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Assessment of the liquid mixture density effect on the prediction of supercritical carbon dioxide volume expansion of organic solvents by Peng-Robinson equation of state

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A B S T R A C T

Volume expansion and liquid mixture density are key-factors to design particle precipitation processes from expanded organic solvents using supercritical fluids such as carbon dioxide. To predict volume expansion it is necessary to know the volume or the density of the liquid mixture that is in equilibrium with its vapor at a certain temperature, pressure and composition. However, equations of state that fail to accurately describe the liquid mixture density are used to predict the volume expansion and results are considered satisfactory. In this work we investigated why this occurs using vapor-liquid equilibrium data of 13 binary systems containing CO_2 and an organic solvent at high pressures with wide spread application in supercritical anti-solvent particle precipitation processes. Peng-Robinson cubic equation of state was applied with quadratic (PR-QMR) and LCVM-UNIFAC mixing rules (PR-LCVM-UNIFAC), and Peneloux's volume correction was adopted too (PR-QMR-Peneloux). The results show that there is an offset of terms during volume expansion calculation that explains why large deviations in the prediction of liquid mixture density from bubble pressure data can lead to small deviations in prediction of organic solvents volume expansion by carbon dioxide.

1. Introduction

Supercritical fluids (SCF) based particle engineering has been widely investigated to modify particle size distribution and characteristics of drugs avoiding high temperatures and residual organic solvent in the final product. For this reason it can be considered as a clean technology compared to conventional micronization techniques such as freeze-drying, spray drying, solvent evaporation or jet milling. Also SCF physical and transport properties are intermediate between those of a gas and a liquid offering the possibility of process intensification [1,2,3].

Particle precipitation processes from expanded organic solvents using supercritical fluids such as gas anti-solvent process (GAS), supercritical anti-solvent micronization (SAS), solution enhanced dispersion by supercritical fluids (SEDS), particles by compressed anti-solvent (PCA) and atomized rapid injection for solvent extraction (ARISE) strongly depend on the extent of volume expansion of the liquid phase that affects proper sizing of precipitation vessels [4,5,6,7]. Certain organic solvents can have increased more than ten times its initial liquid volume when expanded by supercritical fluids. For example, the volumetric expansion of acetone by CO_2 at 40 °C and 80 bar is about 1000% [8]. Therefore, it is important to find optimum process conditions.

Volume expansion of the liquid phase increases with increasing pressure and the degree of this expansion depends on the solvent used and the operation temperature [8]. In order to accurately determine the volume expansion it is necessary to know the volume or the density of the liquid mixture that is in equilibrium with its vapor at a certain temperature, pressure and composition. In practice, volume expansion of organic gases is much easier, faster and cheaper to measure directly using an optical cell than its determination from measurement of the mixture liquid density [8,9,10]. However, one should be sure that vapor-liquid equilibrium has been reached at each point of volume expansion measured. For this reason, the bubble point pressure and the vapor composition of the system organic solvent-supercritical anti-solvent should be well known [11].

Usually, bubble pressure and liquid density data are fitted to a

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cubic equation of state. Thus, it is expected that a well-adjusted cubic equation state should be able to accurately predict volume expansion of organic solvents by supercritical fluids. There is a large number of bubble pressure and composition experimental data for binary systems of organic solvent and supercritical carbon dioxide in literature but most of them does not show the corresponding liquid mixture density experimental data [12,14]. For this reason, it is common to adjust the cubic equations of state using only bubble pressure and composition data. In this case, it is assumed that the model is able to accurately predict the liquid mixture density even if parameter estimation employs an objective function that takes into account only the bubble pressure deviations. However, literature reports that this assumption should not always be done, because large errors can occur in the prediction of density, which consequently would lead to miscalculation of the degree of volume expansion [15]. On the other hand, other reports found in literature show that volume expansion calculated from a cubic equation of state fitted only to bubble pressure data can accurately reproduce volume expansion experimental data even when the model is unable to accurately calculate the respective liquid mixture density [11,16,17]. As volume expansion and liquid density, by definition, are directly related, the following issue arises: why models that fail to accurately describe the liquid mixture density are able to provide a good prediction of volume expansion?

The objective of this study is to try answering this question by assessing the influence of the liquid mixture density on modeling and prediction of the volume expansion of organic solvents by supercritical CO_2 at several conditions of pressure and temperature.

2. Modeling thermodynamics

The relative volume expansion of the liquid phase, by definition, is the difference between the final total volume of the liquid phase and the initial total volume of the liquid phase divided by the initial volume of the liquid phase, noting that the initial total volume of the liquid phase is the total volume of the pure solvent. The classical definition for the volume expansion of the liquid phase is given by:

$$\frac{\Delta V}{V} = \frac{V_L(T,P,x_1) - V_2(T,P_o)}{V_2(T,P_o)} \tag{1}$$

where V_L represents the total volume of mixture liquid phase and V_2 is the total volume of the pure solvent at the same temperature and a reference pressure (usually the atmospheric pressure).

