

# PHASE EQUILIBRIUM MEASUREMENTS FOR BINARY MIXTURES OF METHYL BENZOATE PLUS CO<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> AND C<sub>2</sub>H<sub>4</sub>

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The phase equilibrium data of three binary mixtures composed of methyl benzoate and one of three dense fluids—carbon dioxide, ethane or ethylene—were measured at temperatures from 313.15 to 348.15 K and pressures up to near the critical pressures of the mixtures. The isotherms for the methyl benzoate/ethane system show a double cross-over within the observed pressure range. Meanwhile, the saturated vapor composition of methyl benzoate correlates well with the density of the dense fluids for each isotherm. The Patel-Teja equation of state gives a good representation of the methyl benzoate/CO<sub>2</sub> system, but is not so successful for the ethane- and ethylene-containing systems in the low pressure range.

## Introduction

A series of experimental works is conducted in our laboratory to determine the equilibrium phase compositions of binary mixtures containing a C<sub>8</sub> solute and one of three supercritical fluids: carbon dioxide, ethane or ethylene. The experimental works not only can expand the phase equilibrium database, but also are helpful in model modification for supercritical fluid-containing systems. This paper reports observations for binary systems composed of a strongly polar solute (methyl benzoate) and one of the dense fluids—carbon dioxide, ethane or ethylene—in a temperature range from 313.15 to 348.15 K and at pressures up to near the critical pressures of the mixtures. Each methyl benzoate solubility isotherm was correlated with the solvent's density, and the equilibrium ratios ( $K_i$ ) for all three binary systems are also correlated by using the Patel-Teja equation of state.<sup>3)</sup>

## 1. Experimental

### 1.1 Apparatus

Detailed descriptions of the apparatus and operation were given elsewhere.<sup>2,4)</sup> The equilibrium cell is immersed in a Neslab thermostat (Model: EX-251HT) controlled within  $\pm 0.01^\circ\text{C}$ . The temperature of the equilibrium system is measured with a Micro-Therm thermometer (Model: 1006, Hart Scientific) via a RTD probe. The accuracy of the readings is better generally than  $\pm 0.02^\circ\text{C}$ .

A double-head, constant flow-rate fluid metering pump (Model: ConstaMetric 3200, LDC Analytical

Inc.) is used to compress the dense fluids if high pressures are required. Each head is equipped with a cooling-jacket wherein aqueous ethylene glycol (about  $-10^\circ\text{C}$ ) is circulated to improve the fluid compression. A pressure transducer (Model: PDCR 330, 0–400 bar, Druck products) is connected to the outlet of the equilibrium cell. A digital indicator (Model: DPI 261, Druck products) displays pressure readings calibrated to  $\pm 0.1\%$  by the manufacturer.

### 1.2 Sample analysis

The heavier component (methyl benzoate) in either upper-phase or lower-phase sample is collected in a flask after the pressure is reduced to the ambient condition. To minimize the condensate vaporized into the liberated gas, the sampling flask is cooled with an ice bath. The weight of collected condensate is then determined by electronic balance (Shimadzu AEU-210) with an accuracy of  $\pm 0.0001\text{ g}$ . The volume of the liberated gas from the upper-phase sample is measured by a wet test meter (Model: DM3C, Alexander Wright) with an accuracy better than  $\pm 0.5\%$ , and that from the lower-phase sample is collected in a graduated cylinder. The minor amount of condensate vaporized into the liberated gas is corrected by using its vapor pressure at the collecting condition, while the trace amount of light solvent dissolved in the condensate is calculated from Henry's law. The composition determination was generally reproduced better than  $\pm 2\%$  for the minor component. The uncertainty of the vapor composition of methyl benzoate ( $y_1$ ), however, is about 10–15% at low pressures, where the value of  $y_1$  falls as low as  $10^{-4}$ .

### 1.3 Chemicals

Carbon dioxide (99.8%), ethane (99.0%) and eth-

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ylene (99.5%) were purchased from Matheson Gas Products, and methyl benzoate was supplied by Baker Chemicals with a purity of 99+%. No further purification of those chemicals was made.

