Extended Abstract

Fluid properties simulation challenge
Recommendations for problem II(b): cyclohexane density ☆

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Problem conditions	Recommended values
(1) 0.1 MPa, 300 K	$772.13 \pm 0.3 \, \text{kg m}^{-3}$
(2) 20.0 MPa, 400 K	$702.9 \pm 1.4 \, \text{kg m}^{-3}$

Primary source of recommendation:

The values indicated in this table were calculated from the equation of state of Penoncello et al. [1].

Justification for recommendation:

The equation of state in [1] contains the most accurate formulation for the thermodynamic properties of cyclohexane currently available based on an extensive evaluation of property data available in the literature. The formulation, in the form of a reduced Helmholtz energy correlation, was based on temperatures on the ITS-90 scale. The work of Penoncello et al. [1] considered more than 3100 measured data, including *PVT* data, isobaric and isochoric heat capacities, sound speeds, and saturation properties. Their work summarized the complete data set, including the primary data used in the final regression, and the references are not provided here.

For the current benchmarking exercise, we independently compared calculations based on the formulation of [1] with experimental data, emphasizing the liquid density data in the region of current interest; we have thus confirmed the ability of this formulation to describe the thermodynamic properties of cyclohexane. Further, we have located some additional data, including those for the saturated liquid density available in the NIST TRC Source data system [2]; this source provided some 250 references with about 750 data points. The results again agreed well with the formulation of

Penoncello et al. Finally, we checked the two specific points considered with a predictive, extended corresponding states algorithm [3] with a general uncertainty of 2% for pure fluid densities: the absolute deviation was less than 0.1% for the point at 0.1 MPa specified above and about 0.3% for the 20 MPa benchmark.

Determination of uncertainty:

The overall uncertainty of the formulation of Penoncello et al. is stated in [1] as 0.1% in density; this corresponds to about $0.8 \, \text{kg m}^{-3}$ for the low pressure point and $0.7 \, \text{kg m}^{-3}$ for the point at 20 Mpa.

To produce more refined uncertainty estimates, we have re-examined the liquid-phase data over the temperature range from 280 to 450 K. For the 11 primary data sets used in this region [1], the overall average absolute deviation is 0.08%. However, the deviations are considerably better at the lower-temperature end; an overall average absolute deviation of 0.05% is found for the data less than 330 K. Between 280 and 350 K, the saturated-liquid data from NIST TRC exhibit a cloud of points with an absolute deviation of less than 0.05%; ignoring several outliers, the average absolute deviation becomes 0.034% for these data. Considering these deviations, and the experimental uncertainties of the key data, we conclude that the uncertainty of our benchmark point at 0.1 MPa and 300 K is about 0.04% (corresponding to $0.3 \, \text{kg m}^{-3}$).

Fig. 1 illustrates the deviations for the saturated-liquid data; note that 300 K corresponds to a vapor pressure of about 0.014 MPa, and 0.1 MPa corresponds to a saturation temperature of about 353.5 K. At 300 K, the change in liquid density from saturation to 0.1 MPa is less than 0.01% because of the very small compressibility of the liquid in this region. The critical parameters of cyclohexane are about 554 K and 4 MPa, well away from the state points of interest. To examine the pressure dependence of the equation of state, especially at the higher temperature, we now consider
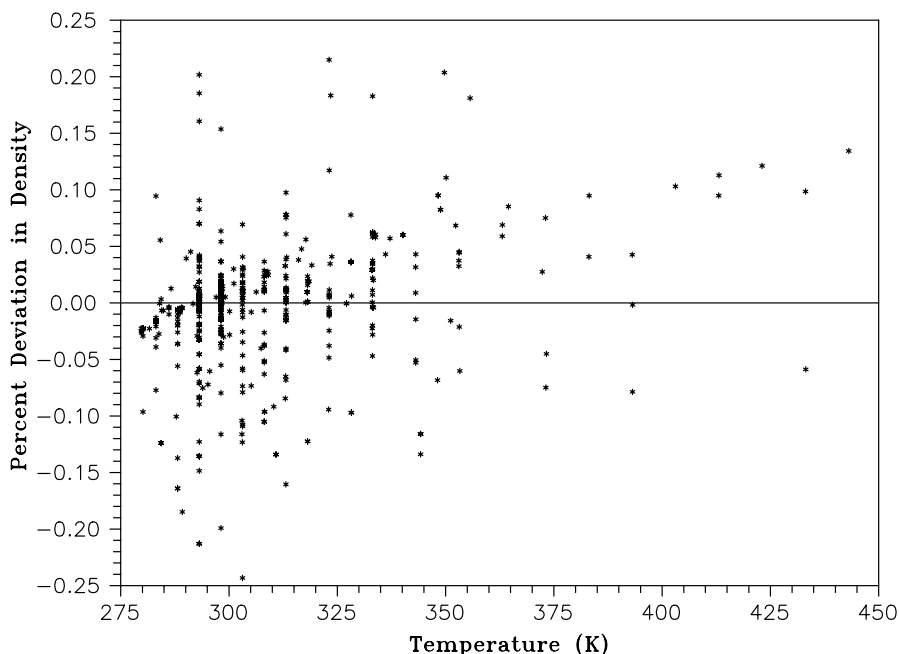

