

Solubility of Methane in Toluene at Temperatures from 313 to 423 K at Pressures to 8.9 MPa

Srinivasa Srivatsan, Wuzi Gao, Khaled A. M. Gasem, and Robert L. Robinson, Jr.*

School of Chemical Engineering, Oklahoma State University, Oklahoma 74078

Solubility data are presented for methane in toluene at temperatures of 313.2, 338.7, and 423.2 K at pressures to 8.9 MPa. The data are in reasonable agreement with the measurements of Lin et al. at 423 K but differ significantly from those of Elbishlawi et al. at 338.7 K. Our data can be described with root-mean-square deviations of about 0.0005 in mole fraction by the Soave–Redlich–Kwong and Peng–Robinson equations of state when a single interaction parameter per isotherm is employed in the equations.

Introduction

As part of our work on the solubilities of light gases in heavy solvents, we have previously reported on the solubility of methane in heavy normal paraffins (Srivatsan et al., 1992; Darwish et al., 1993) and in aromatic hydrocarbons (Darwish et al., 1994). During that time, we also measured the solubility of methane in toluene to bridge the gap between the lower temperature data of Lin et al. (1978) and Chang and Kobayashi (1967) and the higher temperature data of Lin et al. (1979). Our measurements are reported here to complete our studies of methane solubilities.

The measurements of Legret et al. (1982) overlap the temperature range of the present work, but their data are at higher pressures. The lowest isotherm of Lin et al. (1979) coincides with our measurements at 423 K. Measurements by Elbishlawi and Spencer (1951) are in the range of the present work, but their data have been cited as possibly inaccurate (Legret et al., 1982). As a result, we decided to perform the measurements reported here.

Experimental Section

The experimental apparatus and procedures were identical with those described previously (Srivatsan et al., 1995). Estimated uncertainties in the experimental measurements are ± 0.1 K in temperature, ± 0.003 MPa in pressure, and less than ± 0.001 in mole fraction.

The methane used in the measurements had a stated purity of 99.97+ mol % and was supplied by Matheson. Toluene was from E. M. Science Company with quoted purity of 99.90 mol %. No further analysis or purification of the chemicals was attempted.

Results and Discussion

Our experimental data appear in Table 1. The data have been correlated using the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) cubic equations of state (EOS) in order (a) to assess the accuracy of these two equations for the system studied and (b) to facilitate comparisons of our data with the results of earlier studies. Optimum binary interaction parameters, C_{ij} and D_{ij} , in the EOS were obtained by minimizing the sum of squares of the percent

Table 1. Solubility of Methane (1) in Toluene (2)

| x_1 | p/MPa | x_1 | p/MPa |
|---------|----------------|-------|----------------|
| 313.2 K | | | |
| 0.026 | 1.17 | 0.120 | 5.53 |
| 0.055 | 2.38 | 0.136 | 6.30 |
| 0.071 | 3.14 | 0.150 | 7.08 |
| 0.099 | 4.44 | | |
| 338.7 K | | | |
| 0.050 | 2.34 | 0.120 | 5.74 |
| 0.091 | 4.19 | 0.152 | 7.36 |
| 0.107 | 5.10 | 0.181 | 8.92 |
| 423.2 K | | | |
| 0.038 | 2.11 | 0.101 | 5.25 |
| 0.052 | 2.84 | 0.114 | 5.91 |
| 0.074 | 3.88 | 0.140 | 7.24 |

Table 2. Critical Properties and Acentric Factors Used in the SRK and PR Equations of State

| component | critical properties | | | ref |
|-----------|---------------------|----------------|----------|----------------------|
| | P_c/MPa | T_c/K | ω | |
| methane | 4.66 | 190.5 | 0.011 | Goodwin, 1974 |
| toluene | 4.10 | 591.8 | 0.263 | Ely and Hanley, 1981 |

deviations of the calculated pressures from the experimental values. The interaction parameters are applied to the EOS parameters (“a” and “b”) as follows:

$$a_{ij} = (a_i a_j)^{0.5} (1 - C_{ij})$$

$$b_{ij} = \frac{1}{2} (b_i + b_j) (1 + D_{ij})$$

Results are presented for use of a single interaction parameter, C_{ij} ($D_{ij} = 0$), and for both parameters. The detailed procedure for the data reduction is given by Gasem (1989). The EOS input parameters for the pure components (acentric factors, critical temperatures, critical pressures) appear in Table 2.

The EOS, when fitted to individual isotherms, reproduced the measured bubble point pressures with average absolute errors of about 0.5%. Using parameters determined by minimizing the sum of squares of relative errors in bubble point pressures also provided good representations of the methane solubilities (mole fractions at specified pressures), as documented in Table 3.

Both the SRK and PR EOS are capable of describing the data with root-mean-square (rms) deviations of 0.001 in

* To whom correspondence should be addressed. E-mail rrobin@okway.okstate.edu.

