HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA OF FOUR BINARY SYSTEMS CONTAINING CARBON DIOXIDE

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Isothermal vapor-liquid equilibrium data of four binary systems —carbon dioxide+pentane at 311.15 and 329.15 K, +diethyl ether at 313.15 K, +methyl *tert*-butyl ether at 310.15, 329.15 and 338.15 K, and +1-pentene at 303.15, 313.15 and 328.60 K— were determined by using an apparatus with vapor and liquid alternative circulation over a pressure range from 0.5 to 9.1 MPa.

Experimental data were correlated by applying the Soave-Redlich-Kwong equation of state with the conventional quadratic mixing rule and the DDLC-EOS unified model based on the conformal reference state. Results show that both models correlate the present data satisfactorily.

Introduction

Fluid-phase equilibria are basic data eseential to chemical processes. Reliable experimental data are the prerequisite of optimal design. They may also be used for testing the adequacy of thermodynamic models. Thus the determination and correlation of fluid-phase equilibria are not only of great practical value to process design but also of some theoretical significance.

However, reliable equilibrium data under high pressure are not so abundant as those at moderate pressure due to some inherent limitations of specific apparatus or difficulties in the measuring techniques involved.

Recently, phase equilibrium data for carbon dioxide and hydrocarbon mixtures are gaining great industrial importance in enhanced oil recovery and coal gasification. In the field of supercritical fluid extraction, the potential applicability of carbon dioxide as an extractant has long been recognized. It is now being used for the removal of organic solutes from natural compounds or industrial aqueous solutions obtained from biochemical technology.

In this work, isothermal vapor-liquid equilibrium data were determined for four binary systems containing carbon dioxide: carbon dioxide+pentane at 311.15 and 329.15 K, carbon dioxide+diethyl ether at 313.15 K, carbon dioxide+methyl *tert*-butyl ether at 310.15, 329.15 and 338.15 K, and carbon dioxide +1-pentene at 303.15, 313.15 and 328.60 K, by using

an equilibrium apparatus with vapor and liquid alternative circulation over a pressure range from 0.5 to 9.1 MPa.

In addition, experimental data measured in this work were correlated by applying the Soave-Redlich-Kwong equation of state[9] with the conventional quadratic mixing rule and the DDLC-EOS (density-dependent local composition combined with the cubic equation of state) unified model based on the conformal mixture as the reference state.[12] Results show that both models correlate the present data rather satisfactorily except in the vicinity of critical points.

1. Experimental

1.1 Apparatus and operation

Apparatus similar to that used by Kubota *et al.*[2] except for some minor modifications was constructed for the purpose of this investigation. It is shown schematically in **Fig. 1**. The detailed structure of the equilibrium cell was described elsewhere.[2]

By hand-operating the high-pressure circulating pump (3), vapor was taken from the top of the equilibrium cell (1) and recirculated through its bottom. As the vapor was bubbling through the liquid in the cell, the attainment of equilibrium could be accelerated by close contact between the vapor and liquid phases. By turning the 6-port ball valve (2), the circulation mode was switched from vapor to liquid phase in a reversed direction through the same circulating path. During their circulations, both vapor and liquid samples were trapped in the 4-port ball valve (4), and then introduced into the low-pressure circulation system, where they were analyzed on line
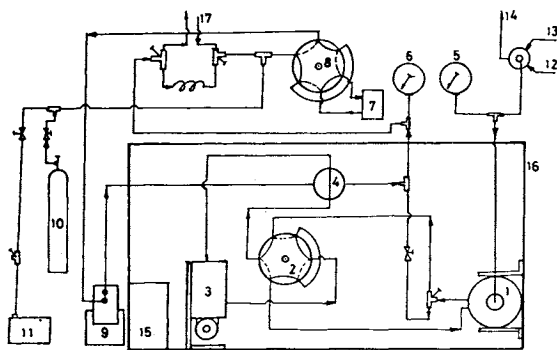
Fig. 1. Schematic diagram of experimental apparatus: 1) equilibrium cell; 2) 6-port high-pressure ball valve; 3) high-pressure circulating pump; 4) 4-port high-pressure ball valve; 5) Bourdon tube gauge; 6) low-pressure gauge; 7) gas chromatograph; 8) 6-port low-pressure valve; 9) low-pressure circulating pump; 10) carrier gas cylinder; 11) vacuum pump; 12) inlet of light component; 13) inlet of heavy component; 14) vent; 15) temperature controller; 16) constant-temperature bath; 17) connection to system for determining calibration curve

by a gas chromatograph (7).