## 2. Results and Discussion

The equilibrium-phase compositions as well as the equilibrium vaporization ratios ( $K_i = y_i/x_i$ ) for methyl benzoate/carbon dioxide, methyl benzoate/ethane, and methyl benzoate/ethylene mixtures are tabulated in **Tables 1, 2, and 3**, respectively. **Figure 1** illustrates the variation of equilibrium ratios with pressure for the ethane-containing system at 318.15, 328.15 and 338.15 K. A remarkable change of  $K_1$  is seen on the 318.15 K isotherm around 65 bar. The phase behavior cannot be observed directly from the blind cell used in this work, but the phenomenon could result from the condition being very close to the upper end point of vapor-liquid-liquid coexistence as indicated in our previous report<sup>5)</sup> for the 1-octanol/CO<sub>2</sub> system. And from the lower portion of Fig. 1 it is seen that  $K_1$ -isotherms show a double cross-over for this binary system within the investigated pressure range. **Figures 2 and 3** present the equilibrium ratios for methyl benzoate/ethylene and methyl benzoate/carbon dioxide systems, respectively. Unlike the above binary system, the upper end points of three-phase coexistence for these two systems would be well below the lowest temperatures of the corresponding systems.

**Figure 4** illustrates the variations of the solubility of methyl benzoate ( $y_1$ ) with the reduced pressure ( $P_r^* = P/P_{c2}$ ) in the three respective dense solvents at 328.15 K. The solubilities are very sparing and vary little over pressures lower than the solvents' critical pressures, whereas they increase dramatically as  $P_r^* > 1$ . The ethane- and carbon dioxide-containing isotherms are at about the same reduced conditions, and these two isotherms almost superpose over the entire pressure range. Moreover, the reduced temperatures ( $T_r^* = T/T_{c2}$ ) of these two isotherms are very close to unity ( $T_r^* = 1.07$ ), leading to an increase in solubilities of about ten-fold as the reduced pressure increases from 1.0 to 1.4. The slightly higher reduced temperature of the ethylene-containing isotherm ( $T_r^* = 1.16$ ) causes the vapor composition of methyl benzoate to become much less sensitive to the pressure. To attain the same level of enhancement, the pressure should be elevated to  $P_r^*$  about 1.8. The comparison also indicates that, as a supercritical extraction solvent, ethane can reach a given extraction level under a relatively low operating pressure.

## 3. Data Correlations

The solubility of methyl benzoate ( $y_1$ ) can be correlated well with the density of the solvent ( $\rho$ ),

**Table 1.** Phase compositions and  $K$ -values of methyl benzoate (1)/carbon dioxide (2) mixture

$T$ (K)	$P$ (bar)	$y_1$	$x_2$	$K_1$	$K_2$
313.15	30.0	0.00015	0.315	0.00022	3.17
	45.0	0.00022	0.430	0.00038	2.32
	55.0	0.00032	0.541	0.00070	1.85
	65.0	0.00055	0.646	0.00154	1.55
	75.0	0.00105	0.755	0.00429	1.32
	80.0	0.00199	0.852	0.0134	1.17
328.15	30.0	0.00030	0.242	0.00040	4.14
	55.0	0.00046	0.425	0.00084	2.35
	70.0	0.00081	0.532	0.00173	1.88
	85.0	0.00170	0.646	0.00479	1.55
	100.0	0.00494	0.761	0.0207	1.31
	105.0	0.00982	0.810	0.0516	1.22
348.15	108.0	0.0169	0.851	0.113	1.16
	30.0	0.00074	0.197	0.00092	5.07
	55.0	0.00094	0.337	0.00142	2.96
	80.0	0.00172	0.467	0.00322	2.14
	110.0	0.00454	0.615	0.0118	1.62
	135.0	0.0158	0.745	0.0621	1.32
145.0	0.0320	0.802	0.162	1.21	

**Table 2.** Phase compositions and  $K$ -values of methyl benzoate (1)/ethane (2) mixture

$T$ (K)	$P$ (bar)	$y_1$	$x_2$	$K_1$	$K_2$
318.15	20.0	0.00014	0.173	0.00017	5.77
	30.0	0.00015	0.258	0.00020	3.88
	45.0	0.00048	0.397	0.00079	2.52
	65.0	0.0269	0.540	0.0585	1.80
	85.0	0.0541	0.585	0.130	1.62
	105.0	0.0806	0.621	0.213	1.48
328.15	120.0	0.0940	0.663	0.279	1.37
	20.0	0.00026	0.152	0.00029	6.59
	30.0	0.00023	0.228	0.00030	4.39
	45.0	0.00061	0.347	0.00094	2.88
	65.0	0.00457	0.509	0.00930	1.96
	85.0	0.0396	0.587	0.0958	1.63
338.15	100.0	0.0622	0.629	0.168	1.49
	120.0	0.0963	0.673	0.295	1.34
	20.0	0.00058	0.134	0.00067	7.49
	30.0	0.00053	0.206	0.00067	4.84
	45.0	0.00077	0.310	0.00111	3.22
	70.0	0.00453	0.479	0.00868	2.08
	95.0	0.0382	0.584	0.0917	1.65
	115.0	0.0759	0.661	0.224	1.40
	130.0	0.116	0.718	0.410	1.23

