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Vapor–Liquid Equilibria for the Methane–Acetone and Ethylene–Acetone Systems at 25 and 50 °C

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Vapor–liquid equilibria for the methane–acetone and ethylene–acetone systems at 25 and 50 °C and pressures up to 10 MPa have been measured by a vapor–liquid recirculation method. To check the reliability of the experimental procedure, vapor–liquid equilibria for the methane–*n*-hexane system at 37.8 °C and pressures up to 2 MPa have also been measured because this system has been studied by several investigators. The thermodynamic consistency test has been applied to the data of this system. The Soave–Redlich–Kwong and Peng–Robinson equations of state have been used to correlate vapor–liquid equilibria for the methane–acetone and ethylene–acetone systems with the use of a temperature-dependent binary interaction parameter.

Introduction

Vapor–liquid equilibrium data for systems containing a light gas and a polar solvent are important for the design of a number of separation processes in the chemical industry. These data provide a background for the development of a prediction method of fluid phase equilibria for such polar asymmetric systems. Since a polar solvent is usually nonvolatile, the content of the solvent in a vapor phase is generally small. Therefore, experimental studies have not been made so extensively for these systems, because of the difficulty of sampling and of composition analysis. In this study, the vapor–liquid equilibria for the methane–*n*-hexane, methane–acetone, and ethylene–acetone systems have been measured by a vapor–liquid recirculation method. The methane–*n*-hexane system was selected to clarify the reliability of the experimental method for the following reasons: this system has already been studied by several investigators (*1–2*) and *n*-hexane and acetone have about the same volatility in the temperature range of this study. Experimental data for the methane–acetone and ethylene–acetone systems are correlated by the Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state with the use of a temperature-dependent binary interaction parameter.

Experimental Section

The vapor–liquid equilibrium equipment used in this study is schematically shown in Figure 1. This equipment consists of an equilibrium system and an analysis system. Experimental procedures are essentially the same as those used by King et al. (*3*) and Kubota et al. (*4*). The equilibrium and analysis systems were enclosed in a thermostated water bath and air bath, respectively. The temperature of the analysis system was kept about 100 °C to avoid the condensation of the heavy component. The temperatures of these systems were measured by mercury thermometers and controlled within ±0.05 °C by mercury–toluene temperature controllers. The pressure of the equilibrium cell was measured with an uncertainty of 0.01 MPa by means of a Bourdon gage calibrated against a deadweight gage. The composition analysis was made by a gas chromatograph and a digital integrater. The calibration curves were obtained by means of mixtures of known compositions prepared in the analysis system. The accuracy of the calibration curves was estimated to be ±0.1%. The analyses of samples are estimated to be accurate to within ±0.5 mol %, while the overall uncertainty in the reported phase compositions is estimated to be ±1.5 mol %. The methane and *n*-hexane were supplied by Takachiho Kagaku Co. Ltd., the ethylene by Nihon Sanso Ltd., and the acetone by Dojin Yakugaku Ltd. In a trace analysis, no impurities were measured and the samples were used without further purification.

Table I. Vapor–Liquid Compositions for the Methane (1)–Acetone (2) System

P, MPa	x_1	y_1	Δx_1[a]	Δy_1[a]
		T = 25.0 °C		
1.71	0.0367	0.9753	−0.0001	−0.0015
2.28	0.0434	0.9789	−0.0052	−0.0019
3.55	0.0670	0.9866	−0.0075	0.0018
4.51	0.0911	0.9871	−0.0023	0.0011
5.49	0.1116	0.9880	−0.0005	0.0015
7.08	0.1443	0.9873	0.0033	0.0010
8.19	0.1598	0.9872	−0.0003	0.0014
9.16	0.1866	0.9870	0.0103	0.0019
10.19	0.1997	0.9868	0.0068	0.0026
11.68	0.2287	0.9853	0.0129	0.0029
		T = 50.0 °C		
1.06	0.0153	0.9124	−0.0024	−0.0004
1.50	0.0223	0.9363	−0.0031	0.0017
2.07	0.0341	0.9523	−0.0012	0.0033
3.07	0.0509	0.9627	−0.0015	0.0017
4.28	0.0725	0.9698	0.0001	0.0025
5.00	0.0822	0.9707	−0.0018	0.0013
5.98	0.0994	0.9713	−0.0001	0.0003
7.05	0.1200	0.9718	0.0044	0.0001
8.25	0.1360	0.9729	0.0023	0.0009
9.59	0.1647	0.9729	0.0119	0.0009
10.73	0.1782	0.9715	0.0096	0.0007
11.75	0.1950	0.9711	0.0127	0.0012

