Vapor-liquid equilibria measurements of binary mixtures CO_2 + Acetone, CO_2 + 3-methyl-2-butanone, and CO_2 + 2-pentanone

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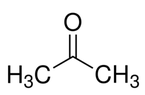
1. Introduction

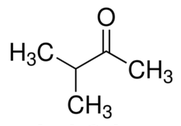
- Carbon dioxide (CO_2) is a popular solvent in industrial applications because it is nontoxic, nonflammable, and cheap and also has a moderate critical temperature and critical pressure.
- It is essential to have phase equilibrium data for systems containing CO_2 for the design and optimization of processes including CO_2.
- In this study, vapor–liquid equilibrium (VLE) data of the binary mixtures CO_2 + acetone, CO_2 + 3-methyl-2-butanone, and CO_2 + 2-pentanone are measured at 313.15 K, 333.15 K, and 373.15 K.
- All present data are compared to the available experimental data, predictions of the Peng–Robinson equation of state (PR EOS) with the van der Waals mixing rule, and the correlation of combining PR EOS with UNIQUAC through the Huron–Vidal mixing rule.

2. Materials and Experiments

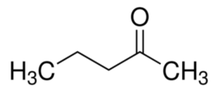
A. Materials



Acetone (purity ≥ 99.9%)



3-methyl-2-butanone (purity 99%)



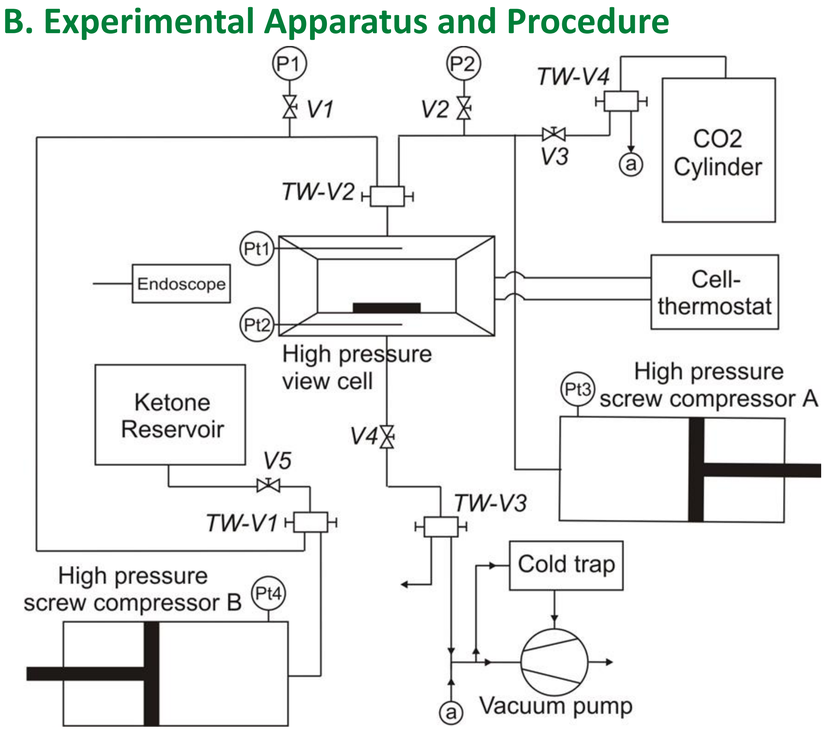
2-pentanone (purity 99.5%)

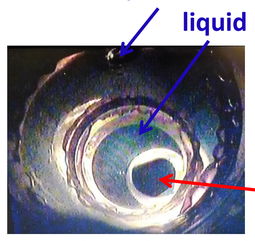
from Sigma-Aldrich, Germany

Carbon dioxide (volume fraction 99.995%) — from Air Liquide, Germany

All chemicals were used without further purification

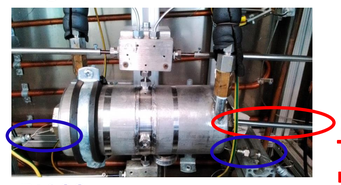
B. Experimental Apparatus and Procedure





Snapshot of view cell from endoscope at the end of a measurement

High pressure view cell



1. The compressor A was cooled down to ~275 K and filled with CO_2 from the gas cylinder.
2. The compressor B was loaded with liquid ketone from the reservoir.
3. The high pressure view cell was heated up to desired measurement temperature.
4. The desired quantity of ketone was added into the view cell from compressor B.
5. Using the compressor A to slowly load liquid CO_2 into the view cell until the CO_2 was completely solved in ketone. (The homogeneous liquid state in the view cell was maintained at least for 20 minutes.)
6. Starting from a homogeneous liquid state in the view cell, compressor A was used to decrease the pressure in the view cell in very small steps, until the first bubbles appeared and thus the saturated liquid state was reached.