Fig. 1. Comparisons of saturated liquid densities calculated with the equation of state of Penoncello et al. [1] to experimental data.
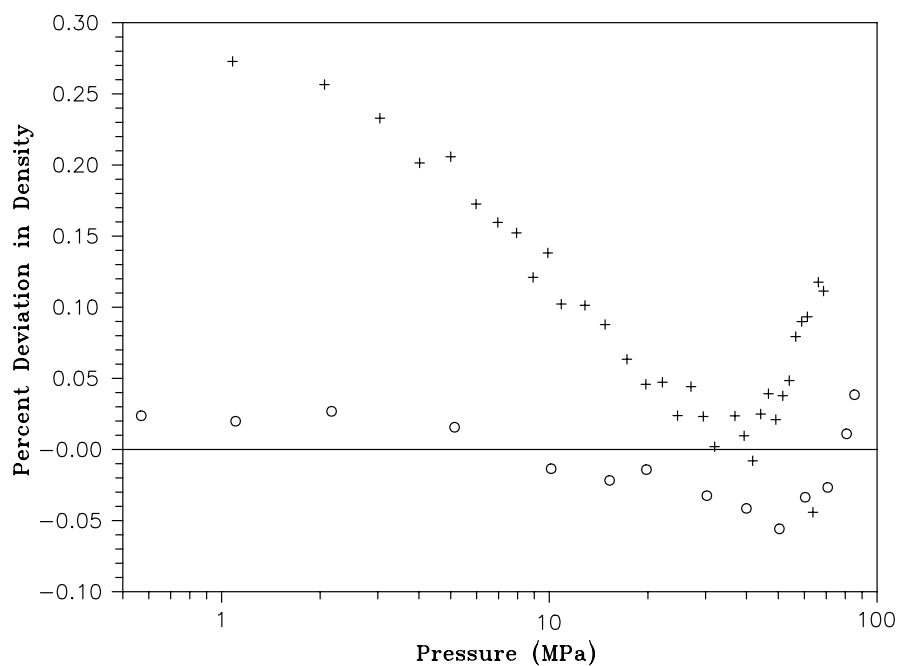

Fig. 2. Comparisons of densities calculated with the equation of state of Penoncello et al. [1] to experimental single-phase data at 398.15 K. Circles: Rastorguev et al. [4]. Pluses: Kerimov and Apaev [5].

the data from Rastorguev et al. [4] and of Kerimov and Apaev [5]. The experimental liquid-phase isotherms at 398.15 K are shown in Fig. 2. For the lower pressures on this isotherm, it is seen that [4,5] exhibit a substantial discrepancy (although there are other low-pressure data for cyclohexane), but these two sources are in better agreement near the pressure of interest. On the basis of this study, we conclude that the uncertainty at 400 K and 20 MPa

is about 0.2%, corresponding to $1.4 \, \mathrm{kg \, m^{-3}}$ as indicated previously.

References

[1] S.G. Penoncello, A.R.H. Goodwin, R. T Jacobsen, A thermodynamic property formulation for cyclohexane, Int. J. Thermophys. 16 (1995) 519.

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