Determination and Study of the Solubility of Methane in Mixtures of Methanol plus Various Hydrocarbons at High Pressures

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It is known that the use of natural gas as a vehicular fuel is advantageous; however, the drawback of this application is the storage limitations of natural gas. One method for storing natural gas at moderate temperatures and pressures is to dissolve it in organic mixtures. In this paper, an apparatus for measuring gas solubility in liquids under high pressures was used. The solubilities of methane in methanol + *n*-hexane, methanol + *n*-heptane, and methanol + cyclohexane at 303.15 K and in methanol + benzene and methanol + methylbenzene at 288.15 K and 303.15 K were measured. The experimental pressures are up to 12.0 MPa. The new solubility measurements are believed to have uncertainties of 0.002 (mole fraction). Meanwhile, the molar volumes of liquid-phase mixtures at high pressures were determined and well-estimated by the Aalto−Keskinen model. Because of the polarity of methanol, the PRSV equation of state with the Huron−Vidal mixing rule was used to estimate the equilibrium data for methane + methanol + hexane, methane + methanol + heptane, and methane + methanol + cyclohexane systems as well as to correlate the data for methane + methanol + benzene and methane + methanol + methylbenzene systems. The average absolute deviations (AAD) of the correlation were 3.0 % and 1.9 %, respectively.

Introduction

The use of natural gas as a vehicular fuel has attracted much attention due to the environmental benefits. For example, the combustion of natural gas as fuels decreases the release of CO, CO_2, and SO_2 by 97, 24, and 90 %, respectively; the amount of lead discharged in exhaust gases is even reduced to zero. Therefore, adapting the natural gas as a vehicular fuel is of great environmental importance.[1] However, the storage limitation of natural gas is a severe drawback in the application of using the natural gas as the vehicular fuel. Conventional storage techniques for natural gas require compression or liquefaction to produce compressed natural gas (CNG) and liquefied natural gas (LNG). However, CNG requires very high-pressure vessels for storage, while LNG needs cryogenic processing equipment and cryogenic storage. Considering the drawbacks associated with CNG and LNG storage techniques, it is highly desirable to develop a safe and more convenient method for storing the natural gas in vehicules.[2]

It has been recognized that when gases are stored with a solvent the critical pressure of the mixture is lower, resulting a lower storage pressure. Based on this principle, dissolving the natural gas in solvents is a potential method for storing it at ambient temperatures and moderate pressures. In this method, the energy storage density can be increased, and the driving range of the vehicle could be extended.

In addition, methanol was originally used as a gasoline extender, and the methanol fuel becomes popular in some countries. For instance, gasoline fuels can be blended with 15 % or 85 % methanol to make so-called the methanol−gasoline blended fuels. In our experiments, the mass fraction of methanol in the mixing solvents ($w(CH_3OH)$ is set as 0.150 or 0.850. Thus, it is of practical significance to study the solubility of methane, the main component of natural gas, in light hydrocarbons, methanol, or other compounds and their mixtures.

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The objectives of this work are to measure the solubility of methane in *n*-C_6H_{14}−CH_3OH, *n*-C_7H_{16}−CH_3OH, and C_6H_{12}−CH_3OH at 303.15 K and in C_6H_6−CH_3OH and C_7H_8−CH_3OH at temperatures of 288.15 and 303.15 K at pressures from 2.0 MPa to 12.0 MPa and compare the results with the predictions by an equation of state (EOS).

Experimental Section

The gas solubility in liquids under high pressures was measured by an apparatus with a variable-volume, stainless steel equilibrium cell. The experimental method was described in ref 3. The overall equipment setup consists of experimental system and sampling system. In this experiment, a water bath with accuracy of ± 0.1 K and a pressure transducer with accuracy of ± 0.01 MPa were used to determine the temperatures and pressures. The estimated uncertainties in experimental measurements are less than 0.002 in mole fraction and 0.5 cm^3/mol in molar volume.