When the equilibrium temperature is below the standard boiling point of the heavy component, it is necessary to check whether the liquid sample trapped in the 4-port ball valve has completely vaporized after expanding to the low-pressure circulation system. Any minor amount of liquid remaining in the 4-port ball valve would cause an enormous error to the next vapor sampling. In this case, it is necessary to turn the 4-port ball valve toward the low-pressure system in order to remove the remaining liquid drop, if there is any, by the vacuum pump before proceeding to the next vapor circulation and sampling.

The pressure of the system was measured with an accuracy of ± 0.07 MPa by means of a Bourdon tube gauge (5) calibrated against a dead-weight gauge. The water bath (16) was maintained within ± 0.02 K. The equilibrium temperature was measured by a platinum resistance thermometer calibrated by the City Bureau of Standards.

1.2 Sample analysis

Samples of both vapor and liquid phases were expanded or evaporated to the low-pressure circulation system, then analyzed on line by a Shanghai Type No. 102 gas chromatograph with a CR-IB type integrator. A column packed with DPX 101 was used at 423 K with hydrogen as a carrier gas.

The relation between the peak-area ratio and the mole ratio, i.e. the calibration curve for each system investigated, was obtained by utilizing a low-pressure circulation system.[11] A glass flask was connected to this system for injection and mixing of the light and heavy component and a mercury manometer was used for measuring pressure changes when components were added. By means of the circulating

pump, the standard sample was thoroughly mixed within a few minutes. The mole ratio of the standard sample was determined by the pressure differences recorded and calculated according to the ideal gas law. The slope of the calibration curve was determined by the least squares method within an accuracy of $\pm 0.5\%$.

1.3 Purity of materials

Carbon dioxide used in this experiment was purified with molecular sieves 5A and was of a minimum purity of 99.8 mol%. Methyl *tert*-butyl ether was supplied by Jingzhou Petroleum Corp. and was purified by redistillation with a high-efficiency packed column. The fraction within the boiling range of 328.4 to 328.8 K was taken. Its minimum purity was 99.6 mol%. Diethyl ether, pentane and 1-pentene were obtained from a commercial source in an analytically pure grade and were used in this work without further purification.

2. Results and Discussion

2.1 Experimental data

Isothermal vapor-liquid equilibrium data of four systems are shown graphically in **Figs. 2, 3, 4** and **5** as plots of equilibrium pressure against composition. The numerical equilibrium compositions for carbon dioxide + methyl *tert*-butyl ether and carbon dioxide + 1-pentene system are presented in **Tables 1** and **2** respectively.

Data of the carbon dioxide + pentane system at 311.15 K measured in this work are very close to those reported by Besserer and Robinson[1] at 311.04 K. Data of the carbon dioxide + diethyl ether system are in good agreement with those measured by Ohgaki and Katayama.[7] Other data have not been published in the literature to date. Therefore, a graphical method was employed to check the consistency of the experimental data. The equilibrium ratio K for the vapor and liquid mole fractions was plotted against total pressure and always gave smooth curves. These curves, together with the smooth isotherms, show the consistency of the present experimental data.

2.2 Data reduction

Phase equilibrium data of carbon dioxide + hydrocarbon systems can be correlated fairly well by the application of cubic equations of state with the quadratic mixing rule, except for those systems with a great disparity in molecular size and shape such as the carbon dioxide and decane system, or in the vicinity of critical points. In the four binary systems investigated in this work, the molecular structure and interaction energy of carbon dioxide are quite different from those of other components.

