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Determination and Study on the Solubility of Methane in Heptane + Cyclohexane and Heptane + Ethanol at High Pressures

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It is known that the use of natural gas as a vehicular fuel is advantageous, but the storage limitation of natural gas is a severe drawback to the use. In this paper, a method for storing natural gas at moderate temperatures and pressures by dissolving natural gas in solvents is studied. A set of experimental equipment for measuring gas solubility in liquids under high pressures was established. The solubilities of methane in heptane + cyclohexane and heptane + ethanol were measured over the temperature range from 291.15 K to 313.15 K and pressures to 12.00 MPa. The new solubility measurements are believed to have uncertainties of 0.002 in the mole fraction. The data were analyzed using the Peng−Robinson equation of state with two kinds of mixing rules. In general, the equation coupled with the simple mixing rule represents the experimental data of methane + heptane + cyclohexane well over the complete temperature and pressure range when the interaction parameters k_{ij} for methane + heptane and methane + cyclohexane were used and the k_{ij} for heptane+cyclohexane was ignored. Owing to the polarity of ethanol, when the experimental data of methane + heptane + ethanol were calculated by the equation, besides the interaction parameters k_{ij} for methane + heptane and methane + cyclohexane, the interaction parameter for heptane + ethanol as well as an additional interaction parameter, l_{ij}, must be employed. At the same time, the molar volumes of liquid-phase mixtures at high pressures for two kinds of ternary systems were measured and calculated.

Introduction

The use of natural gas as vehicular fuel is advantageous from an environmental point of view and has attracted a lot of attention. With respect to environmental protection, the use of natural gas as a vehicular fuel results in the reductions in CO, CO_2, and SO_2 of 97, 24, and 90%, respectively, and the amount of lead discharged in exhaust gases is reduced to zero. Therefore, the potential importance of using natural gas as a vehicular fuel is obvious.[1] However, when the storage volume is limited, the storage limitation of natural gas is a severe drawback to the use of natural gas as the vehicle fuel. Conventional storage techniques for natural gas need compression or liquefaction to give compressed natural gas (CNG) and liquefied natural gas (LNG). But CNG requires very high pressure vessels for storage and, LNG needs cryogenic processing equipment and cryogenic storage. Regarding the drawbacks associated with CNG and LNG storage techniques, it is highly desirable to develop a safe and more convenient way to store natural gas for use as the vehicular fuel.[2]

It has been recognized that, when gases are stored with a solvent, the critical pressure of the mixture is lower so that the storage pressure can be reduced. So, a method for storing natural gas at room temperatures and moderate pressures is to dissolve natural gas in solvents, such as light hydrocarbons. By this method, the energy storage density would be increased and the driving range of the vehicular could be extended.

Therefore it is of practical significance to study the solubility of methane, the main component of natural gas, in light hydrocarbons, ethanol, or other compounds and their mixtures.

The objectives of this work are to develop an apparatus for the measurement of gas solubility at normal temperature and high pressures, to measure the solubilities of CH_4 in n-C_7H_{16}+c-C_6H_{12} and n-C_7H_{16}+C_2H_5OH at temperatures of 291.15 K, 303.15 K, and 318.15 K at pressures from 2.0 MPa to 12.0 MPa, and to compare the results with the equation of state (EOS).

Experimental Method

The experimental apparatus used in this study employs a variable-volume, stainless steel equilibrium cell, which has a volume range from 200 cm^3 to 360 cm^3. In the cell, there is a piston, so the pressure of the cell can be raised by means of a manual oil pump. The cell was immersed in a water bath with a measuring precision of 0.1 K. A high-pressure circulating pump was used to circulate the liquid and provide an excellent mixing of the gas and liquid. A sampling vessel with a volume of 24.1 cm^3 is placed in the circulation flow in order to keep the pressure constant during sampling. The method consists of introducing known compositions of well-degassed binary solvents into the thermostated equilibrium cell. Then methane was introduced into the system, and the pressure was measured by a pressure transducer with measuring precision of 0.01 MPa. If the desired pressure in the apparatus was higher than that of the gas cylinder, the manual oil pump adjusted the gas pressure. The liquid pump was started, and the liquid in the equilibrium cell was cycled continuously at the rate of 15.0 cm^3/min. The system pressures were noted continually. The system was maintained at the temperature until the pressure of the system was changeless for about 30 min. The equipment flowchart is shown in Figure 1.