[a] Deviations are evaluated by the equations $\Delta x_1 = x_{1,\mathrm{exptl}} - x_{1,\mathrm{calcd}}$ and $\Delta y_1 = y_{1,\mathrm{exptl}} - y_{1,\mathrm{calcd}}$, where $x_{1,\mathrm{calcd}}$ and $y_{1,\mathrm{calcd}}$ are obtained from the Peng–Robinson equation with interaction parameters listed in Table V.

Experimental Results

Experimental vapor–liquid equilibrium data for the methane–acetone and ethylene–acetone systems at 25 and 50 °C are summarized in Tables I and II, respectively, and are graphically shown in Figures 2–5. Experimental data for the methane–*n*-hexane system at 37.8 °C are summarized in Table III.

Consistency Test

To evaluate the validity of the experimental procedure, the consistency test of Gunn et al. (*2*) was applied to the data of the methane–*n*-hexane system. In this test, a vapor-phase mole fraction was calculated from T–P–x data by using the virial equation of state truncated after the second virial coefficient. A saturated-liquid molar volume and a vapor pressure of *n*-hexane were obtained from the correlation of Chueh and

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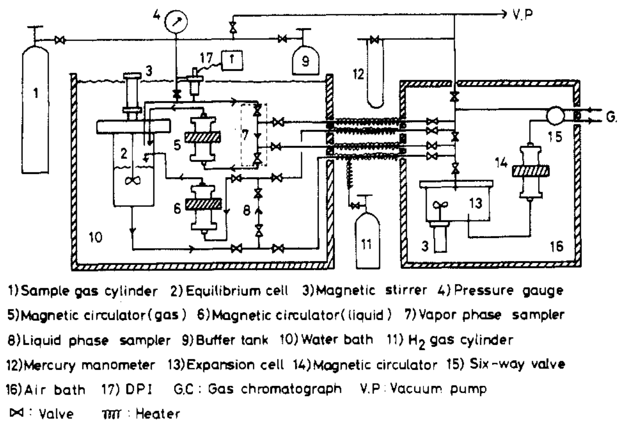

Figure 1. Schematic diagram of experimental apparatus.

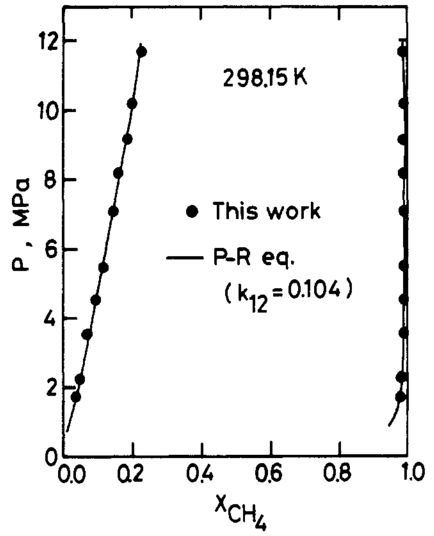

Figure 2. Experimental results and predictions of the Peng-Robinson equation of state for the methane-acetone system at 25 °C.

Table II. Vapor-Liquid Compositions for the Ethylene (1)-Acetone (2) System

P, MPa	x_1	y_1	Δx_1[a]	Δy_1[a]
		T = 25.0 °C		
1.57	0.1721	0.9686	−0.0073	−0.0065
1.87	0.2111	0.9723	−0.0053	−0.0057
2.30	0.2666	0.9765	−0.0029	−0.0040
2.94	0.3713	0.9793	0.0181	−0.0034
3.50	0.4559	0.9813	0.0218	−0.0022
4.16	0.5897	0.9820	0.0494	−0.0016
4.73	0.6805	0.9820	0.0291	−0.0009
5.42	0.8532	0.9801	0.0257	−0.0007
		T = 50.0 °C		
1.35	0.0958	0.9202	−0.0073	−0.0072
1.53	0.1127	0.9257	−0.0054	−0.0085
2.37	0.1904	0.9456	0.0023	−0.0059
2.83	0.2255	0.9487	−0.0012	−0.0073
3.35	0.2715	0.9529	−0.0008	−0.0064
4.45	0.3670	0.9553	−0.0041	−0.0066
5.30	0.4863	0.9584	0.0319	−0.0028
6.73	0.6489	0.9559	0.0277	0.0030
7.26	0.7440	0.9360	0.0397	−0.0082
7.59	0.8132	0.9182	0.0451	−0.0154