The apparatus and the experimental procedure were examined using methanol and *n*-hexane as the standard solvents before measurements. The evaluating data were shown in ref 3.

Materials. Methane with >99.9 % purity from Beijing Analysis Instrument was used for all of the experiments. The other reagents were all purchased from Tianjin Chemical Agents Corp. with a purity of 99.5 %.

Results

Methane + Methanol + Hexane, Methane+ Methanol + Heptane, and Methane+ Methanol + Cyclohexane Systems. The solubility data for methane in methanol + hexane, methanol + heptane, and methanol + cyclohexane binary solvents are presented in Table 2.

EOS Estimation. Data for the ternary systems can be correlated from binary equilibrium data using the PRSV equation

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of state[4] with the Huron−Vidal mixing rule.[5] The PRSV EOS specific relations used are as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \quad (1)$$

where

$$a = \left(\frac{0.45724R^2T_c^{\,2}}{P_c}\right)\alpha(T_r) \quad (2)$$

$$b = \frac{0.0778RT_c}{P_c} \quad (3)$$

and

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \quad (4)$$

$$m = k_0 + k_1(1 + T_r^{0.5})(0.7 - T_r) \quad (5)$$

$$k_0 = 0.378893 + 1.4897153\omega - 0.17131848\omega^2 + 0.0196554\omega^3 \quad (6)$$

where k_1 is an adjustable parameter characteristic of each pure compound.[4]

To apply the PRSV equation to mixtures, the values of a and b can be determined using the HV mixing rules:

$$a_M = \sum_i \sum_j x_i x_j a_{ij} \quad (7)$$

$$b_M = \sum_i x_i b_i \quad (8)$$

$$a_{ij} = \frac{1}{2}\left(a_{ii}\frac{b_j}{b_i} + a_{jj}\frac{b_i}{b_j}\right) - \frac{c}{2}(x_i b_i + x_j b_j)\frac{g^E_{ij,\infty}}{x_i x_j} \quad (9)$$

where

$$c = \frac{2\sqrt{2}}{\ln[(2+\sqrt{2})/(2-\sqrt{2})]} \quad (10)$$

For $g^E_{ij,\infty}$, Huron and Vidal[5] have used the NRTL equation proposed by Renon and Prausnitz[6]:

$$\frac{g^E_{ij,\infty}}{x_i x_j} = \frac{\Delta g_{ij} G_{ij}}{x_i G_{ij} + x_j} + \frac{\Delta g_{ji} G_{ji}}{x_i + x_j G_{ji}} \quad (11)$$

and

$$G_{ij} = \exp\left[\frac{-0.3\Delta g_{ij}}{RT}\right] \quad (12)$$

Δg_{ij} and Δg_{ji} are the parameters for the NRTL equation. The values of these parameters were determined by fitting experimental binary mixture data to minimize the objective function, F, which is expressed as

$$F = \sum_{i=1}^{N} (\hat{f}_i^{\,g} - \hat{f}_i^{\,l})^2 \quad (13)$$

The calculation procedure is follows. First, the gas−liquid equilibrium data for four binary systems, methane + methanol, methane + hexane, methane + heptane, and methane + cyclohexane were collected from the literature.[7−9] The fugacity coefficients of methane in both gas and liquid phases were calculated by PRSV EOS. Meanwhile, the vapor−liquid equilibrium data for three binary systems, methanol + hexane, methanol + heptane, and methanol + cyclohexane were collected from the literature.[10] The fugacity coefficients of methanol in both vapor and liquid phases were calculated by PRSV EOS. The binary interaction parameters Δg_{ij} and Δg_{ji} in the mixing rules for every binary system were correlated by the Simplex method.[11] The results are listed in Table 1. Using these parameters, the experimental data for the ternary system were correlated by the PRSV equation. The estimation average absolute deviations (AADs) from the experimental solubility data for the three systems are 11 %, 4.9 %, and 6.6 %, respectively. These results are presented in Table 2. The calculated and experimental solubility data of methane in methanol + hexane system are illustrated in Figure 1.