Therefore, all the experimental data measured in this work were correlated by applying the Soave-
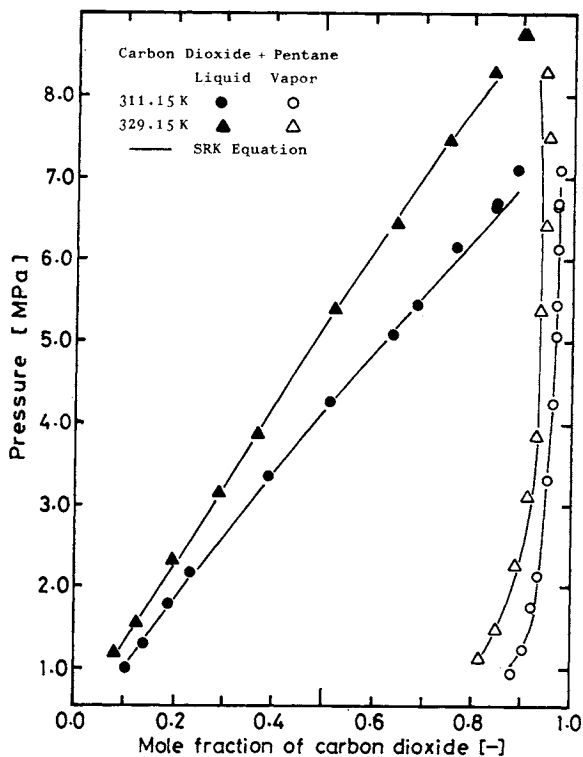
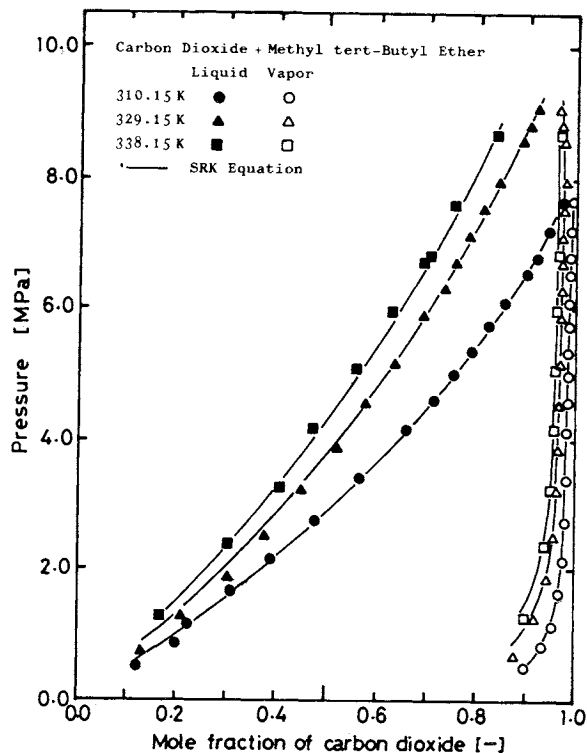**Fig. 2.** Experimental and calculated phase diagram for $CO_2 + C_5H_{12}$ system

Fig. 3. Experimental and calculated phase diagram for $CO_2 + C_2H_5OC_2H_5$ system