Table 3. SRK and PR Equation-of-State Representations of Solubility of Methane in Toluene

| T/K | Soave parameters (P-R parameters) | | deviations in predicted methane mole fraction ^a | |
|---------------------|-----------------------------------|----------|--|---------|
| | C_{12} | D_{12} | RMS | maximum |
| 313.2 | 0.065 | 0.003 | 0.0004 | 0.0008 |
| | (0.066) | (0.007) | | |
| 338.7 | 0.072 | | 0.0004 | 0.0009 |
| | (0.081) | | | |
| 423.2 | 0.056 | 0.004 | 0.0008 | 0.0016 |
| | (0.058) | (0.008) | | |
| 313.2, 338.7, 423.2 | 0.065 | | 0.0008 | 0.0013 |
| | (0.074) | | | |
| 313.2, 338.7, 423.2 | 0.031 | 0.020 | 0.0001 | 0.0002 |
| | (0.036) | (0.020) | | |
| 313.2, 338.7, 423.2 | 0.073 | | 0.0005 | 0.0008 |
| | (0.075) | | | |
| 313.2, 338.7, 423.2 | 0.043 | 0.012 | 0.0012 | 0.0030 |
| | (0.047) | (0.017) | | |
| 313.2, 338.7, 423.2 | 0.068 | | 0.0013 | 0.0027 |
| | (0.078) | | | |

^a Errors are essentially identical for the SRK and PR EOS.

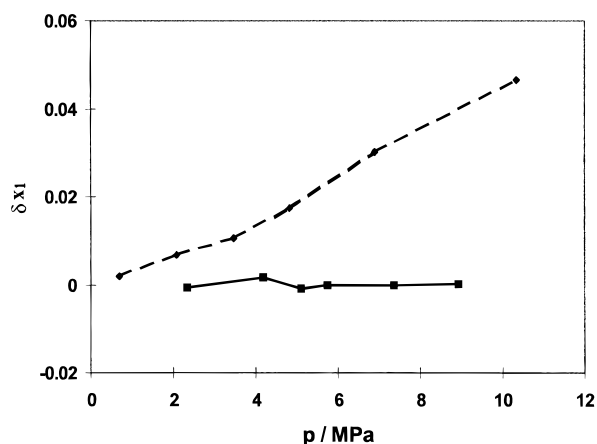


Figure 1. Comparison of methane solubilities in toluene at 338.7 K. Solid line is this work (■) and dashed line is Elbishlawi et al., 1951 (◆). δx_1 is the deviation (mole fraction methane) of the data from the PR EOS fit to our data.

mole fraction when a single interaction parameter, C_{ij} , is used over the complete temperature range of this study. However, when a C_{ij} value is optimized for each isotherm of data, the rms deviations for either EOS drop to less than 0.0008, which is within the expected experimental uncertainty of the data. Introduction of an additional interaction parameter, D_{ij} , produces negligible improvements, as shown in Table 3. The excellent fit of the EOS to the data on an isotherm-by-isotherm basis illustrates both the abilities of the EOS and the precision of our data. The absence of clear temperature trends in the regressed interaction parameters is attributed to their sensitivity to small errors in the experimental data.

Comparisons of our results with those reported by others appear in Figures 1 and 2. The comparisons are shown in terms of deviations (δx) of the solubilities from values predicted by the PR EOS, using C_{ij} , D_{ij} values determined from the present data at the temperature of interest. These figures facilitate a sensitive analysis of differences in data sets. The difference in the deviations between data sets (not the magnitude of the deviation of either set from the reference equation) is of interest in these data comparisons, since the difference in deviations (δx) between data sets is independent of the reference model employed.

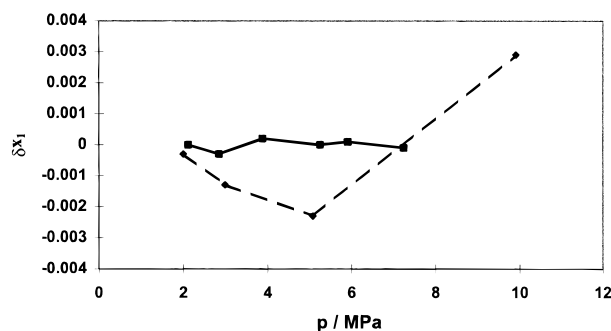


Figure 2. Comparison of methane solubilities in toluene at 423 K. Solid line is this work (■, 423.2 K), and dashed line is Lin et al., 1979 (◆, 422.5 K). δx_1 is the deviation (mole fraction methane) of the data from the PR EOS fit to our data.

That is, for two data sets A and B, at a fixed temperature and pressure:

$$\delta x_A - \delta x_B = [(x_{\text{expt}})_A - (x_{\text{EOS}})] - [(x_{\text{expt}})_B - (x_{\text{EOS}})] = (x_{\text{expt}})_A - (x_{\text{expt}})_B$$

Figure 1 shows rather significant disagreement between our measurements and the data of Elbishlawi and Spencer (1951) at 338.7 K, where the two data sets differ by as much as 0.047 in mole fraction. However, better agreement is seen in Figure 2 with the data of Lin et al. (1979) at 423.2 K, since the two deviation curves are separated by no more than about 0.003. (Note the different scales for δx in Figures 1 and 2.)

Conclusion

Data are reported on the solubility of methane in toluene from 323 to 423 K at pressures to 8.9 MPa. The data are described well by the Soave-Redlich-Kwong and Peng-Robinson equations of state.

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Received for review January 20, 1998. Accepted April 10, 1998. This work was supported by the U.S. Department of Energy under Contract No. DE-FG-22-90PC90302.

JE9800151