Table 1. NRTL Parameters Δg_{ij} and Δg_{ji} for the Binary Systems

	Δg_{12} / J·mol^{-1}	Δg_{21} / J·mol^{-1}	standard error
methane (1) + methanol (2)	7672.7	−2624.6	1.9 %
methane (1) + hexane (2)	3089.4	−1677.3	1.5 %
methane (1) + heptane (2)	3393.5	−1824.1	1.8 %
methane (1) + cyclohexane (2)	2809.4	−1071.3	1.7 %
methanol (1) + hexane (2)	8508.7	8614.0	2.0 %
methanol (1) + heptane (2)	11034.3	2167.0	1.4 %
methanol (1) + cyclohexane (2)	8999.9	−1253.9	1.8 %

Table 2. Experimental and Estimation Data for Methane (1) + Methanol (2) + Hexane, Methane (1) + Methanol (2) + Heptane, and Methane (1) + Methanol (2) + Cyclohexane Systems at 303.15 K (w(CH$_3$OH = 0.85)

P / MPa	x_2	$x_{1(exp)}$	$x_{1(cal)}$	RD % (x)	$V_{m,exp}$ / cm^3·mol^{-1}	$V_{m,cal}$ / cm^3·mol^{-1}	RD % (V)
Methane (1) + Methanol (2) + Hexane							
12.02	0.808	0.139	0.139	−0.24	46.4	46.6	0.36
8.02	0.848	0.0958	0.106	−11	47.0	45.8	−2.6
4.99	0.883	0.0589	0.0700	−14	47.2	45.4	−3.8
2.00	0.915	0.0242	0.0292	−21	47.1	45.1	−4.2
AAD %				11			2.7
Methane (1) + Methanol (2) + Heptane							
12.00	0.819	0.135	0.125	7.2	47.2	46.2	−2.1
8.00	0.861	0.0911	0.0901	1.1	47.1	45.9	−2.7
5.00	0.893	0.0573	0.0587	−2.5	47.4	45.5	−4.0
1.99	0.926	0.0225	0.0244	−8.7	47.3	45.1	−4.6
AAD %				4.9			3.4
Methane (1) + Methanol (2) + Cyclohexane							
11.99	0.820	0.125	0.124	0.75	45.3	45.5	0.36
7.99	0.859	0.0830	0.0861	−3.7	45.1	45.5	0.90
4.99	0.889	0.0507	0.0560	−11	45.5	44.4	−2.5
2.00	0.917	0.0212	0.0236	−11	45.7	44.1	−3.5
AAD %				6.6			1.8

It is noticeable that the ternary gas−liquid equilibrium data can be correlated approximately with the binary equilibrium data. But the results are not satisfactory.

The molar volumes of liquid-phase mixtures at high pressures were estimated by the Aalto−Keskinen model.[12,13] In the model, the correlation of Hankinson and Thomson[14]was used to predict the densities of saturated liquids, and the modified Chang-Zhao equation[15,16] was applied to predict the compressed liquid molar volume. The calculation AADs from the experimental molar volumes for the three systems are 2.7 %, 3.4 %, and 1.8 %, respectively, and the results are also presented in Table 2.

Methane + Methanol + Benzene and Methane + Methanol + Methylbenzene Systems. The solubility data for methane in methanol + benzene and methanol + methylbenzene binary solvents are presented in Table 3.

