

Isothermal Vapor–Liquid Equilibria of the Carbon Dioxide (CO_2)–*N,N*-Dimethylformamide (DMF) System at Temperatures from 293.95 K to 338.05 K and Pressures up to 12 MPa

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Vapor–liquid equilibrium data are presented for the binary system carbon dioxide–*N,N*-dimethylformamide at 293.95, 313.05, and 338.05 K and pressures up to 12 MPa. The data are correlated using the Peng–Robinson equation of state with Wong–Sandler mixing rules. Agreement between the calculated and the measured equilibrium data has been found within 0.03% for vapor mole fractions and within 0.6% for pressures.

Introduction

Vapor–liquid equilibrium (VLE) data of compressed gas and low-volatile solvents have been the object of increasing interest due to their application in extraction processes under supercritical conditions. In the literature, little information exists about the carbon dioxide–*N,N*-dimethylformamide (CO_2 –DMF) system; only liquid-phase compositions¹ were available. In this work, both liquid and vapor phases are analyzed to have complete liquid–vapor equilibrium data and to provide accurate binary interaction parameters that are used in the design and analysis of the performance of supercritical extraction equipment.

Experimental Section

Apparatus. The apparatus used in this work (Figure 1) is the same as described by Laugier and Richon.² A static method was used with liquid- and vapor-phase sampling and analyses for each phase. The equilibrium cell was maintained at constant temperature in a liquid bath. It contains an efficient magnetic stirrer to ensure fast equilibrium and is equipped with two sampling systems that allow withdrawal of microsamples (to avoid disturbing the thermodynamic equilibrium), connected to a gas chromatograph. The temperature was measured using two thermocouples placed inside wells drilled directly into the body of the equilibrium cell. They allow temperature readings through an electronic display within 0.1 K as a result of a calibration against a 25 Ω platinum probe. The pressure was measured by means of a pressure transducer (SEDEME type TFO1 160 S241) for which the accuracy of pressure readings was found to be better than 0.01 MPa. This results from a calibration against a dead weight balance (Desgranges and Huot model 5202S, 0.3–40 MPa).

Liquid and vapor samples were both analyzed using a gas chromatograph (Stang Instruments type ST200),

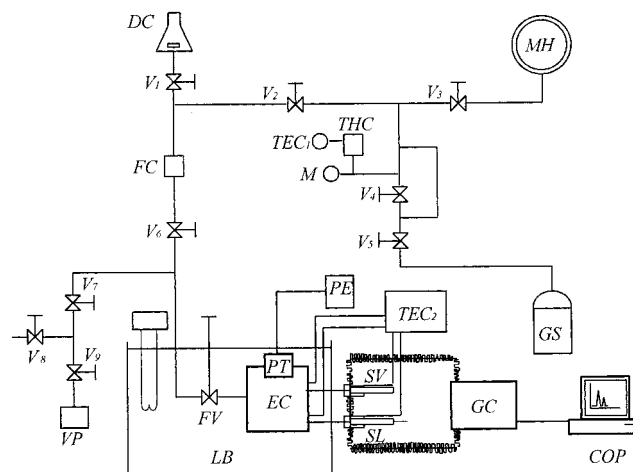


Figure 1. Flow diagram of the apparatus: DC, degassing cell; V, valve “Autoclave Engineers”; FC, feeding cell; THC, thermal compressor; M, manometer; TEC, temperature control; MH, manometer Heise; FV, feeding valve; EC, equilibrium cell; LB, liquid bath; PT, pressure transducer; SV, sampling vapor; SL, sampling liquid; GC, gas chromatograph; GS, gas supplier; PE, pressure electronic display.

equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) connected in series. They were repeatedly calibrated by introducing pure components through a syringe. In this work, the uncertainty reported for the analysis of the composition in mole fraction for both vapor and liquid phases was estimated to be within <1%. This uncertainty comes essentially from the calibration itself; samplings from the Rolsi samplers are very accurate and reliable as described in a paper from Guilbot et al.³ The column used for analysis purposes is a 5% Stabilwax column, 79 in. \times 1/8 in. silcosteel.