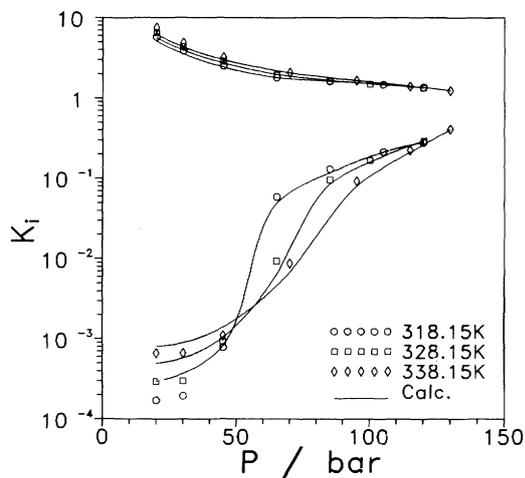
which is predicted from the Patel-Teja equation<sup>3)</sup> at the mixture's condition. As an example, **Fig. 5** presents the correlation for the methyl benzoate/CO<sub>2</sub> system. It appears that a quadratic relationship exists between  $\ln(y_1)$  and  $\rho$  for each isotherm; that is,

$$\ln(y_1) = A + B\rho + C\rho^2 \quad (1)$$

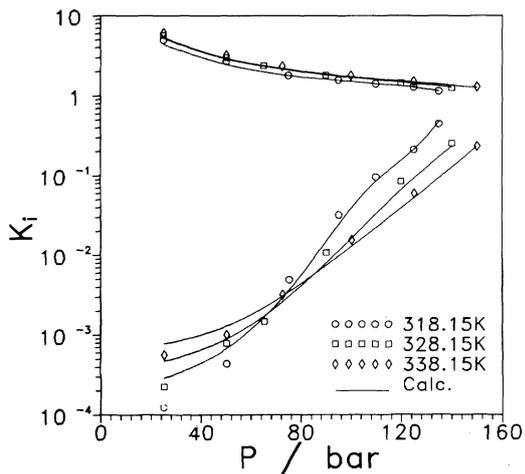
The best-fitted values of the coefficients  $A$ ,  $B$  and  $C$  as well as the average absolute deviations (AAD) of the solubility correlations for these three binary systems are reported in **Table 4**.

**Table 3.** Phase compositions and  $K$ -values of methyl benzoate (1)/ethylene (2) mixture

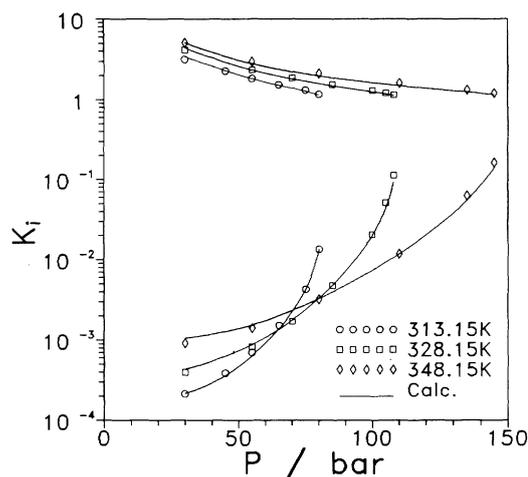
$T$ (K)	$P$ (bar)	$y_1$	$x_2$	$K_1$	$K_2$
318.15	25.0	0.00010	0.200	0.00013	4.99
	50.0	0.00027	0.372	0.00043	2.69
	75.0	0.00219	0.554	0.00490	1.80
	95.0	0.0120	0.627	0.0321	1.58
	110.0	0.0302	0.684	0.0954	1.42
	125.0	0.0573	0.729	0.212	1.29
328.15	135.0	0.0916	0.795	0.446	1.14
	25.0	0.00019	0.175	0.00023	5.71
	50.0	0.00052	0.335	0.00078	2.98
	65.0	0.00086	0.419	0.00148	2.38
	90.0	0.00484	0.552	0.0108	1.80
	120.0	0.0282	0.667	0.0847	1.46
338.15	140.0	0.0650	0.744	0.2541	1.26
	25.0	0.00047	0.163	0.00056	6.12
	50.0	0.00069	0.312	0.00100	3.20
	72.5	0.00182	0.428	0.00319	2.33
	100.0	0.00683	0.558	0.0155	1.78
	125.0	0.0212	0.644	0.0594	1.52
150.0	0.0611	0.746	0.229	1.28	