Table 3. Experimental and Correlation Results for Methane (1) + Methanol (2) + Benzene and Methane (1) + Methanol (2) + Methylbenzene[a]

T / K	P / MPa	x_2	$x_{1(\mathrm{exp})}$	$x_{1(\mathrm{cal})}$	RD % (x)	$V_{\mathrm{m,exp}}$ / cm^3·mol^{-1}	$V_{\mathrm{m,cal}}$ / cm^3·mol^{-1}	RD % (V)
			Methane (1) + methanol (2) + Benzene System					
303.15	11.99	0.829	0.110	0.103	−6.2	44.0	44.2	0.44
303.15	7.99	0.863	0.0741	0.0720	−2.9	44.9	43.82	−2.4
303.15	5.00	0.888	0.0474	0.0458	−3.3	44.9	43.5	−3.0
303.15	2.01	0.915	0.0180	0.0158	−12	44.4	43.3	−2.6
288.15	12.01	0.828	0.112	0.114	1.8	44.8	43.3	−3.4
288.15	8.00	0.862	0.0754	0.0754	0.0	44.7	42.93	−4.0
288.15	5.00	0.886	0.0491	0.0552	12	45.3	42.63	−5.9
288.15	2.01	0.913	0.0207	0.0212	2.3	45.9	42.4	−7.7
303.15	12.00	0.240	0.202	0.200	−0.89	69. 9	69.3	−0.82
303.15	8.00	0.260	0.137	0.139	1.5	72.5	70.7	−2.5
303.15	5.00	0.275	0.0848	0.0860	1.4	74.1	71.8	−3.1
303.15	2.00	0.291	0.0339	0.0351	3.7	75.1	73.0	−2.8
288.15	11.99	0.238	0.208	0.208	−0.01	68.9	67.7	−1.8
288.15	7.99	0.259	0.141	0.135	−4.2	71.7	69.27	−3.4
288.15	4.99	0.275	0.0880	0.0840	−4.5	73.3	70.4	−4.0
288.15	1.99	0.290	0.0354	0.0348	−1.7	75.1	71.6	−4.6
AAD %					3.0			3.3
			Methane (1) + Methanol (2) + Methylbenzene System					
303.15	12.00	0.842	0.106	0.106	0.14	44.9	44.5	−0.84
303.15	7.99	0.875	0.0710	0.0703	−0.91	44.8	44.2	−1.4
303.15	5.01	0.900	0.0449	0.0442	−1.6	44.8	43.9	−2.0
303.15	2.00	0.925	0.0179	0.0174	−2.6	45.0	43.6	−3.1
288.15	12.00	0.840	0.108	0.110	2.0	44.7	43.5	−2.8
288.15	8.00	0.873	0.0732	0.0737	0.69	44.8	43.2	−3.5
288.15	5.01	0.898	0.0464	0.0463	−0.15	45.1	43.0	−4.7
288.15	2.01	0.923	0.0198	0.0206	4.0	44.8	42.7	−4.6
303.15	12.01	0.266	0.211	0.2156	2.2	76.4	75.7	−0.86
303.15	8.00	0.289	0.141	0.140	−0.38	81.0	77.9	−3.9
303.15	5.00	0.307	0.0905	0.0903	−0.25	82.2	79. 4	−3.4
303.15	2.00	0.324	0.0390	0.0411	5.4	84.1	80.9	−3.8
288.15	12.00	0.265	0.213	0.213	0.0	76.5	74.2	−3.0
288.15	8.00	0.289	0.142	0.136	−4.5	79.3	76.3	−3.8
288.15	4.99	0.306	0.0913	0.0865	−5.3	81.7	77.9	−4.7
288.15	2.00	0.324	0.0395	0.0395	0.00	84.0	79.5	−5.4
AAD %					1.9			3.3

[a] Key: RD is the relative deviation of calculated vs experimental data, RD(x) = (x(cal) − x(exp))/x(exp), RD(V) = (V(cal) − V(exp))/V(exp). AAD is the average absolute deviation of calculated vs the experimental data, AAD = $|\sum_i^N \mathrm{RD}|/N$.