After equilibrium was reached, the sample valves were closed and the sample can was uninstalled and linked to a

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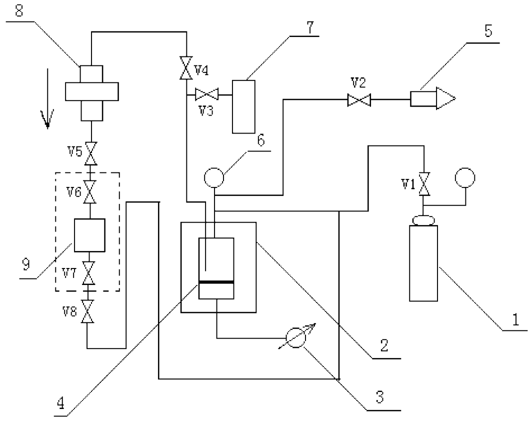

Figure 1. Schematic flow diagram of experimental system. 1, gas cylinder; 2, water bath; 3, manual oil pump; 4, equilibrium cell; 5, vacuum pump; 6, pressure transducer; 7, introduction vessel; 8, high-pressure pump for liquid circulating; 9, sample vessel; V1−V9 valves.

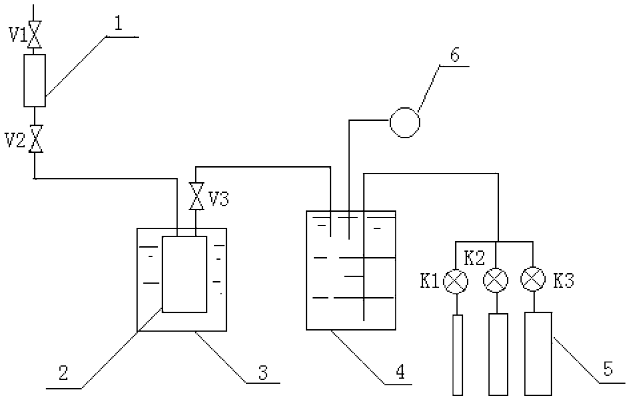

Figure 2. Schematic flow diagram of sampling system. 1, sample vessel; 2, trapper; 3, ice−water bath; 4, drainage; 5, gas-flow meter; V1−V3, high-pressure valves; K1−K3, vitric valves.

trapper. Then the sample process was started. The liquid sample was drawn and flashed into the trapper, which was immersed in an ice−water bath. The separated liquid was kept in the tube, while the effluent gas was collected with the drainage. The sampling flowchart is shown in Figure 2. The collected liquid was weighed using an electronic balance, and the measuring range and precision of the balance were 0 to 200 g and 0.0001 g, respectively. The volume of the gas collected was measured at ambient temperature and atmosphere pressure by a gas meter, which has a measuring range of 0 to 3 × 10^3 cm^3 and a precision of 0.1 cm^3. On the basis of the amount of the liquid collected and the volume of the gas meter, the gas solubility of methane in the solvent at the condition could be calculated. At the same time, the molar volumes of the equilibrium liquid phase could be calculated.

Estimated uncertainties in experimental measurements are less than 0.002 in mole fraction and 0.5 cm^3/mol in molar volume.

Evaluation of the Apparatus

The apparatus and the experimental procedure were checked using methanol and *n*-hexane as the standard solvents, respectively, before the experiment. The evaluating data were listed in Tables 1 and 2.

From Tables 1 and 2, the experimental solubility of methane in methanol and *n*-hexane at different temperatures and pressures are in good agreement with the data in refs 3 and 4, which were classed as credible. It can be seen from the data that the experimental apparatus and procedure are reliable.

Table 1. Solubility Data of Methane (x_1) in Methanol (T = 298.15 K)

x_1	P/MPa
This Work	
0.04418	5.45
0.09121	12.00
Reference 3	
0.04401	5.45
0.09092	11.96

Table 2. Solubility Data of Methane (x_1) in Hexane (T = 310.9 K)

x_1	P/MPa
This Work	
0.0985	2.15
0.1921	4.50
0.2540	6.00
Reference 4	
0.0996	2.18
0.1898	4.30
0.2573	6.03

Table 3. Binary Interaction Parameters k_{ij} of Methane (1) + Heptane (2) and Methane (1) + Cyclohexane (3)

	methane + heptane	methane + cyclohexane
k_{ij}	0.03320	0.04883
standard error	0.861%	1.09%

Table 4. Experimental and Estimation Data for Methane + Heptane + Cyclohexane at 303.15 K

