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# Solubility of Methane in Tetrahydrofuran + Ethanol at High Pressures

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The solubility of methane in tetrahydrofuran + ethanol has been measured at (300.15 and 274.45) K at pressures from (2.71 to 9.40) MPa. The experimental data were analyzed using the Soave−Redlich−Kwong equation of state with three kinds of mixing rules, and the estimation average deviation from the experimental solubility data is less than 3.7 %.

## Introduction

Gas hydrates are crystalline compounds that are formed by host water molecules with small guest molecules. It has been reported that the world reserves of natural gas trapped in the hydrate state have been estimated to be several times the known reserves of conventional natural gas.[1] Methane hydrates are therefore viewed as the main energy supply resource for the 21st century.[2] Several methods for commercial production of natural gas from hydrates have attracted considerable attention, namely, heating, depressurization, and inhibitor injection methods.[3] The inhibitor injection method is proposed by the injection of alcohol or tetrahydrofuran (THF) into the natural gas hydrates to dissociate the hydrate.[4,5] Therefore, the solubility data of methane are important not only in water but also in THF + ethanol for the decomposition of hydrates.

The phase equilibrium properties of the methane + ethanol and methane + THF systems have been widely investigated by various researchers.[4–8] Unfortunately, solubility data for methane in THF + ethanol at high pressure are scarce. In the present study, the solubility of methane was measured at (300.15 and 274.45) K at pressures from (2.71 to 9.40) MPa in THF + ethanol. The present experimental data obtained were correlated using the Soave−Redlich−Kwong (SRK)[9] cubic equations of state (EOS) with three kinds of mixing rules.

## Experimental Section

***Materials.*** Methane of 99.99 % purity was supplied by Beijing Analysis Instruments. The THF and ethanol were purchased from Tianjin Chemical Agents Corp. with a purity of 99.9 %. All chemicals were used without further purification.

***Apparatus and Operation.*** The experimental apparatus is similar to that described in previous studies.[10,11] The apparatus consists of an equilibrium cell equipped with a magnetic stirring bar to provide an excellent mixing of gas and liquid. A high-pressure circulating pump was used to circulate the liquid, and a sample vessel with a volume of 20.2 cm$^3$ was placed in the circulation flow to keep the pressure in the cell constant during sampling. The pressure in the cell was measured by a calibrated digital transducer (TPT530 and an indicator AI-518P from Yudian) with an estimated uncertainty of 0.1 % of the scale range (10 MPa). The temperature in the cell was measured by a calibrated thermal resistance thermometer (Pt100). The main parts of the apparatus were placed in a constant-temperature liquid bath controlled within an accuracy of ± 0.1 K.

**Table 1. Solubility Data of Methane ($x_1$) in *n*-Hexane ($T$ = 298.15 K)**

| $x_1$ | $P$/MPa |
|---|---|
| This work | |
| 0.0982 | 2.05 |
| 0.2283 | 5.05 |
| 0.3451 | 8.10 |
| Ref 12 | |
| 0.0978 | 2.03 |
| 0.2316 | 5.07 |
| 0.3447 | 8.11 |

Prior to the introduction of the liquids, the cell was evacuated. About 500 cm$^3$ of the solvent was transferred into the cell, and then methane was added by the cylinder pressure. The mixer and circulation pump were started and kept in operation for (4 to 6) h until the pressure remained the same for more than 30 min. The sample valves were closed, and the sample vessel can be removed and linked to a 60 cm$^3$ sample bomb that had previously been evacuated and weighed. The liquid sample was drawn and flashed into the bomb. The separated liquid was kept in the bomb, and the effluent gas was collected with a drainage. The bomb was reweighed to determine the mass of the separated liquid. The collected liquid was weighted using an electronic balance, and the measuring range and precision of the balance were (0 to 200) and 0.0001 g, respectively. The volume of the gas collected was measured at the local atmospheric pressure and room temperature by a $3 \cdot 10^3$ cm$^3$ buret, which has a precision of 0.1 cm$^3$. The moles collected were calculated from the $P-V-T$ data, assuming ideal gas behavior. The residual gas left in the solvent at atmospheric pressure was measured using a gas chromatograph. A 2 $\mu$L sample of separated liquid sample was injected directly into the gas chromatograph. Estimated uncertainties in experimental measurements are less than 0.002 in mole fraction and 0.5 cm$^3 \cdot$mol$^{-1}$ in molar volume.