[a] Deviations are the same as Table I.

Prausnitz (*5*) and the Antoine equation (*6*), respectively. Second virial coefficients for methane and *n*-hexane were quoted from Dymond and Smith (*7*), and a cross second virial coefficient from Danzler et al. (*8*). The results are shown in Table IV. For comparison, the results obtained from the data of Shim and Kohn (*1*) and Gunn et al. (*2*) are shown in the same

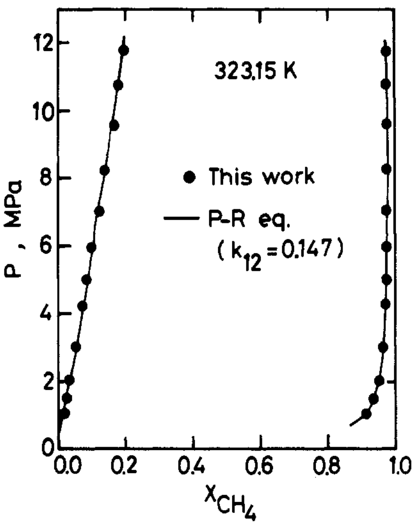

Figure 3. Experimental results and predictions of the Peng-Robinson equation of state for the methane-acetone system at 50 °C.

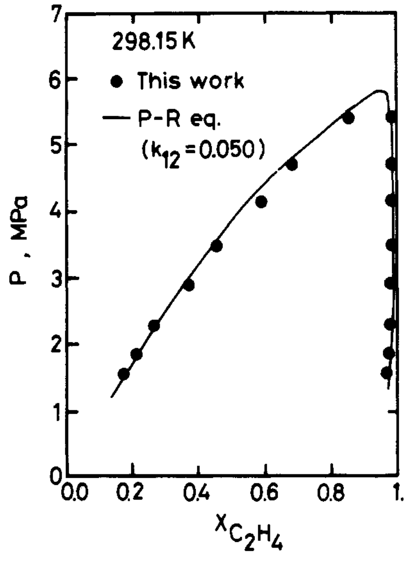

Figure 4. Experimental results and predictions of the Peng-Robinson equation of state for the ethylene-acetone system at 25 °C.

Table III. Experimental Vapor-Liquid Compositions for the Methane (1)-*n*-Hexane (2) System at 37.8 °C

P, MPa	x_1	y_1	P, MPa	x_1	y_1
0.57		0.9264	1.53	0.0734	0.9680
0.59		0.9256	1.58	0.0757	
0.83		0.9468	1.77	0.0860	0.9696
1.06		0.9468	1.79	0.0892	
1.20	0.0567	0.9607	1.81	0.0880	0.9724
1.30	0.0616	0.9627	1.98	0.0965	

Table IV. Vapor-Phase Compositions from Second Virial Cross Coefficient[a] and Liquid-Phase Compositions for the Methane (1)-*n*-Hexane (2) System at 37.8 °C

workers	P, MPa	$y_{1,\text{exptl}}$	$y_{1,\text{calcd}}$	AAD[b]
Shim and Kohn	1.01	0.9275	0.9587	3.36
Gunn et al.	1.034	0.9606	0.9595	0.11
this work	1.20	0.9607	0.9639	0.33
this work	1.30	0.9627	0.9661	0.35
this work	1.53	0.9680	0.9700	0.21
this work	1.77	0.9696	0.9729	0.34
this work	1.81	0.9724	0.9733	0.09

[a] $B_1 = -39\ \text{cm}^3\cdot\text{mol}^{-1}$, $B_2 = -1680\ \text{cm}^3\cdot\text{mol}^{-1}$, $B_{12} = -243\ \text{cm}^3\cdot\text{mol}^{-1}$. [b] $\text{AAD} = 100|(y_{1,\text{exptl}} - y_{1,\text{calcd}})/y_{1,\text{exptl}}|$.

