The Solubility of Organic Compounds in Supercritical CO_2

Guillermo A. Alvarez[a], Wolfram Baumann[b], Martha Bohrer Adaime[b], and Frank Neitzel[b]

[a] Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Carrera 1 No. 18A-10/70, Bogotá, Colombia
[b] Institute of Physical Chemistry, University of Mainz, D-55099 Mainz, Germany

Reprint requests to Prof. G. A. A.; Fax: 00571 3324366; E-mail: gualvare@uniandes.edu.co

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A simple liquid solution model is proposed to describe the effect of solvent-solute interactions on the solubility of nonpolar and slightly polar substances in supercritical solvents. Treating the system as an ideal solution, the effect of pressure on the solubility is zero or nearly zero, as it is governed by the difference in molar volume of the pure supercooled liquid solute and the pure solid solute, and this may be nearly zero. Deviations from ideal behavior are given by activity coefficients of the Margules type with the interaction parameter *w* interpreted as interchange energy as in the lattice theory. The hypothesis is put forward that the interchange energy is of the same form as a function proposed by Liptay and others to describe the effect of the solvent on the wavelength of the absorption maximum of the solute dissolved in the solvent. The function consists of a radius of interaction *a* and a function $g(\varepsilon)$ of the dielectric constant ε of the solvent, treated as a continuum. The function g depends on pressure through the pressure dependence of the dielectric constant $\varepsilon(P)$. The attractive feature of this formalism, introduced by Baumann et al. and here justified thermodynamically, is that plots of the logarithm of solubility vs. g are linear, except for polar solutes near the solvent's critical point. Changes in slope then admit interpretation as changes in the radius of interaction *a* with possible clues about the mechanism of solvation of these molecules.

Key words: Dielectric Interactions; Solubility; Supercritical CO_2; Thermodynamic Model; Activity Coefficient.