Measurement and mathematical description of the ternary phase equilibrium of carbon dioxide, acetone and isopropanol

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1. Introduction

Experimental and computational studies of phase equilibria often reveal underlying thermodynamic effects in and can be used to support the design of separation processes in high-pressure media. While in some processes (dissolution in extraction, recrystallization, RESS) setting parameters in the single-phase region of the phase diagram is necessary, in other cases, the presence of a multiphase system is preferrable (in the separator of supercritical extractors, spraying processes). Studies on multicomponent, high-pressure phase equilibria are still able to contribute to the knowledge on complex high-pressure phase behavior. [1,2]

In the current study, the ternary system of carbon dioxide, acetone and isopropanol was investigated in order to collect the necessary data to model the ternary equilibrium and compare the results to predictions based on binary data available in the literature.

2. Materials and Methods

High-pressure equilibrium studies in systems containing carbon dioxide were conducted in a variable volume view-cell. (*Figure 1.*) The synthetic cloud-point – redissolution point method was applied. The procedure is based on the variation of the volume of the tempered cell that is filled with a mixture of precisely known composition. Increasing the volume of the apparatus results in pressure-reduction and eventually phase separation. It is recognized by the internals of the view-cell becoming opaque. Redissolution points are determined the opposite way: isothermal compression of a multi-phase system results in the formation of a single, homogeneous, usually transparent phase.

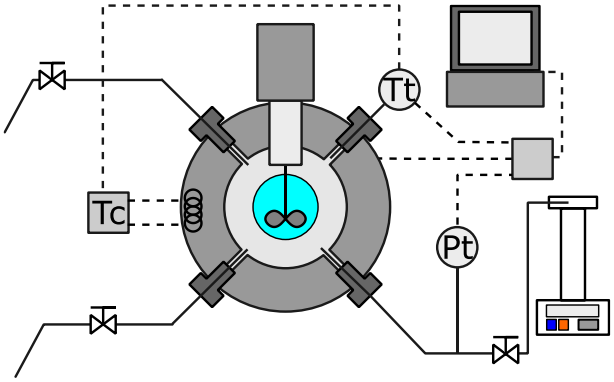

Figure 1. Variable volume view-cell used in the investigation of the ternary mixtures of carbon dioxide, acetone and isopropanol.

3. Results and discussion

Cloud-point pressures and redissolution point pressures were measured in the approximate composition ranges of $x_{CO_2} \in [0.7; 0.99]$; $x_{acetone} \in [0.001; 0.24]$ and $x_{isopropanol} \in [0.0003; 0.14]$, specified for the mole fractions of the components in different measurements. As results were grouped based on the volumetric ratio of acetone and isopropanol in the mixtures, the general tendencies may be illustrated on an example (*Figure 2.*). Circles mark clouds points, triangles correspond to redissolution pressures. While cloud-points and redissolution points do not remarkably differ at given temperature and composition, the measured pressures of phase transition show an increasing trend with increasing temperature. The proximity of the mixture-critical point (at each temperature) is visible: results in the marked area can hardly be distinguished, albeit belonging to different compositions.

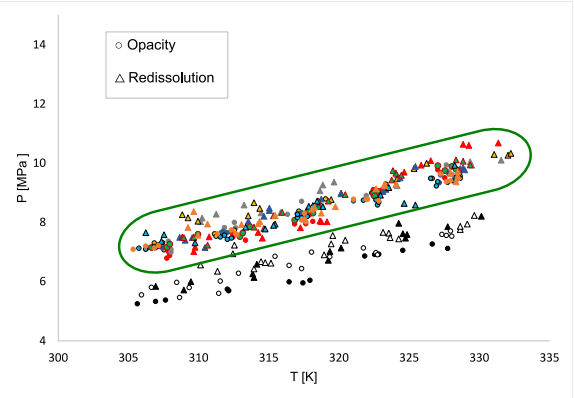

Figure 2. Cloud-points and redissolution points measured on a 1:1 volumetric mixture of acetone and isopropanol. The mole fraction of carbon dioxide ranges from 0.71 to approx. 0.99. In the area marked with the green boundary, it is over 0.89.

Due to the vicinity to the mixture-critical point, numerous data had to be omitted from the binary interaction parameter fitting in AspenPlus. The capability of the original Peng-Robinson[3] and Soave-Redlich-Kwong[4] equations of state were tested by directly fitting binary interaction parameters to the measured ternary phase equilibrium data.

The PR-EOS gives a closer prediction to the phase-transition pressure in the studied range, even more so when the temperature-dependence of the binary interaction parameters is included. However, the applicability of binary interaction parameters fitted to the ternary system for the description of binary systems (and vice versa) is currently being tested.

4. Conclusions

The phase equilibrium behavior of the ternary mixture of carbon dioxide, acetone and isopropanol was investigated using a static synthetic method. The organic compounds could serve as co-solvents in supercritical carbon dioxide extraction processes or could be used in antisolvent procedures. Measurement data was correlated using the Peng-Robinson and Soave-Redlich-Kwong equations of state, albeit the general applicability of the obtained BIPs is currently being reviewed.

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