Based on 1 mol of solvent [15], the relative volume expansion of the liquid phase in which the CO_2 is dissolved can also be calculated from:

$$\frac{\Delta V}{V} = \frac{\rho_2(T,P_0)}{\rho_L(T,P,x_1)}\cdot\left[\frac{x_1}{(1-x_1)}\cdot\frac{M_1}{M_2}+1\right] - 1 \tag{2}$$

where $\Delta V/V$ indicates the relative volume expansion of the solvent due to the addition of CO_2, x_1 is the CO_2 molar fraction in solution, ρ_L and ρ_2 are the density of mixed and the pure solvent, respectively. M_1 and M_2 are the molecular weights of CO_2 and solvent, respectively, P and T are the temperature and pressure at which the expansion is performed, and P_0 is the atmospheric pressure.

Vapor-liquid equilibrium for the binary system solvent-supercritical anti-solvent was calculated using Peng-Robinson equation of state with quadratic mixing rule (QMR) and LCVM-UNIFAC mixing rules was chosen to calculate the fugacity coefficient of the components in the mixture [18].

In order to improve the quality of the density calculation from PR-QMR EOS and maintain the quality of phase equilibrium description, the Peneloux's correction was adopted. This method is widely applied for oil products [19].

Due to a relative greater availability of high pressure vapor-liquid equilibrium data than liquid density data in literature, parameter estimation was done considering only an objective function calculated based on minimization of bubble pressure deviations. Nonetheless, it is assumed that if the EOS well describes the bubble point curve it will be able to give a good prediction of the liquid mixture density.

Simplex method was applied to minimize the following objective function [20]:

$$FO = \min \sum_{i=1}^{NEP} \frac{|P_{\exp} - P_{calc}|}{P_{\exp}} \tag{3}$$

Despite parameter estimation takes into account only bubble pressure deviation, assessment of both PR-LCVM-UNIFAC and PR-QMR EOS was based on bubble pressure, liquid mixture density and volume expansion deviations, i.e., the predictive capacity of these EOS regarding liquid mixture density and volume expansion was evaluated from its capacity to well describe phase behavior.

To monitor the EOS performance, bubble pressure, liquid mixture density and volume expansion deviations are expressed in mean relative deviation $\Delta P/\%$, $\Delta\rho/\%$ and $\Delta[\Delta V/V]/\%$, respectively, as follows:

$$\Delta P/\% = \frac{100}{NEP}\sum_{i=1}^{NEP} \frac{\left|P_i^{\exp} - P_i^{calc}\right|}{P_i^{\exp}} \tag{4}$$

$$\Delta\rho/\% = \frac{100}{NEP}\sum_{i=1}^{NEP} \frac{\left|\rho_i^{\exp} - \rho_i^{calc}\right|}{\rho_i^{\exp}} \tag{5}$$

$$\Delta\left(\frac{\Delta V}{V}\right)\Big/\% = \frac{100}{NEP}\sum_{i=1}^{NEP} \frac{\left|\left(\frac{\Delta V}{V}\right)_i^{\exp} - \left(\frac{\Delta V}{V}\right)_i^{cal}\right|}{\left(\frac{\Delta V}{V}\right)_i^{\exp}} \tag{6}$$

where P_i is the bubble pressure, ρ_i is the liquid mixture density and $\Delta V/V$ is the volume expansion for each point of temperature, pressure and composition.

3. Results

In this study, volume expansion of organic solvents by supercritical CO_2 is calculated using PR-LCVM-UNIFAC and PR-QMR equations of state. Pure component properties (critical temperature, critical pressure, acentric factor and the Peneloux's correction factor) required to calculate the EOS parameters a and b of CO_2 and 12 organic solvents were taken from literature [18].

Parameter a is related to the intensity of intermolecular forces and parameter b, namely as covolume, represents the volume occupied by the molecules of the components.The Peneloux's correction factor has always positive values for acentric factor values higher than 0.352.

Table 1 shows the results of bubble pressure calculation using PR-LCVM-UNIFAC and PR-QMR EOS for 13 binary systems of the type CO_2-organic solvent. These organic solvents have been wide spread used in particle precipitation processes where CO_2 acts as an anti-solvent [21–24]. It is noteworthy that for this calculation parameter λ of PR-LCVM-UNIFAC as well as parameters k_{ij} and l_{ij} of PR-QMR EOS were regressed for each binary system using the objective function expressed by Eq. (3). The values of parameters k_{ij} and l_{ij} are in the range between 0 and 0.02 but for polar