P/MPa	x_2 (exp)	x_1 (exp)	x_1 (cal)	RD% (x)	$V_{m,exp}$/ ($cm^3 \cdot mol^{-1}$)	$V_{m,cal}$/ ($cm^3 \cdot mol^{-1}$)	RD% (V)
2.64	0.683	0.112	0.115	1.47	130.8	130.7	−0.945
5.12	0.604	0.216	0.211	−2.65	122.1	122.0	−1.35
8.06	0.521	0.323	0.314	−3.05	111.7	111.5	−0.333
12.00	0.421	0.453	0.439	−3.24	99.4	99.2	−1.06
2.64	0.409	0.102	0.104	0.530	120.5	120.4	−1.04
5.12	0.368	0.193	0.191	−1.09	112.9	112.8	−0.529
8.06	0.320	0.298	0.287	−3.94	105.4	105.3	−0.886
12.00	0.266	0.415	0.403	−3.21	96.8	96.6	−0.823
2.64	0.158	0.091	0.0919	0.520	109.4	109.3	0.557
5.12	0.143	0.173	0.171	−1.07	105.3	105.2	−0.797
8.06	0.127	0.268	0.258	−4.02	99.2	99.2	−0.882
12.00	0.108	0.374	0.363	−3.33	91.8	91.7	−0.108
AAD%				2.40			−0.558

Materials. All chemicals used in this study were purchased from commercial suppliers. Methane with >99.9% purity from Beijing Analysis Instrument was used for all experiments. Other reagents were all purchased from Tianjin Chemical Agents Corp. with a purity of 99.5%.

Results

Methane + Heptane + Cyclohexane System. The solubility data for methane in heptane + cyclohexane binary solvents are presented in Table 4. The fugacity coefficient of methane in gas phase was calculated by the Peng−Robinson (PR) EOS. The relation of methane fugacity and methane solubility in heptane + cyclohexane were shown in Figure 3.

The methane fugacity and the solubility can be fitted to the equation $f_i = Hx_i$ well, because the binary solvents is a nearly ideal system, and the activity coefficient of the component almost is 1.

EOS Estimation. The mixtures of methane + heptane + cyclohexane were considered as ideal mixtures. The experimental data for the ternary systems can be predicted by binary equilibrium data of methane + heptane and methane + cyclohexane using the PR EOS.[5] The PR EOS

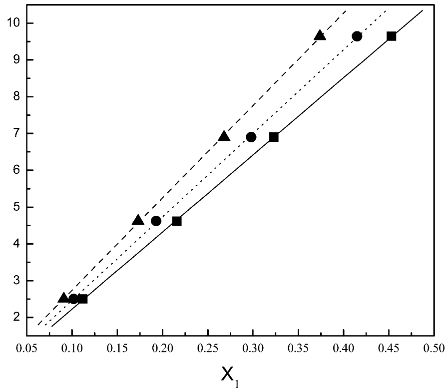

Figure 3. The curves of methane fugacity with methane (1) solubility (x_1) in cyclehexane (3) + heptane (2). ■, $w_3 = 0.2000$; ●, $w_3 = 0.5000$; ▲, $w_3 = 0.8000$. Note: w_3 is the mass percent of cyclohexane in the solvent.

specific relations used are

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

where

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

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

and

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

$$m = f(\omega) = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (5)$$

To apply the PR equation to mixtures, the values of a and b can be determined using the mixing rules[3]

$$a = \sum_i^N \sum_j^N x_i x_j (1 - k_{ij})(a_i a_j)^{1/2} \qquad (6)$$

$$b = \sum_i^N x_i b_i \qquad (7)$$

In eq 6, k_{ij} is an empirical interaction parameter characterizing the binary interactions between components "i" and "j". Values of these parameters were determined by fitting experimental binary mixture data to minimize the objective function, F, which is expressed as

$$F = \sum_i^N (\hat{f}_i^{\,g} - \hat{f}_i^{\,l})^2 \qquad (8)$$

The calculation procedure is the following. First, the solubility data of methane in heptane and in cyclohexane were collected from the literature.[6] The fugacity coefficients of methane in both the liquid and gas phases were calculated by the PR EOS. The binary interaction parameters k_{ij} in the PR EOS of methane + heptane and methane + cyclohexane were correlated by the simplex method.[7] The results were listed in Table 3. Then the binary interaction parameters k_{ij} of methane with each pure solvent were used, and the binary interaction parameter k_{ij} of heptane + cyclohexane was considered as zero, and the experimental data for the ternary system were predicted by the PR equation. The estimation average absolute deviation (AAD) from the experimental solubility data is 2.4%, and the results are presented in Table 4.