C. Thermodynamic Models for Correlation and Prediction

➢ Peng-Robinson (PR) EOS

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b)+v(v-b)}$$

$$a(T) = 0.457235\frac{RT_c^2}{P_c}\left[1+\kappa\left(1-\sqrt{\frac{T}{T_c}}\right)\right]^2$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$$

$$b = 0.077796\frac{RT_c}{P_c}$$

Critical properties (T_c, P_c) and acentric factor (ω) were taken from literature

➢ van der Waals mixing rule (VMDmr)

$$a(T,\underline{x}) = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j \sqrt{a_i a_j}$$

$$b(\underline{x}) = \sum_{i=1}^{n} x_i b_i$$

➢ Huron-Vidal mixing rule with UNIQUAC model (HV+UNIQUAC)

$$\frac{a(T,\underline{x})}{b(\underline{x})} = \sum_i^n x_i \frac{a_i}{b_i} + \frac{G^{ex}}{C_{\mathrm{HV}}} \qquad C_{\mathrm{HV}} = \frac{1}{2\sqrt{2}}\ln\left(\frac{2+\sqrt{2}}{2-\sqrt{2}}\right)$$

$$b(\underline{x}) = \sum_{i=1}^{n} x_i b_i \qquad \underline{G}^{ex} = RT\sum_i x_i \ln\gamma_i$$

γ_i from UNIQUAC model

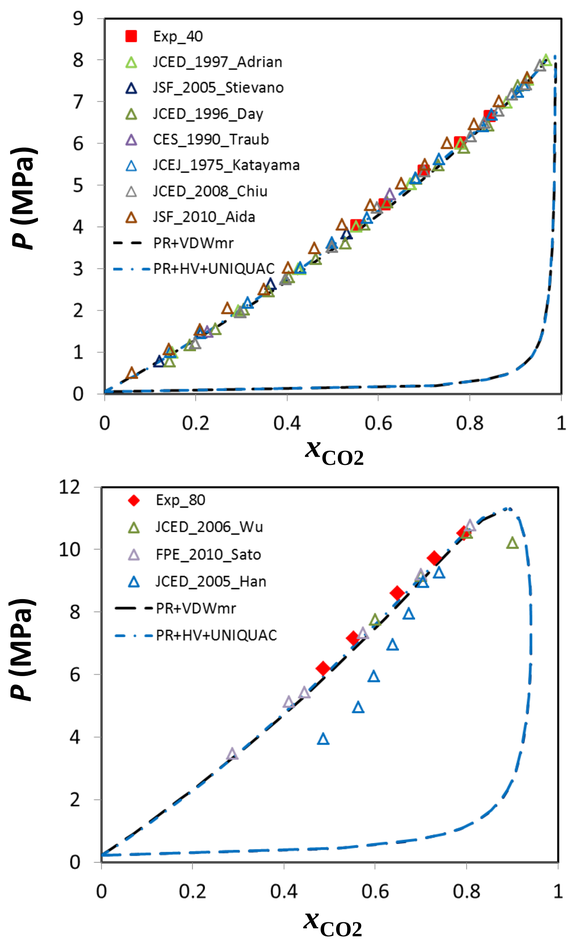
$$\ln\gamma_i = q_i\left[1-\ln\frac{\sum_j x_j q_j \tau_{ji}}{\sum_j x_j q_j} - \sum_j \frac{x_j q_j \tau_{ij}}{\sum_k x_k q_k \tau_{kj}}\right] + 1 - \frac{r_i}{\sum_j x_j r_j} + \ln\frac{r_i}{\sum_j x_j r_j} - \frac{z}{2}q_i\left[1-\frac{r_i}{q_i}\frac{\sum_j x_j q_j}{\sum_j x_j r_j} + \ln\frac{r_i}{q_i}\frac{\sum_j x_j q_j}{\sum_j x_j r_j}\right]$$

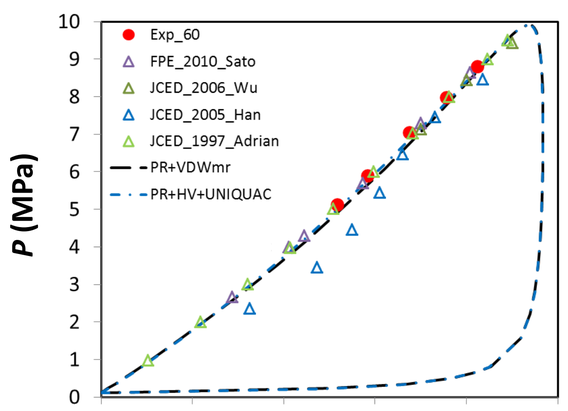
$$\tau_{ij} = \exp\left(-\Delta u_{ij}/RT\right)$$

r_i and q_i are relative van der Waals volume and surface area of substance i. The values of binary interaction parameters Δu_{ij} and Δu_{ji} were obtained from regression.

