Cage Effect and Critical Fluctuations: Photolysis of Diazene in Supercritical Fluids

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Supercritical Fluids (SCFs) are currently used in several technological processes. One of the more interesting properties of SCFs as solvents is their high compressibility: most equilibrium and transport properties (solvation power, dielectric constant, viscosity, etc.) scale with the density and can be tuned near the critical point by modest changes of pressure and/or temperature.[1] The high compressibility of SCFs near a critical point, coupled with attractive solvent-solute interactions, cause a local enhancement of solvent density around low-volatile solutes, a phenomenon usually referred to as critical clustering. There has been some debate about the characteristics of this solvation shell in the near-critical region, in particular about its strength and persistence against disruption. Several studies indicate that, in the critical vicinity, reaction products display a distinctive feature of condensed matter: a cage effect due to the enhanced local density.[2]

In this work we examine the cage effect in SCFs by measuring the escape probability of 1-biphenyl-4-il-1-methyl-ethyl radicals, generated from the photolysis of (1-biphenyl-4-il-1-methyl-ethyl)-*tert*-butyl diazene. The diazene compound is a relatively volatile solid, thermally stable up to 343 K, and dissolves in SCFs at densities below the critical value, allowing photoreaction experiments to be performed less than 2 K above T_c. Results in CO_2, Xe and Kr show that the escape probability, which is clearly a function of the solvent's density, does not change significantly with the reduced temperature T_r in the near-critical region ($T_r = T/T_c$ between 1.004 and 1.08). These results do not support the existence of enhanced cage effect due to critical fluctuations.

[1] Levelt Sengers, J. M. H. In Supercritical-Fluid Technology: Reviews in Modern Theory and Applications; Bruno, T.J., Ely, J.F., Eds.; CRC Press: Boca Raton, 1991.
[2] Brennecke, J.F.; Chateauneuf, J.E. Chem. Rev. 1999, 99, 433-452; Tanko, J.M.; Pacut, R.J. Am. Chem. Soc. 2001, *123*, 5703-5709.