Fig. 4. Experimental and calculated phase diagram for $CO_2 + CH_3OC(CH_3)_3$
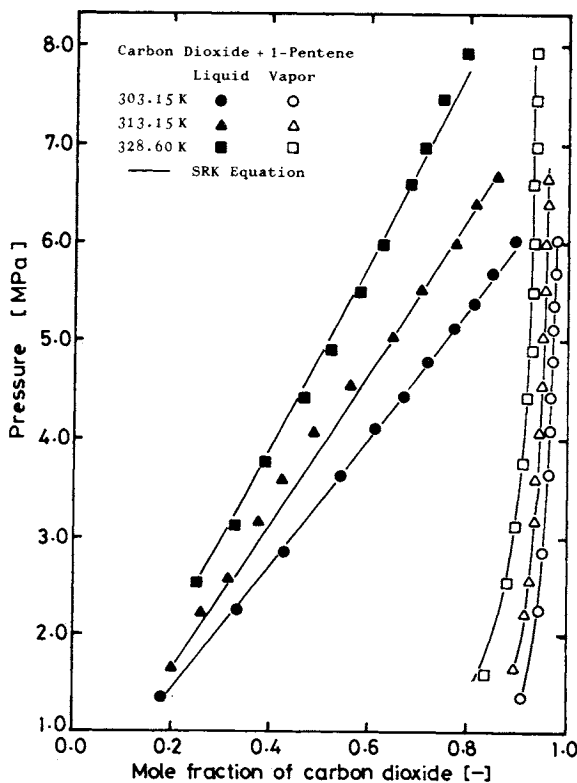
Fig. 5. Experimental and calculated phase diagram for $CO_2 + 1\text{-}C_5H_{10}$

Redlich-Kwong equation of state with the conventional mixing rule and a simple DDLC-SRK unified model based on the conformal reference state.[4,5,12)]

(1) The Conventional SRK Equation of State:[9)]

$$P = RT/(v-b) - \sum x_i \sum x_j a_{ij}^{\circ}(T)/v(v+b) \qquad (1)$$

$$a_{ij}^{\circ}(T) = [a_i(Tc_i)a_j(Tc_j)\alpha_i(Tr_i, \omega_i)$$

$$\cdot \alpha_j(Tr_j, \omega_j)]^{0.5}(1 - k_{ij}) \qquad (2)$$

Table 1. Vapor-liquid equilibria of carbon dioxide (1) + methyl *tert*-butyl ether (2)

P (MPa)	x_1	y_1	K_1	K_2
		310.15 K		
0.54	0.1233	0.9099	7.299	0.1140
0.89	0.2025	0.9363	4.624	0.0799
1.17	0.2254	0.9566	4.244	0.0560
1.69	0.3120	0.9680	3.103	0.0465
2.16	0.3698	0.9762	2.504	0.0390
2.77	0.4889	0.9802	2.051	0.0379
3.44	0.5668	0.9838	1.735	0.0379
4.20	0.6606	0.9859	1.492	0.0415
4.65	0.7152	0.9866	1.380	0.0471
5.03	0.7523	0.9865	1.311	0.0545
5.36	0.7894	0.9865	1.250	0.0641
5.79	0.8231	0.9874	1.200	0.0712
6.15	0.8542	0.9879	1.157	0.0830
6.57	0.9016	0.9888	1.097	0.1138
6.82	0.9202	0.9890	1.075	0.1378
7.23	0.9457	0.9914	1.048	0.1584
7.69	0.9734	0.9933	1.020	0.2519
		329.15 K		
0.74	0.1310	0.8800	6.718	0.1381
1.28	0.2124	0.9195	4.329	0.1022
1.88	0.3063	0.9465	3.090	0.0771
2.51	0.3783	0.9580	2.532	0.0676
3.24	0.4521	0.9657	2.136	0.0626
3.89	0.5204	0.9693	1.861	0.0661
4.56	0.5812	0.9700	1.669	0.0716
5.19	0.6353	0.9729	1.531	0.0746
5.90	0.6940	0.9750	1.405	0.0817
6.31	0.7370	0.9764	1.325	0.0897
6.72	0.7568	0.9743	1.287	0.1057
7.14	0.7841	0.9754	1.244	0.1139
7.53	0.8134	0.9751	1.199	0.1334
7.97	0.8465	0.9756	1.153	0.1590
8.56	0.8956	0.9752	1.099	0.2375
8.80	0.9087	0.9732	1.071	0.2935
9.07	0.9231	0.9675	1.048	0.4226
		338.15 K		
1.29	0.1698	0.9040	5.324	0.1156
2.41	0.3033	0.9415	3.104	0.0840
3.30	0.4087	0.9531	2.332	0.0793
4.21	0.4734	0.9623	2.033	0.0716
5.12	0.5579	0.9617	1.724	0.0866
5.96	0.6299	0.9663	1.534	0.0911
6.75	0.6920	0.9648	1.394	0.1143
6.86	0.7068	0.9687	1.371	0.1067
7.61	0.7538	0.9704	1.287	0.1202
8.68	0.8413	0.9720	1.155	0.1764