Table 5. Solubility Data for Methane (1) in Heptane (2) + Ethanol (3)[a]

T/K	P/MPa	x_2	x_1	RD1% (x)	RD2% (x)	V_m/($cm^3 \cdot mol^{-1}$)	RD1% (V)	RD2% (V)
291.15	2.67	0.718	0.0993	−8.37	1.38	121.8	−2.66	−1.95
	5.11	0.638	0.196	1.61	2.34	117.4	−5.13	−5.03
	8.06	0.553	0.305	4.52	0.423	107.2	−2.85	−3.21
	12.00	0.445	0.441	6.53	−1.62	93.3	1.06	0.348
303.15	2.65	0.722	0.0943	−7.73	−0.824	118.0	2.45	3.13
	5.09	0.646	0.190	−1.80	2.72	112.0	1.79	1.88
	8.07	0.560	0.297	5.17	1.19	108.5	−2.00	−2.36
	12.00	0.453	0.431	6.84	−1.22	94.8	2.21	1.52
318.15	2.65	0.730	0.0842	−14.5	−6.92	125. 9	−1.36	−0.751
	5.12	0.654	0.180	0.413	1.55	117.1	0.152	0.216
	8.06	0.565	0.290	6.13	2.18	107.5	1.78	1.39
	12.01	0.469	0.412	5.60	−2.23	97.0	3.98	3.32
291.15	2.65	0.594	0.0950	−6.40	3.15	132.2	−3.71	−2.41
	5.11	0.533	0.188	1.57	4.04	111.7	−4.93	−4.55
	8.06	0.471	0.283	2.34	−0.578	95.9	−3.54	−3.67
	11.98	0.381	0.420	6.25	−1.92	76.8	2.55	1.95
303.15	2.64	0.601	0.0850	11.9	−1.44	112.7	−3.08	−1.79
	5.10	0.540	0.180	0.980	3.85	107.6	−3.33	−2.97
	8.07	0.478	0.273	2.27	−0.272	98.5	0.241	0.114
	12.00	0.387	0.410	6.52	−1.39	85.9	5.98	5.39
318.15	2.66	0.606	0.0772	−17.9	−6.70	113.8	−1.56	−0.304
	5.11	0.549	0.165	−2.66	0.962	105.1	1.93	2.31
	8.04	0.485	0.262	1.95	−0.206	98.8	2.95	2.82
	12.00	0.394	0.400	6.24	−1.43	88.4	6.51	5.95
303.15	2.64	0.0990	0.0393	−10.7	−2.19	68.3	−4.62	−0.481
	5.12	0.0946	0.0822	0.660	3.01	67.4	−3.69	−0.391
	8.06	0.0901	0.126	2.35	−0.200	66.8	−3.27	−0.731
	12.00	0.0835	0.190	6.88	−1.28	64.5	−0.440	1.24
AAD%				5.60	2.04		2.85	2.26

[a] Key: RD is the relative deviation of calculation from the experimental data, $x\text{RD} = x(\text{cal}) - x(\text{exp})/x(\text{exp})$, $V\text{RD} = V(\text{cal}) - V(\text{exp})/V(\text{exp})$. RD1($x$) is the relative deviation for x when only a single interaction parameter, k_{ij}, was used. RD2(x) is the relative deviation for x when two interaction parameters, k_{ij} and l_{ij},were used. RD1(V) is the relative deviation for molar volume calculated by Aalto−Keskinen model. RD2(V) is the relative deviation for molar volume calculated by the YWAK model. AAD is the average absolute deviation of calculation form the experimental data, AAD $= |\Sigma_i^N RD|/N$.

The molar volumes of liquid-phase mixtures at high pressures were estimated by the Aalto−Keskinen model.[8,9] In the model, the correlation of Hankinson and Thomson[10] is used to predict the densities of saturated liquids, and the modified Chang−Zhao equation[11,12] is applied to predicting compressed liquid molar volume. The calculation AAD from the experimental molar volume is 0.59%, and the results are also presented in Table 4.

Methane + Heptane + Ethanol System. The solubility data for methane in heptane + ethanol binary solvents are presented in Table 5.