Procedure. The experimental procedure consists of three main steps: filling the cell, setting up experimental conditions, and performing measurements at equilibrium.

The liquid component, *N,N*-dimethylformamide, was introduced into the degassing cell (see Figure 1) and then degassed under vacuum and efficient stirring. After com-

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Table 1. Vapor–Liquid Equilibrium Data for the Carbon Dioxide–*N,N*-Dimethylformamide System at Different Temperatures

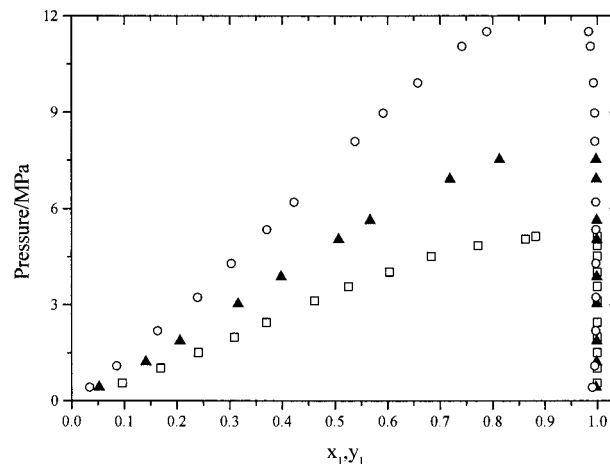
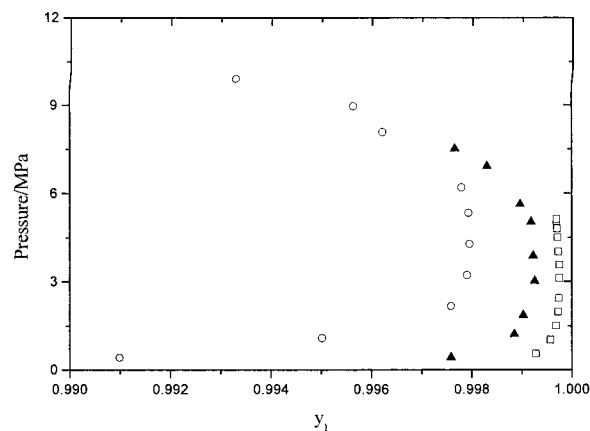
pressure <i>P</i> /MPa	mole fraction				
	liquid $x_{\text{exptl,CO}_2}$	vapor $y_{\text{exptl,CO}_2}$	vapor $y_{\text{calcd,CO}_2}$	vapor $y_{\text{exptl,DMF}}$	vapor $y_{\text{calcd,DMF}}$
<i>T</i> = 293.95 K					
0.56	0.0962	0.9993	0.9994	0.0007	0.0006
1.03	0.1691	0.9996	0.9996	0.0004	0.0004
1.51	0.2402	0.9997	0.9997	0.0003	0.0003
1.99	0.3088	0.9997	0.9997	0.0003	0.0003
2.45	0.3694	0.9997	0.9998	0.0003	0.0002
3.12	0.4610	0.9998	0.9998	0.0002	0.0002
3.57	0.5256	0.9998	0.9998	0.0002	0.0002
4.02	0.6031	0.9997	0.9998	0.0003	0.0002
4.51	0.6832	0.9997	0.9997	0.0003	0.0003
4.85	0.7723	0.9997	0.9997	0.0003	0.0003
5.04	0.8627	0.9997	0.9997	0.0003	0.0003
5.13	0.8823	0.9997	0.9997	0.0003	0.0003
<i>T</i> = 313.05 K					
0.43	0.0528	0.9976	0.9973	0.0024	0.0027
1.22	0.1414	0.9989	0.9989	0.0011	0.0011
1.86	0.2062	0.9990	0.9991	0.0010	0.0009
3.02	0.3165	0.9993	0.9992	0.0007	0.0008
3.87	0.3980	0.9992	0.9992	0.0008	0.0008
5.03	0.5075	0.9992	0.9991	0.0008	0.0009
5.63	0.5672	0.9990	0.9990	0.0010	0.0010
6.92	0.7194	0.9983	0.9985	0.0017	0.0015
7.51	0.8137	0.9977	0.9981	0.0023	0.0019
<i>T</i> = 338.05 K					
0.43	0.0345	0.9910	0.9896	0.0090	0.0104
1.09	0.0861	0.9950	0.9953	0.0050	0.0047
2.18	0.1641	0.9976	0.9970	0.0024	0.0030
3.23	0.2395	0.9980	0.9974	0.0020	0.0026
4.29	0.3037	0.9980	0.9975	0.0020	0.0025
5.34	0.3712	0.9979	0.9973	0.0021	0.0027
6.20	0.4233	0.9978	0.9970	0.0022	0.0030
8.09	0.5385	0.9962	0.9956	0.0038	0.0044
8.97	0.5921	0.9957	0.9945	0.0043	0.0055
9.91	0.6583	0.9933	0.9923	0.0067	0.0077
11.05	0.7422	0.9874	0.9878	0.0126	0.0122
11.51	0.7894	0.9836	0.9840	0.0164	0.0160