Table 2. Vapor-liquid equilibria of carbon dioxide (1) + 1-pentene (2)

P (MPa)	x_1	y_1	K_1	K_2
		303.15 K		
1.35	0.1790	0.9108	5.088	0.109
2.24	0.3323	0.9428	2.837	0.086
2.85	0.4271	0.9513	2.227	0.085
3.64	0.5432	0.9662	1.779	0.074
4.09	0.6107	0.9682	1.585	0.082
4.42	0.6700	0.9666	1.443	0.101
4.69	0.7155	0.9693	1.355	0.108
5.13	0.7714	0.9721	1.260	0.122
5.37	0.8101	0.9739	1.202	0.137
5.67	0.8487	0.9755	1.149	0.162
6.02	0.8922	0.9762	1.094	0.221
6.32	0.9300	0.9826	1.057	0.249
		313.15 K		
1.66	0.2045	0.8982	4.392	0.128
2.13	0.2621	0.9163	3.496	0.113
2.55	0.3137	0.9271	2.955	0.106
3.16	0.3782	0.9372	2.478	0.101
3.57	0.4277	0.9420	2.203	0.102
4.05	0.4906	0.9479	1.932	0.102
4.53	0.5643	0.9516	1.686	0.111
5.03	0.6489	0.9526	1.468	0.135
5.50	0.7046	0.9581	1.360	0.142
5.98	0.7804	0.9603	1.231	0.181
6.37	0.8176	0.9626	1.177	0.205
6.67	0.8618	0.9629	1.117	0.269
		328.60 K		
1.59	0.1462	0.8390	5.739	0.189
2.53	0.2524	0.8848	3.506	0.154
3.12	0.3316	0.8997	2.713	0.150
3.75	0.3793	0.9135	2.408	0.139
4.43	0.4699	0.9239	1.966	0.144
4.89	0.5259	0.9329	1.774	0.142
5.49	0.5829	0.9346	1.603	0.157
5.99	0.6322	0.9357	1.480	0.175
6.59	0.6825	0.9396	1.377	0.190
6.96	0.7175	0.9415	1.312	0.207
7.44	0.7526	0.9363	1.244	0.257
7.91	0.8014	0.9393	1.172	0.306
8.43	0.8464	0.9297	1.098	0.458

$$\alpha_i(Tr_i, \omega_i) = [(1 + m_i(1 - Tr_i^{0.5})]^2 \qquad (3)$$

$$m_i = 0.48 + 1.574\omega_i - 0.176\omega_i^2 \qquad (4)$$

The binary interaction parameter k_{ij} for each system was estimated by minimizing the following objective function with the Golden Section Method:[10]

$$OF = \sum_j^m [(P_{exp} - P_{cal})/P_{exp}]_j^2 + (y_{1,exp} - y_{1,cal})_j^2 \qquad (5)$$

(2) A Simple DDLC-SRK Unified Model Based on Conformal Reference State:[12]

$$P = RT/(v - b) - \sum_i x_i \sum_j x_j a_{ij}^\circ(T)/v(v + b)$$
$$+ \sum_i x_i (\sum_j x_j C_{ij} E_{ij} a_{ij}^\circ(T)/\sum_k x_k E_{ki})/v(v + b) \qquad (6)$$

where

$$a_{ij}^\circ(T) = [a_i(Tc_i)a_j(Tc_j)\alpha_i(Tr_i, \omega_i)\alpha_j(Tr_j, \omega_j)]^{0.5}$$

$$E_{ij} = \exp[(-C_{ij}a_{ij}^\circ(T)/RTb)\ln(1 + b/v)] \qquad (7)$$

The binary pair-parameters C_{ij} and C_{ji} for each system were estimated by applying the Simplex method of Nelder and Mead[6] with the same objective function as Eq. (5).

