Irregular Pressure Induced Shift of the First UV-Absorption Band of 4-Nitroanisole in CO_2 and CHF_3

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The first UV-absorption band of the polar molecules trans-4-dimethylamino-4′-nitrostilbene (DMANS), 5-dimethylamino-5′-nitro-2,2′-bithiophene (DMANBT), and 4-nitroanisole (NA), and of the slightly polar pesticide diclofop-methyl in the nonpolar supercritical solvent carbon dioxide (CO_2) and in the slightly polar supercritical solvent trifluoromethane (CHF_3) was measured in the pressure range from 1.5 to 30 MPa and the temperature range from 298 to 353 K with the purpose of studying the solvent-solute interactions in these molecules. The theory of Liptay for the effect of the solvent on the wave number of the electronic absorption of the solute molecule was applied. In this theory the solvent is represented by an isotropic and homogeneous dielectric continuum characterized by a pressure and temperature dependent dielectric constant $\varepsilon(P,T)$, and an optical refraction index n. For the isotherms which approach the critical point in both solvents there is a change in the slope of the plot of the wave number maximum against the solvent parameter $g = (\varepsilon-1)/(2\varepsilon+1)$ which is reminiscent of complex formation. A possible mechanism for this phenomenon is the arrangement of the solvent molecules around the dilute solute in the intermediate region at the (continuous) transition of the solvent from the dense vapour to the supercritical fluid.

Key words: Dielectric Interactions; Dispersion; Pressure Dependent UV-Absorption; Supercritical CO_2; Supercritical CHF_3; Complex Formation.