plete degassing, the liquid was loaded by gravity into the equilibrium cell. The gaseous component, CO₂, was loaded into the thermal compressor. At constant temperature, pressure in the equilibrium cell was adjusted by adding CO₂ from the thermal compressor. When equilibrium was reached, samples of liquid and vapor were withdrawn using pneumatic samplers³ (Rolsi) and analyzed by gas chromatography. At a given temperature and pressure condition, at least five samples of each phase were taken to check for reproducibility.

Chemicals. Carbon dioxide was provided by Air Liquide with a certified purity of 99.995%. DMF was supplied by Merck (99.5%). Both products were used without any further purification except careful degassing of DMF.

Results and Discussion

Isothermal vapor–liquid equilibrium results are reported in Table 1 for the CO₂–DMF system and plotted on a pressure–composition diagram in Figure 2. For clarity, the vapor-phase compositions are plotted again in Figure 3. The isothermal VLE data are correlated using the Peng–Robinson⁴ (PR) equation of state (EOS) with Wong–Sandler⁵ (WS) mixing rules. The binary interaction parameters of the EOS are fitted by using VLE data at 293.95 K. VLE data at higher temperatures are then predicted and found to be in good agreement with other isothermal

**Figure 2.** Pressure as a function of carbon dioxide mole fraction in the system CO₂–DMF at 293.95 K (□), 313.05 K (▲), and 338.05 K (○).**Figure 3.** Vapor-phase compositions for the CO₂ (1)–DMF (2) system at 293.95 K (□), 313.05 K (▲), and 338.05 K (○).**Table 2. Critical Parameters and Acentric Factors (from Dortmund Data Bank⁷ Version 97)**

component	<i>P</i> _c /MPa	<i>T</i> _c /K	ω
carbon dioxide	7.375	304.2	0.225
<i>N,N</i> -dimethylformamide	5.499	650.0	0.389

data reported in this work, displaying a null temperature difference of the binary interaction parameters.

The PR EOS⁴ is

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

where, for pure compounds

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

and

$$b = 0.07780 \frac{RT_c}{P_c} \quad (3)$$

The critical parameters *T*_c, *P*_c, and acentric factors used in this work are reported in Table 2.

The temperature dependence of $\alpha(T)$ is given by

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

where

$$m = 0.3746 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

and ω is the acentric factor.

For mixtures, the WS mixing rule are given by eqs 6 and 7.

$$b_m = \frac{\sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij}}{\left[1 - \sum_i x_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{CRT} \right]} \quad (6)$$

$$a_m = b_m RT \left(\sum_i x_i \frac{a_i}{b_i RT} + \frac{A_\infty^E}{CRT} \right) \quad (7)$$

In eqs 6 and 7, a_i and b_i are the pure component EOS parameters, A_∞^E is the Helmholtz energy at the infinite pressure limit, x_i is the mole fraction of component i in either the liquid or vapor phase, and C is a numerical constant equal to $\ln(\sqrt{2} - 1)/\sqrt{2}$. The following combining rule developed by Wong and Sandler for the second cross virial coefficient is used in this work

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2} \left[\left(b_i - \frac{a_i}{RT} \right) + \left(b_j - \frac{a_j}{RT} \right) \right] (1 - k_{ij}) \quad (8)$$

where k_{ij} is a binary interaction parameter. Note that $k_{ij} = k_{ji} = 0$.