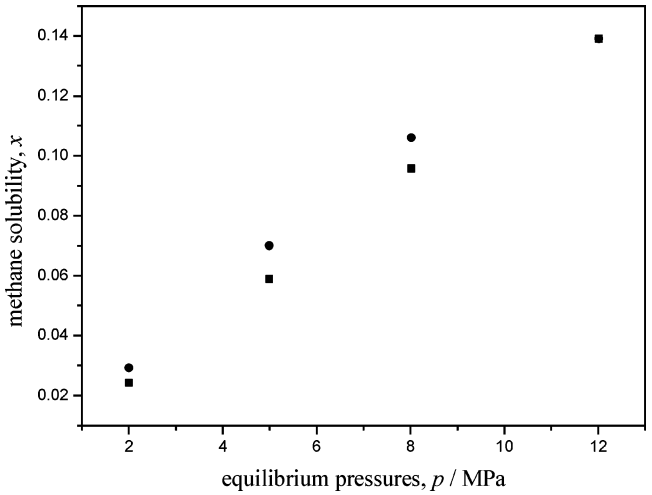

Figure 1. Methane solubility in mixtures of methanol + hexane at 303.15 K (w(CH_3OH = 0.85): ●, calculated data; ■, experimental data.

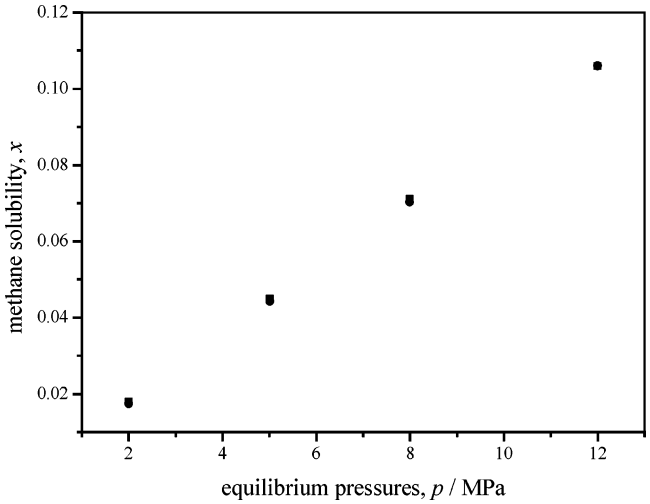

Figure 2. Methane solubility in mixtures of methanol + methylbenzene at 303.15 K (w(CH_3OH = 0.85): ●, calculated data; ■, experimental data.

EOS Correlation. The experimental data for the two systems were correlated using the PRSV cubic EOS with the HV mixing rule by the Simplex method. The binary interaction parameters Δg_{ij} and Δg_{ji} in the mixing rules were determined by fitting experimental data to minimize the objective function, F. The correlation results are shown in Table 3. The correlation average absolute deviations (AADs) for the experimental solubility data for methane + methanol + benzene and methane + methanol + methylbenzene system are 3.0 % and 1.9 %, respectively. The calculated and experimental solubility data of methane in methanol + methylbenzene system at 303.15 K are shown in Figure 2.

The molar volumes of the liquid-phase mixtures at high pressures were estimated by the Aalto−Keskinen model. The calculated AADs for the experimental molar volume for methane

+ methanol + benzene and methane + methanol + methylbenzene systems are 3.3 % and 3.3 %, respectively. The results are also presented in Table 3.

Conclusion

The solubility data of methane in methanol + hexane, methanol + heptane, and methanol + cyclohexane at 303.15 K and in methanol + benzene and methanol + methylbenzene at 288.15 K and 303.15 K were obtained in this study. The experimental pressures are up to 12.0 MPa. The equilibrium data of three systems, methane + methanol + hexane, methane + methanol + heptane, and methane + methanol + cyclohexane, were correlated from binary data using PRSV EOS with the HV mixing rule. However, the results are not satisfactory. The PRSV EOS with the HV mixing rule was also used to correlate the data for methane + methanol + benzene and methane + methanol + methylbenzene systems. The results indicate that the PRSV EOS with the HV mixing rule can be used to correlate the equilibrium data well for the systems containing methanol, which is a polar compound. But it was unable to predict the ternary gas−liquid equilibrium data accurately from the binary data. The acquired solubility data will be of value in the development and evaluation of solution theories of mixing and for natural gas storage.

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