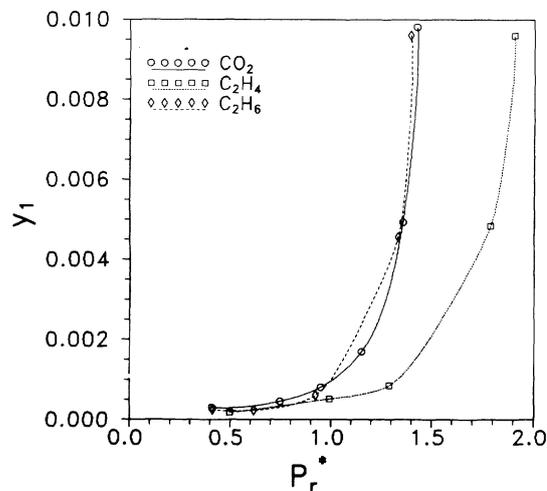
**Fig. 1.** Equilibrium ratios for the methyl benzoate/ethane system



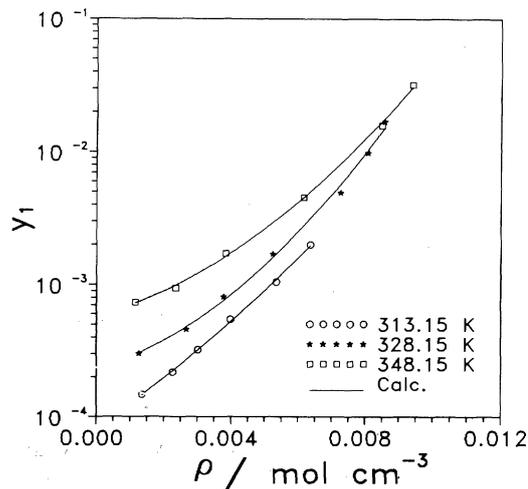
**Fig. 2.** Equilibrium ratios for the methyl benzoate/ethylene system



**Fig. 3.** Equilibrium ratios for the methyl benzoate/carbon dioxide system



**Fig. 4.** Variations of saturated vapor composition of methyl benzoate with reduced pressure at 328.15 K



**Fig. 5.** Correlation between saturated vapor composition of methyl benzoate and carbon dioxide density (curves represent the best-fitted results from Eq. (1))

**Table 4.** Empirical correlations for methyl benzoate solubilities

Solvent	<i>T</i> (K)	Data pts.	<i>A</i>	<i>B</i>	<i>C</i> (× 10 <sup>5</sup> )	AAD* (× 10 <sup>-3</sup> )
CO <sub>2</sub>	313.15	6	-9.4086	412.561	0.13615	0.018
	328.15	7	-8.3859	184.950	0.35610	0.454
	348.15	6	-7.4497	163.321	0.27548	0.421
C <sub>2</sub> H <sub>6</sub>	318.15	7	-10.2644	1208.398	-0.44803	2.412
	328.15	7	-9.2954	889.147	-0.19522	2.465
	338.15	7	-8.1832	567.209	0.06329	3.240
C <sub>2</sub> H <sub>4</sub>	318.15	7	-10.1470	807.903	-0.05894	1.823
	328.15	6	-9.2306	636.516	0.04021	0.169
	338.15	6	-8.1860	424.511	0.16981	0.310

$$* \text{AAD} = \sum_{k=1}^n |y_1^{\text{calc}} - y_1^{\text{expt}}|_k / n$$

The equilibrium ratios determined in this study were also correlated by the Patel-Teja equation of state.<sup>3)</sup> Quadratic mixing rules with two adjustable binary interaction constants,  $k_{a12}$  and  $k_{b12}$ , were applied to the calculations, i.e.,

$$a_m = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j a_{ij} \quad (2)$$

$$b_m = \sum_{i=1}^2 \sum_{j=1}^2 x_i x_j b_{ij} \quad (3)$$

with

$$a_{12} = (1 - k_{a12})(a_1 a_2)^{0.5} \quad (4)$$

$$b_{12} = (1 - k_{b12})(b_1 + b_2)/2 \quad (5)$$

The optimal interaction parameters for each isotherm were obtained by minimization of the following objective function,  $\pi$ , with a modified Levenberg-Marquardt algorithm:

$$\pi = \left( \frac{1}{2n} \right) \sum_{k=1}^n \left[ \frac{|K_1^{\text{calc}} - K_1^{\text{expt}}|}{K_1^{\text{expt}}} + \frac{|K_2^{\text{calc}} - K_2^{\text{expt}}|}{K_2^{\text{expt}}} \right]_k \quad (6)$$

where  $K_i^{\text{expt}} = y_i^{\text{expt}}/x_i^{\text{expt}}$  and  $K_i^{\text{calc}}$  denotes the  $K$ -value for the component  $i$  calculated from the Patel-Teja equation accompanying the given  $k_{a12}$  and  $k_{b12}$ ; that is,

$$\left( \frac{\Phi_i^l}{\Phi_i^v} \right)^{\text{calc}} = \left( \frac{y_i}{x_i} \right)^{\text{calc}} = K_i^{\text{calc}} \quad (7)$$