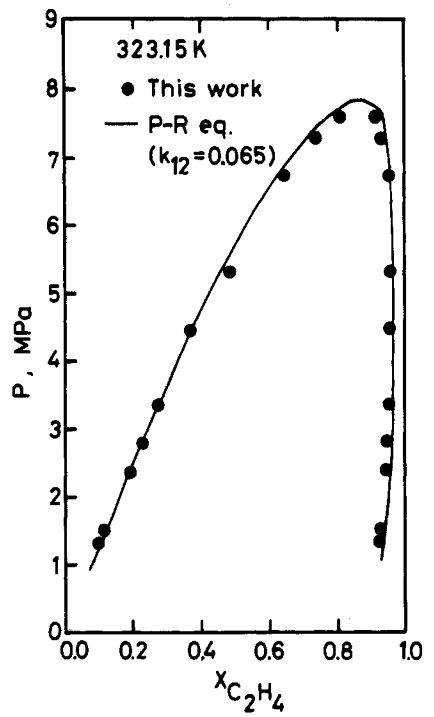

Figure 5. Experimental results and predictions of the Peng–Robinson equation of state for the ethylene–acetone system at 50 °C.

table. The data of Shim and Kohn used in this test were quoted from Gunn et al. (*2*). It was found that the experimental data and the calculated results agree well with each other.

Equation of State Calculation

Vapor-liquid equilibrium data for the methane–acetone and ethylene–acetone systems were compared with the calculated results from Soave–Redlich–Kwong (SRK) and Peng–Robinson (PR) equations of state. Parameters a and b of each equation were obtained from the generalized expressions given in the original references (*9*, *10*). The parameters for a mixture were expressed as follows:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad (1)$$

$$b = \sum_i x_i b_i \qquad (2)$$

with

$$a_{ij} = (1 - k_{ij})(a_i a_{ij})^{1/2} \qquad (3)$$

where k_{ij} is a binary interaction parameter. The value of k_{ij} was determined by minimizing the difference of compositions between the experimental results and the calculated results. Figures 2–5 show the comparisons of the experimental data and the results from the PR equation. It was found the k_{ij} should be temperature dependent if better results are obtained. The deviations of compositions between the experimental results and the calculated results from the PR equation are shown in Tables I and II. The values of k_{ij} and predicted results from the SRK and PR equations for the methane–acetone and ethylene–acetone systems are listed in Tables V and VI, respectively.

Table V. Comparison of Calculated and Experimental Data for the Methane (1)–Acetone (2) System

eq	T, °C	n[a]	k_{12}	Δx_{av}[b]	Δy_{av}[c]
PR	25	10	0.104	4.33	0.18
PR	50	12	0.147	5.22	0.13
SRK	25	10	0.097	4.06	0.11
SRK	50	12	0.145	4.87	0.10

[a] Number of data points. [b] $\Delta x_{av} = 100\sum_{i=1}^{n}|(x_{1,\mathrm{exptl}} - x_{1,\mathrm{calcd}})/x_{1,\mathrm{exptl}}|/n$. [c] $\Delta y_{av} = 100\sum_{i=1}^{n}|(y_{1,\mathrm{exptl}} - y_{1,\mathrm{calcd}})/y_{1,\mathrm{exptl}}|/n$.

Table VI. Comparison of Calculated and Experimental Data for the Ethylene (1)–Acetone (2) System[a]

eq	T, °C	n	k_{12}	Δx_{av}	Δy_{av}
PR	25	8	0.050	4.15	0.320
PR	50	10	0.065	3.75	0.766
SRK	25	8	0.045	4.18	0.414
SRK	50	10	0.062	3.35	0.902

[a] Symbols are the same as in Table V.

Glossary

a, b	equation of state constants
B	second virial coefficient
k_{ij}	binary interaction parameter
P	pressure
R	gas constant
T	temperature
x	liquid-phase mole fraction
y	vapor-phase mole fraction

Registry No. Acetone, 67-64-1; methane, 74-82-8; ethylene, 74-85-1.

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