

Binary interaction parameters estimated from experimental data for solid-supercritical fluid equilibrium (S-SCF)

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Solid - supercritical fluid phase equilibria are of key importance in designing supercritical extraction processes. High temperatures and pressures at which such phenomena take place can only be quantitatively described by equation-of-state (EoS) models, at least for the (multicomponent) fluid phase. When modelling a fluid binary system with pure solid phase, it is necessary to know solute critical parameters. Often critical parameters are estimated (e.g. with group contribution methods (Shilpi et al., 2013)), mainly when, for chemical reasons, the solute may decompose far below its (theoretical) critical point. The solubility of the compounds in supercritical fluids is an important issue in the whole extraction process as this is one of the factors that dictate the technological and economic viability of such a process. The solubility of the solid in the supercritical fluid represents the concentration of the solid in the supercritical phase. In order to understand the behavior of the phases of a mixture containing several solutions of interest, it is useful to start from the simple case of the binary system. For this purpose it is proposed an algorithm for determination of solid-supercritical fluid equilibrium data by estimating the binary interaction parameters k_{ij} from experimental data and from critical data, using the least squares method to minimize the objective function formed by the square of the difference between the solute fugacity in the solid phase calculated from experimental data and the solute fugacity in the supercritical phase calculated from experimental data and critical data.

In this study caffeine and β -carotene are selected to estimate binary interaction parameters. The solid solute sublimation pressures for β -carotene (Skerget et al., 1997) and caffeine (Emelyanenko & Verevkin, 2008) were determined from experimental data from literature. Critical data for caffeine was obtained by group contribution methods and critical data for β -carotene was obtained from PROPRED module from ICAS software and from literature (Skerget et al., 1997). For the validation of the proposed model for caffeine solubility in supercritical CO_2 five experimental data sets at temperatures between 313 and 393 K at different pressures were used and for β -carotene solubility in supercritical CO_2 eight experimental data sets at temperatures between 307.6 and 353 K at different pressures were used.

Finally, the solubilities data calculated with estimated binary interaction parameters are compared with experimental solubility data from literature. Calculated solubility data for caffeine-supercritical CO_2 mixture was compared with solubility experimental data and lower errors between them are obtained. For β -carotene-supercritical CO_2 mixture it was observed that calculated solubilities at low temperatures with estimated binary interaction parameters using critical data from the literature (Skerget et al., 1997) for all eight experimental data sets have lower errors than solubilities obtained with estimated binary interaction parameters using critical data from ICAS. It can also be noticed that calculated solubilities belonging to the lowest temperatures exhibit high errors and as the temperature increases, these errors are greatly diminished as a result of the fact that the molar volumes of the two substances (β -carotene and CO_2) is negligible.

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