Solubility data of methane in *n*-hexane have been measured to check the reliability of the experimental apparatus and procedure. The average uncertainties were estimated to be 4 %

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when compared with values in the literature.[12] The evaluating data were listed in Table 1.

***Phase Equilibria Modeling.*** Our experimental data appear in Table 2. The data have been correlated using the SRK cubic equation of state. To account for interaction taking place between components in the mixture, the classical mixing rules, two-parameter Margules mixing rules,[13] and the mixing rules developed by Huron and Vidal[14] are used.

(1) Classical mixing rules (method I)

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{1}$$

$$a_{\mathrm{M}} = \sum_i \sum_j x_i x_j a_{ij} \tag{2}$$

$$b_{\mathrm{M}} = \sum_i x_i b_i \tag{3}$$

with $k_{ij} = k_{ji}$.

In eq 1, $k_{ij}$ is an empirical interaction parameter characterizing the binary interactions between components $i$ and $j$.

(2) Margules mixing rules (method II)

$$a_{ij} = (a_{ii} a_{jj})^{0.5}(1 - x_i k_{ij} - x_j k_{ji}) \tag{4}$$

with $k_{ij} \neq k_{ji}$.

(3) Huron−Vidal mixing rules (method III)

Mixing rules are proposed by the activity coefficient model.

$$\frac{g^{\mathrm{E}}}{RT} = \ln \phi - \sum_i x_i \ln \phi_i \tag{5}$$

To use eq 5, the excess Gibbs energy has to be first calculated. In our work, it is obtained using the NRTL activity coefficient model.[15,16]

$$a_{ij} = \frac{1}{2}\left(a_{ii}\frac{b_j}{b_i} + a_{jj}\frac{b_i}{b_j}\right) - \frac{c}{2}(x_i b_i + x_j b_j)\frac{g^{\mathrm{E}}_{ij\infty}}{x_i x_j} \tag{6}$$

with

$$c = \frac{2\sqrt{2}}{\ln[(2+\sqrt{2})/(2-\sqrt{2})]} \tag{7}$$

$$\frac{g^{\mathrm{E}}_{ij\infty}}{x_i x_j} = \frac{\Delta g_{ij} G_{ij}}{x_i G_{ij} + x_j} + \frac{\Delta g_{ji} G_{ji}}{x_i + x_j G_{ji}} \tag{8}$$

$$G_{ij} = \exp\left[\frac{-0.3\Delta g_{ij}}{RT}\right] \tag{9}$$

Values of these parameters were determined by fitting experimental binary mixture data to minimize the objective function, $Q$, which is expressed as

$$\mathrm{Min}\ Q = \sum_{i=1}^{N} (\hat{f}_i^{\mathrm{g}} - \hat{f}_i^{\mathrm{l}})^2 \tag{10}$$

where $\hat{f}_i^{\mathrm{g}}$ and $\hat{f}_i^{\mathrm{l}}$ are, respectively, the fugacity of methane in the gas phase and liquid phase.

The use of these methods requires the knowledge of pure component parameters $T_{\mathrm{C}}$, $P_{\mathrm{C}}$, and $\omega$ referring to the equation of state. For each component, these parameters can be found in the DIPPR database (Design Institute for Physical Properties data).

## Results

Adjustable parameters, such as $k_{ij}$ and $\Delta g_{ij}$ in the proposed mixing rules, are calculated by regression analysis of experimental phase equilibrium data. The results are given in Table 3.

Table 2 compared the predicted results with the experimental measurements for the methane solubility in the solvent. It can be seen that the SRK equation describes the data with an average absolute deviation (AAD) of 3.7 % when the method I is used. The quality of the SRK EOS representation is improved when Margules mixing rules and Huron−Vidal mixing rules are employed, resulting in an AAD of 1.6 % and 1.2 %, respectively. Apparently, the SRK EOS simulated the methane solubility very well in the range of experimental conditions.