Wong and Sandler have shown that the excess Helmholtz energy of mixing at infinite pressure, A_∞^E is approximately equal to the excess Gibbs energy at low pressure.⁵ Consequently, they assumed that

$$\frac{A_\infty^E}{RT} = \frac{G^E}{RT} \quad (9)$$

Therefore, for the liquid phase, the A^E (or G^E) obtained from the equation of state (with the WS mixing rules) has to be that of the chosen liquid solution model described by G^E . We used the NRTL model of Renon and Prausnitz⁶ given by

$$\frac{G^E}{RT} = \sum_i x_i \frac{\sum_j x_j \tau_{ij} g_{ji}}{\sum_k g_{ki} x_k} \quad (10)$$

where

$$g_{ij} = \exp(-\alpha_{ij} \tau_{ij}) \quad (11)$$

The temperature-independent parameters τ_{ij} , τ_{ji} , and k_{ij} are fitted for the NRTL model, whereas α_{ij} has a fixed value of 0.3. The VLE calculation algorithm was used in combination with the Levenberg–Marquardt method (IMSL, 1979) with the objective function (F)

$$F = \sum_{i=1}^N \left[\left(\frac{P_{i,\text{calcd}} - P_{i,\text{exptl}}}{P_{i,\text{exptl}}} \right)^2 + \left(\frac{y_{i,\text{calcd}} - y_{i,\text{exptl}}}{y_{i,\text{exptl}}} \right)^2 \right] \quad (12)$$

where N is the total number of data ($i = 1, \dots, N$), $P_{i,\text{calcd}}$ and $P_{i,\text{exptl}}$ are the calculated and experimental total pressures, respectively, and, $y_{i,\text{calcd}}$ and $y_{i,\text{exptl}}$ are the

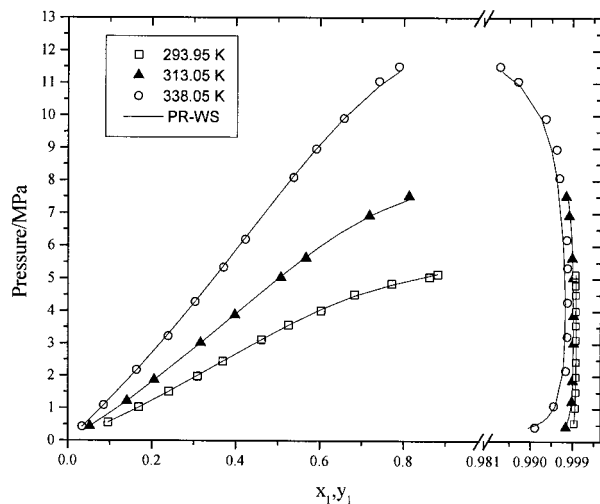


Figure 4. Pressure as function of the carbon dioxide mole fraction in the system CO₂ (1)–DMF (2) at different temperatures: (experimental data) □, 293.95 K; ▲, 313.05 K; ○, 338.05 K; (results calculated with the PR EOS) —.

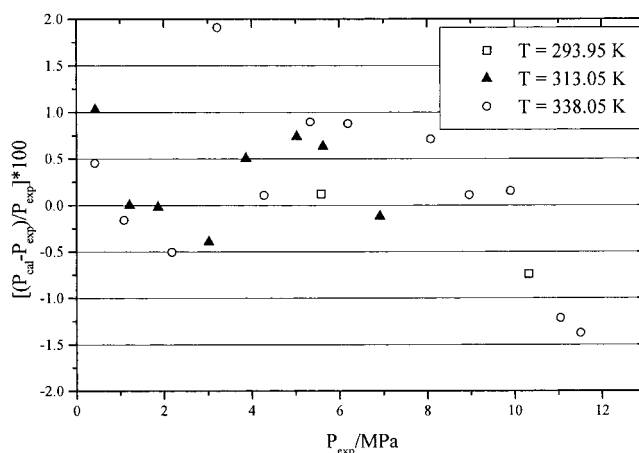


Figure 5. Relative deviation of the total pressure.

calculated and experimental CO₂ vapor mole fractions, respectively.

