

EXPERIMENTAL STUDY OF PHASE EQUILIBRIA IN BINARY MIXTURES OF SUPERCRITICAL FLUIDS WITH ORGANIC COMPONENTS*Khabriev I.Sh., Kabirov R.R., Khairutdinov V.F., Yarullin L.Yu., Abdulagatov I.M.*

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Pyridine is an important solvent and precursor in the pharmaceutical and chemical industries, and is also used as a component of ionic liquids for CO₂ capture. Accurate data on the phase equilibrium in the CO₂ + pyridine system are necessary for the development of supercritical fluid extraction processes and the verification of thermodynamic models. However, at the time of this study, vapor–liquid equilibrium (VLE) data for this binary system were absent in the open literature.

The objective of this work is the experimental determination of isothermal VLE data (PTxy) for the binary mixture CO₂ + pyridine, the estimation of mixture critical parameters, the calculation of the Krichevskii parameter, and the modeling of phase equilibrium using the Peng–Robinson equation of state (PR78).

The measurements were performed in a high-temperature, high-pressure optical cell with an internal volume of 117 cm³, equipped with sapphire windows. Three isotherms were investigated: 313.15 K, 333.15 K, and 353.15 K at pressures up to 12.35 MPa. The compositions of the equilibrium liquid (x) and vapor (y) phases were determined by a gravimetric method after component separation by cooling. The mixture critical parameters were determined according to the criterion of equality of coexisting phase compositions (x = y) [1].

New experimental PTxy data for the CO₂ + pyridine system were obtained. The mixture critical parameters were: at 313.15 K – Pc = 8.251 MPa, x (pyridine) = 0.028; at 333.15 K – Pc = 10.523 MPa, x = 0.061; at 353.15 K – Pc = 12.854 MPa, x = 0.089. Based on the initial slopes of the critical curves, the Krichevskii parameter was calculated: $(\partial P / \partial x_{Tcvc}^{\infty}) = -22.8$ MPa. The negative value of the parameter indicates that near the critical point of pure CO₂, the partial molar volume of pyridine tends to $-\infty$, and the size of solvent clusters around the solute molecule tends to $+\infty$, classifying this system as "attractive." Modeling using the PR78 equation of state showed good agreement with the experiment: with a binary interaction parameter value of $k_{ij}=0.022$, the average absolute deviations for the liquid and vapor phases were 0.32% and 2.89%, respectively.

1. Khairutdinov V.F., Gumerov F.M., Gabitov F.R., Zaripov Z.I., Khabriev I.Sh., Akhmetzhanov T.R., Abdulagatov I.M. New design of the high-pressure optical cell for VLE measurements. Supercritical binary mixture (propane/n-butane) +acetophenone. *J. Chem. Eng. Data* 2020, 65, 3306-3317. <https://doi.org/10.1021/acs.jced.0c00104>

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