3. Results

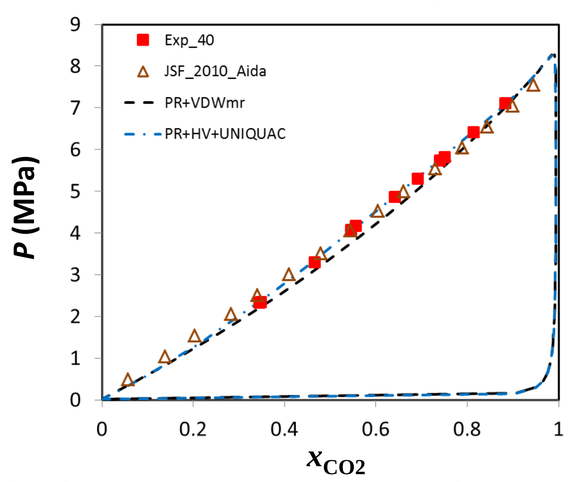
A. VLE measurements of CO_2 + acetone

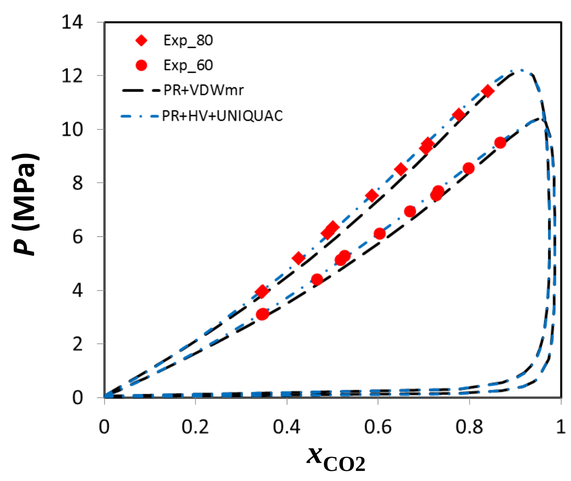




- The measurement results from the apparatus have a good agreement with available experimental data in literature.
- Both the prediction of PR+VDWmr and the correlation of PR+HV+UNIQUAC match the experimental results.
- Not all experimental data from the literature are reliable, e.g., JCED_2006_Han.

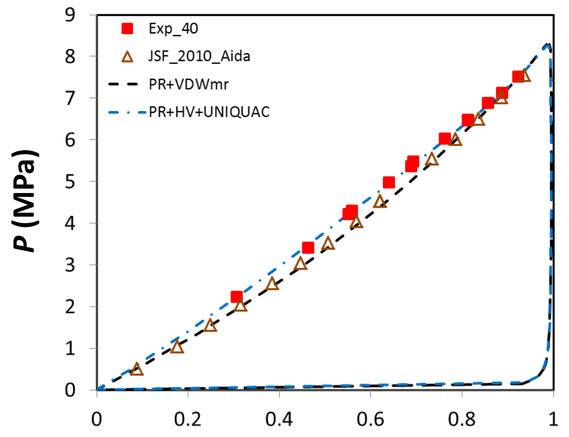
B. VLE measurements of CO_2 + 3-methyl-2-butanone

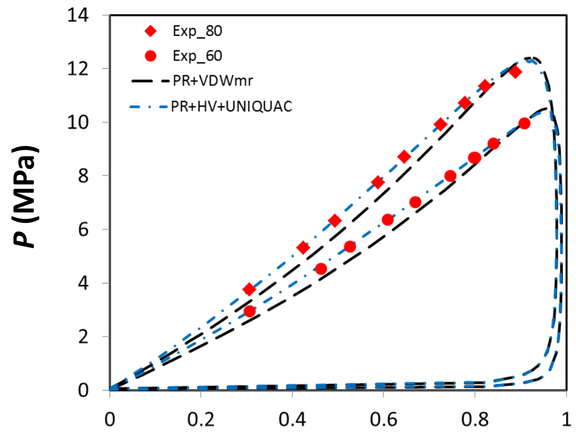




- The present measurement results at 313.15 K are in very good agreement with the experimental data by Aida et al.
- Only the correlation of PR+HV+UNIQUAC matches with the experimental results.
- New experimental data at 333.15 K and 353.15 K were generated.

C. VLE measurements of CO_2 + 2-pentanone





- The measurement results at 313.15 K from the apparatus are not consistent with Aida's experimental data. This is because the purity of 2-pentanone in their measurement was only 95% and these 5% heavy impurity components will lead to a lower vapor pressure.
- The correlation of PR+HV+UNIQUAC matches the experimental results better.
- New experimental data at 333.15 K and 353.15 K were generated.

4. Conclusions

- **The apparatus was validated by measuring the VLE of CO_2 + acetone.**
- **New experimental VLE data for CO_2 + 3-methyl-2-butanone and CO_2 + 2-pentanone at 313.15, 333.15, and 353.15 were measured.**
- **The correlation PR+HV+UNIQUAC is in good agreement with the experiments.**

5. References

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Acknowledgements

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