The values of the adjusted parameters for the PR EOS with WS mixing rules (fitted at 293.95 K with data of the CO₂–DMF system) are τ_{12} (J·mol⁻¹) = 6661.98, τ_{21} (J·mol⁻¹) = -2969.59, and $k_{12} = 0.4145$.

These sets of parameters are used to predict the vapor–liquid equilibria at two other temperatures, namely, 313.05 K and 338.05 K (Figure 4). The percentage deviations for the vapor pressure and the vapor-phase composition are plotted in Figures 5 and 6, respectively. Thus, it is justifiable to take the adjusted parameters as independent of temperature. The mean relative percentage deviation of pressures (ΔP) is 0.6%, and the mean relative percentage deviation of vapor-phase mole fractions (Δy) is 0.03%. They are defined by

$$(\Delta P\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{P_{\text{calcd}} - P_{\text{exptl}}}{P_{\text{exptl}}} \right|_i \times 100 \quad (13)$$

and

$$(\Delta y\%) = \frac{1}{N} \sum_{i=1}^N \left| \frac{y_{\text{calcd}} - y_{\text{exptl}}}{y_{\text{exptl}}} \right|_i \times 100 \quad (14)$$

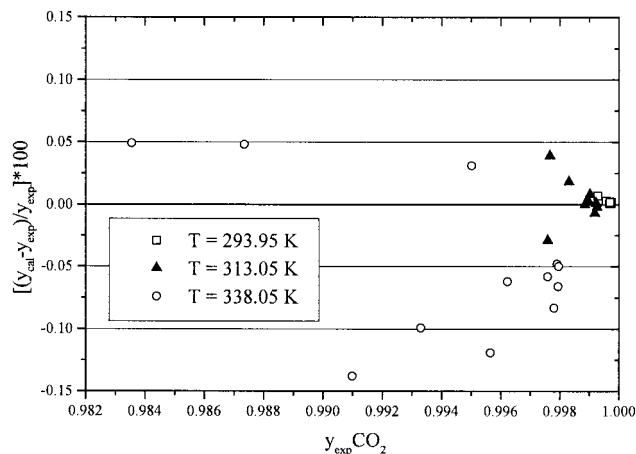


Figure 6. Relative deviation of the CO₂ vapor mole fraction.

Conclusions

In this paper we present VLE data for the CO₂–DMF system. The data obtained for each mixture covers several compositions and different temperatures (293.95, 313.05, and 338.05 K). The experimental data for all of the mixtures were analyzed and fitted with the Peng–Robinson equation of state. In each case the data were consistent with this model. The parameters employed in the isothermal prediction at 313.05 K and 338.05 K were obtained from the experimental data at 293.95 K. The predictions gave good results, with deviations of P around 1% and less than 0.15% for the CO₂ vapor mole fraction.

Glossary

a	parameter of the equation of state (energy parameter)
b	parameter of the equation of state (covolume parameter)
A	Helmholtz energy
G	Gibbs free energy
C	numerical constant = $\ln(\sqrt{2} - 1)/\sqrt{2}$
F	objective function
g	local composition factor for the NRTL model, eq 11
P	pressure in MPa

k_{ij}	binary interaction parameter
R	gas constant in J·mol ⁻¹ ·K ⁻¹
T	temperature in K
V	molar volume in cm ³ ·mol ⁻¹
x	liquid mole fraction
y	vapor mole fraction

Greek letters

α_{ij}	NRTL model parameter, eq 11
τ_{ij}	NRTL model binary interaction parameter, eq 10
ω	acentric factor

Superscript

E	excess property
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Subscripts

c	critical property
r	reduced property
calcd	calculated property
exptl	experimental property
i, j	molecular species
m	mixture property
∞	infinite pressure reference state

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Received for review February 21, 2001. Accepted August 20, 2001.

JE010055W