EOS Correlation. The experimental data for methane + heptane + ethanol have been correlated using the PR cubic equation of state. To apply the PR equation to mixtures, the values of b can also be determined using the mixing rules as eq 9 except eq 7. In eq 9, l_{ij} also is the binary interaction between components "i" and "j"

$$b = 0.5\sum\sum x_i x_j (1 - l_{ij})(b_i + b_j) \qquad (9)$$

The PR EOS representation of the solubility for the system is shown in Table 5. In general, the PR equation describes the data with an AAD of 5.6% when a single interaction parameter, k_{ij}, is used over the complete temperature range. The quality of the EOS representation is

Table 6. Binary Interaction Parameters k_{ij} and l_{ij} for Methane + Heptane + Ethanol System

	methane + heptane	methane + ethanol	heptane + ethanol
k_{ij}	0.04003	0.09299	0.08554
l_{ij}	−0.1619	−0.1653	0.1370
standard error		1.52%	

improved when an additional interaction parameter, l_{ij}, is employed, resulting in an AAD of 2.0%. The correlation results were shown in Table 5, and the parameters k_{ij} and l_{ij} acquired in the method are given in Table 6.

The molar volumes of liquid-phase mixtures for the system at high pressures were also estimated by the Aalto−Keskinen model. Because of the polarity of ethanol, the calculation of AAD is 2.9%, which is much larger than the result for the methane + heptane + cyclohexane system. To improve the calculation accuracy, the Aalto−Keskinen model was modified to predict the liquid molar volumes for methane + heptane + ethanol. In the modified model, the Hankinson and Thomson correlation, which is used to predict the densities of saturated liquids, was replaced by the Yen−Woods model.[13] The modified model is called the YWAK model. All the calculation results were presented in Table 5.

Conclusion

Data have been obtained on the solubility of methane in heptane + cyclohexane and heptane + ethanol at temperatures of 291.15 K, 303.15 K, and 318.15 K at four different pressures. The data for the methane + heptane + cyclohexane system are well described by the PR EOS when the interaction parameters k_{ij} were used. And the experimental data for the methane + heptane + ethanol system can be well calculated by the PR equation when an additional interaction parameter, l_{ij}, is employed. The acquired solubility data will be of value in the development and evaluation of solution theories of mixing and in the use for natural gas storage.

Appendix

Aalto−Keskinen Model.

$$\frac{V_s}{V^*} = V_R^{(0)}[1 - \omega_{SRK} V_R^{(\delta)}]$$

$$V_R^{(0)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3}$$

$$V_R^{(\delta)} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001}$$

$$\frac{V}{V_s} = \frac{A + C^{(D-T_r)B}(P_r - P_{s,r})^E}{A + C(P_r - P_{s,r})^E}$$

$$A = a_0 + a_1 T_r + a_2 T_r^3 + a_3 T_r^6 + a_4/T_r$$

$$B = b_0 + \frac{b_1}{b_2 + \omega_{SRK}}$$

$$C = c_1(1 - T_r)^{c_2} + [1 - (1 - T_r)^{c}{}_2]\exp[c_3 + c_4(P_r - P_{s,r})]$$

where V_s is the molar volumes of saturated liquids and $V^*\omega_{SRK}$ and $T_{c,HBT}$ are the characteristic parameters for every compound. $P_{s,r}$ is reduced vapor pressure.

The mixing rules for V^*, ω_{SRK}, $T_{c,HBT}$, and P_c are

$$T_{c,m} = (\sum\sum x_i x_j V_{ij}^* T_{cij})/V_m^*$$

$$V_{ij}^* T_{cij} = (V_i^* V_j^* T_{ci} T_{cj})^{1/2}$$

$$V_m^* = 1/4[\sum x_i V_i^* + 3(\sum x_i V_i^{*1/3})(\sum x_i V_i^{*2/3})]$$

$$\omega_{SRK,m} = \sum\sum x_i x_j (\omega_{SRK,i}\omega_{SRK,j})^{1/2}$$

$$P_{c,m} = (0.291 - 0.080\omega_{SRK,m})RT_{c,m}/V_m^*$$

The Yen−Wood Model. The Yen−Wood model, which was used to predict the molar volumes of saturated liquids in the YWAK model, is expressed as follows

$$\frac{V_c}{V_s} = 1 + A(1 - T_r)^{1/3} + B(1 - T_r)^{2/3} + (0.93 - B)(1 - T_r)^{4/3}$$

$$A = 17.4425 - 214.578Z_c + 989.625Z_c^2 - 1522.06Z_c^3$$

$$B = -3.28257 + 13.6377Z_c + 107.4844Z_c^2 - 384.211Z_c^3 \quad (Z_c \le 0.26)$$

$$B = 60.2091 - 402.063Z_c + 501.0Z_c^2 + 641.0Z_c^3 \quad (Z_c > 0.26)$$

$$Z_{c,m} = \sum\sum x_i x_j (Z_{c,i} + Z_{c,j})/2$$

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