## Conclusions

In this work, data have been obtained on the solubility of methane in THF + ethanol at (300.15 and 274.45) K and pressures up to 9.40 MPa. The data are well described by the SRK equations of state. The quality of SRK EOS is different with different mixing rules. Introduction of Margules mixing rules and Huron−Vidal mixing rules produces obvious im

**Table 2. Solubility Data for Methane (1) in Ethanol (2) + THF (3)[a]**

| | | | method I | | method II | | method III | |
|---|---|---|---|---|---|---|---|---|
| $T$/K | $P$/MPa | $x_1$(exptl) | $x_1$(calcd) | RD % | $x_1$(calcd) | RD % | $x_1$(calcd) | RD % |
| 300.15 | 9.40 | 0.173 | 0.157 | −9.3 | 0.175 | 1.0 | 0.174 | 0.6 |
| | 8.40 | 0.155 | 0.154 | −1.0 | 0.156 | 0.6 | 0.156 | 0.5 |
| | 7.42 | 0.139 | 0.138 | −1.0 | 0.139 | 0.2 | 0.139 | −0.1 |
| | 6.32 | 0.118 | 0.119 | 0.9 | 0.116 | −1.3 | 0.118 | −0.4 |
| | 5.50 | 0.103 | 0.105 | 1.7 | 0.101 | −2.1 | 0.102 | −0.8 |
| | 4.59 | 0.086 | 0.087 | 2. 7 | 0.084 | −2.6 | 0.086 | −0.1 |
| | 3.65 | 0.069 | 0.071 | 3.5 | 0.067 | −3.0 | 0.068 | −1.4 |
| | 2.71 | 0.052 | 0.054 | 3.7 | 0.051 | −2.2 | 0.051 | −1.7 |
| 274.45 | 9.37 | 0.176 | 0.177 | 0.6 | 0.177 | 0.3 | 0.172 | −2.4 |
| | 8.88 | 0.171 | 0.169 | −1.3 | 0.174 | 1.7 | 0.17 | −0.7 |
| | 7.54 | 0.150 | 0.148 | −1.3 | 0.154 | 2.4 | 0.154 | 2.7 |
| | 6.32 | 0.130 | 0.127 | −1.9 | 0.134 | 2.8 | 0.131 | 1.1 |
| | 5.37 | 0.104 | 0.111 | 6.3 | 0.106 | 2.0 | 0.105 | 1.4 |
| | 4.54 | 0.087 | 0.095 | 8.7 | 0.088 | 1.7 | 0.089 | 2.4 |
| | 3.63 | 0.072 | 0.077 | 6.9 | 0.073 | 1.0 | 0.073 | 1.6 |
| | 2.70 | 0.054 | 0.057 | 8.5 | 0.054 | 0.5 | 0.054 | 0.7 |
| AAD % | | | | 3.7 | | 1.6 | | 1.2 |

[a] Subscripts: The mass percent of ethanol in the solvent is 0.1500; RD is the relative deviation of calculation from the experimental data, RD = $x_1$(calcd) − $x_1$(exptl)/$x_1$(exptl). AAD is the average absolute deviation of calculation from the experimental data, AAD = $|\Sigma_i^N \mathrm{RD}|/N$.

**Table 3. Binary Interaction Parameters *k* and Δ*g***

| | | | |
|---|---|---|---|
| method I | $k_{12} = 0.081$ | $k_{13} = 0.069$ | $k_{23} = 0.111$ |
| method II | $k_{12} = 0.035$ | $k_{13} = 0.382$ | $k_{23} = 0.142$ |
| | $k_{21} = 0.011$ | $k_{31} = -0.116$ | $k_{32} = -0.079$ |
| method III | $\Delta g_{12} = -174.547$ | $\Delta g_{13} = -178.633$ | $\Delta g_{23} = -953.224$ |
| | $\Delta g_{21} = 1722.189$ | $\Delta g_{31} = 2135.901$ | $\Delta g_{32} = -142.973$ |

provements. These results will be of value in the use of THF and ethanol in the decomposition of hydrates.

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