



Solubility of supercritical gases in organic liquids

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ABSTRACT

Chrastil (1982) [6] demonstrated that the solubility of a substance in a supercritical fluid (SCF) can be correlated with the density of the pure supercritical gas. Therefore, Chrastil's equation permits calculation of the supercritical phase composition of binary SCF + substance mixture based on the knowledge of the supercritical gas density and avoiding the use of equation of state based models.

In this work, it is demonstrated that the supercritical fluid density also defines the liquid phase composition of binary systems; a density-dependent relationship is presented to calculate the solubility of supercritical gases in organic liquids. The isothermal solubility of several gases commonly employed in supercritical processing, such as carbon dioxide, methane, and ethane, in different organic liquids, including alkanes, alkenes, alcohols, acids, ketones, esters, terpenes and aromatic compounds, was successfully correlated as a function solely of the pure supercritical fluid density. As an application, pressure vs. composition phase diagrams of binary SCF + substance mixtures were obtained circumventing the use of equation of state models.

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1. Introduction

The use of supercritical fluids (SCFs) in extraction, separation or fractionation processes has been intensively investigated since the last decades. Knowledge of phase behavior is essential for the design of these processes. Experimental information on multicomponent systems is usually difficult to obtain and thus, literature data are relatively scarce. Nevertheless, the study of simpler binary systems can provide valuable information on the fundamentals of phase equilibria behavior, which can further be used in the interpretation of multicomponent behavior. Around 200 CO₂ + compound binary systems had been measured from 1988 to 1993 [1] and more than 300 during 1994–1999 [2]. Particular interest has been given to the solubility behavior of different solutes in supercritical CO₂ as affected by operating conditions and solute properties.

Besides experimental measurement, thermodynamic phase equilibria modeling is widely applied as a simulation and optimization tool in supercritical process design. High pressure vapor–liquid phase equilibria modeling is accomplished by using an equation of state to solve Gibbs isofugacity criteria and calculate the equilibrium composition of both phases, at a given temperature and pressure [3].

In the case of binary mixtures, vapor and liquid phase composition exclusively depends on equilibrium temperature and pressure.

Moreover, the SCF density also exclusively depends on temperature and pressure. Thus, it is reasonable to wonder a direct relationship between phase composition and SCF density. In fact, the effect of the SCF density on phase equilibria composition is clearly referred in the literature with sentences such as “solvent power depends on SCF density” or “process selectivity can be turned according to SCF density” [4].

Stahl et al. [5] firstly observed a close relationship between the solute solubility (i.e. the composition of the high pressure vapor phase) and the supercritical solvent density. In 1982, Chrastil [6] presented an equation based on the solvato complex model, which establishes a linear dependency, in logarithmic basis, between the isothermal solute solubility and the SCF density (ρ_{SCF}). This equation has been widely employed to correlate solubility data [7,8] and has been also used to judge the goodness of experimental solubility measurements [9–11]. However, few works were reported in the literature modifying or improving Chrastil's equation [12].

In this work, it is demonstrated that not only the composition of the vapor phase but also the composition of the liquid phase is straightforward related with the SCF density. Based on a modification of Henry's law, the solubility of a supercritical gas in a liquid (i.e. the SCF molar fraction in the liquid phase, X_{SCF}) is correlated with ρ_{SCF} . This Chrastil-type equation proved to be valid for mixtures presenting positive deviations to Henry's law: at constant temperature, a linear relationship between $\ln(X_{CO_2})$ and $\ln(\rho_{CO_2})$ was obtained for 13 different CO₂ + low molecular weight substance mixtures, in a wide range of temperature and pressure, with linear regression coefficients greater than 0.98. In the case of systems

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