If  $K_i^{\text{calc}}$  equals  $K_i^{\text{expt}}$ , the model exactly reproduces the equilibrium ratio. Therefore, the values of the objective function defined in Eq. (6) is a measure of the quality of the model.<sup>1)</sup> The results of the data reduction are tabulated in **Table 5**. The smooth curves of the calculated values given in Figure 3 indicate that the Patel-Teja equation yields a good representation for the methyl benzoate/CO<sub>2</sub> system over the entire pressure range. However, the curves presented in Figures 1 and 2 show that the accuracy

**Table 5.** Phase equilibrium calculations from the Patel-Teja equation of state

Mixture (1)+(2)	<i>T</i> (K)	$k_{a12}$	$k_{b12}$	$K_1^*$ AAD (%)	$K_2^*$ AAD (%)
MBA + CO <sub>2</sub>	313.15	0.0837	-0.2771	4.2	2.8
	328.15	0.0891	-0.3069	8.6	3.1
	348.15	0.0618	-0.2379	9.2	4.6
MBA + C <sub>2</sub> H <sub>6</sub>	318.15	0.0341	0.0322	27.2	3.6
	328.15	0.0306	0.0322	31.3	5.0
	338.15	0.0297	0.2213	18.2	5.3
MBA + C <sub>2</sub> H <sub>4</sub>	318.15	-0.0201	0.0247	35.5	3.0
	328.15	-0.0067	0.0215	32.6	3.0
	338.15	-0.0209	0.0035	17.4	5.1

$$* K_i \text{ AAD (\%)} = \left( \frac{100}{n} \right) \sum_{k=1}^n \left[ \frac{|K_i^{\text{calc}} - K_i^{\text{expt}}|}{K_i^{\text{expt}}} \right]_k$$

for the heavier component (methyl benzoate) is not so good for ethane- and ethylene-containing systems at low pressures. Further modification of the mixing rules for such systems appears to be necessary.

## Conclusion

1. The phase equilibrium data for three binary systems composed of methyl benzoate plus either carbon dioxide, ethane or ethylene were measured at temperatures between 313.15 and 348.15 K and pressures up to near the critical pressures of the mixtures.

2. Dense ethane is capable of extracting methyl benzoate to a given level under a relatively low operating pressure as compared with the other two dense solvents at 328.15 K.

3. Each methyl benzoate solubility isotherm correlates well with the solvent's density. Moreover, the Patel-Teja equation of state with two binary interaction parameters represents the equilibrium ratios ( $K_i$ ) for the methyl benzoate/CO<sub>2</sub> system reasonably well, but it is not so successful for the other two binary systems at low pressures.

### Acknowledgment

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### Nomenclature

$a, b$	= parameters in the Patel-Teja equation of state	
$A, B, C$	= coefficients in Eq. (1)	
$k_{a12}$	= binary interaction constant in the combining rule of $a_{12}$	[—]
$k_{b12}$	= binary interaction constant in the combining rule of $b_{12}$	[—]
$K_i$	= equilibrium vaporization ratio	[—]
$n$	= number of data points	[—]
$p$	= pressure	[bar]
$P_r^*$	= reduced pressure ( $= P/P_{c2}$ )	[—]
$T$	= temperature	[K]
$T_r^*$	= reduced temperature ( $= T/T_{c2}$ )	[—]
$x_i$	= mole fraction of liquid phase for component $i$	[—]
$y_i$	= mole fraction of vapor phase for component $i$	[—]
$\rho$	= solvent density	[mol cm <sup>-3</sup> ]
$\Phi_i$	= fugacity coefficient for component $i$	[—]

### <Subscripts>

1	= component 1 (solute)
12	= 1-2 pair interaction
2	= component 2 (solvent)
$c$	= critical property
$i$	= component $i$
$ij$	= $i$ - $j$ pair interaction
$j$	= component $j$
$r$	= reduced property

### <Superscripts>

calc	= calculated value
expt	= experimental data
$l$	= liquid phase
$v$	= vapor phase

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