The fitting accuracies and binary interaction parameters estimated are summarized in **Table 3**. It can be seen that both models correlate the present data rather satisfactorily.

The physical properties of methyl *tert*-butyl ether essential for data regression were estimated by meth-

Table 3. Fitting Accuracies and Binary Interaction Parameters

System	Temperature K	Datum point	DDLC-SRK				SRK		
			C_{12}	C_{21}	ΔP	Δy	k_{12}	ΔP	Δy
Carbon dioxide (1)+	311.15	13	0.205	0.006	0.09	0.28	0.117	0.12	0.32
Pentane (2)	329.15	9	0.077	0.183	0.06	0.62	0.116	0.08	0.85
Carbon dioxide (1)+ Diethyl ether (2)	313.15	11	−0.017	0.013	0.12	0.87	0.000	0.12	0.86
Carbon dioxide (1)+	310.15	17	−0.110	0.095	0.07	0.46	−0.029	0.10	0.42
Methyl tert-	329.15	17	−0.156	0.070	0.13	0.43	−0.033	0.12	0.32
butyl ether (2)	338.15	10	−0.085	0.058	0.10	0.93	−0.034	0.13	0.96
Carbon dioxide (1)+	303.15	12	0.114	0.036	0.06	0.32	0.073	0.09	0.27
1-Pentene (2)	313.15	12	0.063	0.096	0.09	0.22	0.065	0.14	0.29
	328.60	13	−0.031	0.197	0.14	0.86	0.066	0.12	0.85

$$\Delta P = \sqrt{\sum_{j=1}^{m} (P_{\mathrm{exp}} - P_{\mathrm{cal}})_j^2 / m} \quad \mathrm{MPa}; \quad \Delta y = \sqrt{\sum_{j=1}^{m} (y_{1,\mathrm{exp}} - y_{1,\mathrm{cal}})_j^2 / m} \times 100$$

ods as suggested by Reid et al.[3,8]

Conclusions

1. Isothermal vapor-liquid equilibrium data of four binary systems containing alkane, alkene and ether with carbon dioxide as a common component were determined at one to three temperatures over a pressure range from 0.5 to 9.1 MPa by using an equilibrium apparatus with vapor and liquid alternative circulation.

2. Data of carbon dioxide+diethyl ether at 313.15 K and carbon dioxide+pentane at 311.15 K are in good agreement with those reported by earlier investigators.

Other data were tested by an empirical method and proved to be in thermodynamic consistency. The apparatus and operation method employed in this investigation have been confirmed to be capable of producing reliable vapor-liquid equilibrium data.

3. All data were correlated by applying the Soave-Redlich-Kwong equation of state with the quadratic mixing rule and the DDLC-EOS unified model based on the conformal reference state. Results show that both models correlate the present data with fairly good accuracies, except in the vicinity of critical points.

Nomenclature

a_{ij}°	= attractive constant of $i-j$ pair	$[\mu\mathrm{Pa\,m^6\,mol^{-2}}]$
b	= repulsive constant	$[\mathrm{cm^3\,mol^{-1}}]$
C_{ij}	= empirical parameter	[—]
E_{ij}	= model energy parameter for $i-j$ pair	[—]
K	= equilibrium ratio	[—]
m	= number of datum points	[—]
N	= number of components	[—]
P	= pressure	[MPa]
R	= gas constant	$[\mathrm{J\,mol^{-1}\,K^{-1}}]$
T	= absolute temperature	[K]
T_r	= reduced temperature	[—]
v	= molar volume	$[\mathrm{cm^3\,mol^{-1}}]$
x	= mole fraction of liquid phase	[—]
y	= mole fraction of vapor phase	[—]
α_i	= correction factor for a_i	[—]
ω_i	= acentric factor of component i	[—]

⟨Subscripts⟩

i, j, k	= component	
c	= critical	
exp	= experimental	
cal	= calculated	

⟨Superscript⟩

$\circ$	= conformal mixture

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