diffusion simulation), characterization of the physical properties under exposure to a liquid phase is critical. However, direct assessment of permeability into a silica sol-gel material has not yet been fully explored. Therefore, our study focuses on elucidating diffusional dynamics of the solvent located at the interfacial region between

liquid media and the nanoporous structures of a silica sol-gel surface. Our approach takes advantage of the phosphorescence lifetime since it sensitively varies with the entrapment environment.^[1] This variation in time constant can probe the diffusional motion affecting the pore and reflects upon the entrapment conditions caused by the solvent. A

comparative study among various solvents enables us to model a plausible inter-molecular interaction existent between silica-sol gel pores and a given solvent.

The $[\text{Ru}(\text{bpy})_3]^{2+}$ ion dopant encapsulated in a silica based sol-gel thin film (film thickness = 500 ± 20 nm) was immersed in solvent, and the phosphorescence decay time from photo-excited MLCT (metal-ligand-charge-transfer) state was observed at 620 nm under 450 nm excitation. The solvents used in this study were water, methanol, ethanol, 1-butanol, 2-propanol, and glycerol. For one day aged film, the phosphorescence decay time of a $[\text{Ru}(\text{bpy})_3]^{2+}$ doped in a silica sol-gel film generally resulted in a relatively significant increase. Thus, encapsulation was found to reduce or prevent direct contact of solvent with a dopant.

Solvent intrusion into the sol-gel entrapment environment over time was observed during a four weeks period at 25 °C. (Figure 1) While most of the solvents caused minimal changes in the phosphorescence over time, the dopant when immersed in water exhibited a linear monotonic increase dependent on the number of days immersed. The decay time observed in water approaches that of an aqueous solution after 21st days. This indicates that all cavities were becoming occupied by sufficient water to cause a freely mobile dopant analogous to an aqueous solution. These results strongly suggest that the permeability rate at a silica gel - liquid interface is dominated by a hydrogen bonding formation between solvent and a lone pair of oxygen of silanol groups and not by an electrostatic interaction with solvent and the $[\text{Ru}(\text{bpy})_3]^{2+}$ ion dopant.

References:

- [1] F. N. Castellano, T. A. Heimer, M. T. Tandhasetti, G. J. Meyer, *Chem. Mater.* **1994**, 6, 1041
- [2] G. R. Lee, J. A. Crayston, *Advanced Materials* **1993**, 5, 434.
- [3] P. Kiernan, C. McDonagh, B. D. MacCraith, K. Mongey, *Sol-Gel Sci. Technol.* **1994**, 2, 513.
- [4] O. Dvorak, M. K. De Armond, *J. Phys. Chem.* **1993**, 97, 2646
- [5] K. Matsui, K. Sasaki, N. Takahashi, *Langmuir* **1991**, 7, 2866
- [6] E. S. Handy, A. J. Pal, M. F. Rubner, *J. Am. Chem. Soc.* **1999**, 121, 3525.
- [7] S. Bernhard, J. A. Barron, P. L. Houston, H. D. Abruna, J. L. Ruglovsky, X. Gao, G. G. Malliara, *J. Am. Chem. Soc.* **2002**, 124, 13624.