

Phase Equilibria of Acrylonitrile and *p*-Bromobenzaldehyde in Carbon Dioxide

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Vapor–liquid equilibrium (VLE) of acrylonitrile and the solubility of *p*-bromobenzaldehyde in compressed and/or supercritical carbon dioxide were measured using a synthetic static method with a variable-volume cell with a front sapphire window for visualization of phase transitions. For CO₂ + acrylonitrile, the bubble point (BP) and dew point (DP) were verified at temperatures ranging from (303 to 333) K and pressure up to 100 bar. For CO₂ + *p*-bromobenzaldehyde, solid–fluid (SF) transitions were verified at the same temperatures over a pressure range of (90 to 135) bar. The experimental data obtained here (VLE and SFE) were modeled with the Peng–Robinson equation of state (PR-EOS) with the classical quadratic mixing rule. The correlation between experimental and calculated values showed good agreement in both cases.

Introduction

Supercritical fluids (SCFs) have received great attention as an alternative medium for chemical reactions because they present some advantages such as controllable reaction rate, improved yield, or tunable selectivity.^{1–6} One additional attractive feature of SCFs as a medium for chemical reactions is that they can lower mass transfer limitations.⁷ Also, it allows us to combine advantageously the reaction, separation, and purification steps.^{8,9}

Supercritical carbon dioxide (scCO₂) is one of the most commonly used SCFs. The advantage of scCO₂ arises from its easily accessible critical temperature, moderate critical pressure, nonflammability, nontoxicity, abundance, chemical inertness, and tunable solvent power.^{10,11} Therefore, scCO₂ becomes an interesting possibility to replace organic solvents in many chemical reactions, like the Baylis–Hillman (B–H) reaction.^{12,13} This type of reaction is a synthetically useful carbon–carbon bond-forming reaction between an aldehyde and an electrophilic alkene, usually in the presence of a tertiary amine.¹⁴ One of its main characteristics is the high degree of functionality present in the products and their resultant potential transformations. At high pressures, Oishi et al.¹⁵ observed that rates of the B–H reaction are increased.

The main aim of this work was to investigate the high-pressure phase equilibrium behavior of binary systems formed by CO₂ with two reactants of B–H reaction, acrylonitrile and *p*-bromobenzaldehyde. This reaction is shown in Figure 1. Phase transitions were recorded visually as bubble or dew points for the vapor–liquid equilibrium of the CO₂ (1) + acrylonitrile (2) system and solid–fluid equilibrium for CO₂ (1) + *p*-bromobenzaldehyde (2). The experiments were carried out at temperatures ranging from (303 to 333) K and pressures ranging up to 135 bar. Such ranges were used due to reactions previously carried out in similar conditions.¹⁶ Experimental data obtained were

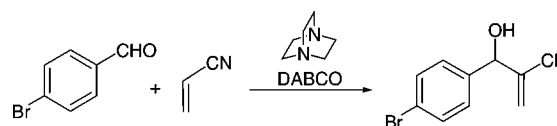


Figure 1. Baylis–Hillman reaction between *p*-bromobenzaldehyde and acrylonitrile.

Table 1. Critical Properties and Acentric Factors of Pure Components

compound	<i>M</i>	<i>T</i> _c /K	<i>P</i> _c /bar	<i>ω</i>
CO ₂ ¹⁷	44.01	304.21	73.8	0.2236
acrylonitrile ¹⁷	53.06	536.0	45.6	0.35
<i>p</i> -bromobenzaldehyde ^a	185.02	744.40	48.33	0.529

^a Estimated by the group contribution method.¹⁷

modeled with the Peng–Robinson equation of state (PR-EOS) and the classical quadratic mixing rule.

Experimental Section

Materials. The solvent CO₂ was acquired from AGA with 99.9 % purity. Acrylonitrile and *p*-bromobenzaldehyde were obtained from ACROS with a minimum purity of 99 %. All materials were used without further purification. The critical properties of pure compounds are presented in Table 1. The *p*-bromobenzaldehyde was characterized by differential scanning calorimetry (DSC-50, Shimadzu). From this analysis, the enthalpy of fusion, $\Delta_{\text{fus}}H = (122.4 \pm 0.2) \text{ J} \cdot \text{g}^{-1}$, and melting temperature, $T_{\text{fus}} = (334.2 \pm 0.1) \text{ K}$, values were obtained.

Procedure. Measurements of the vapor–liquid equilibrium (VLE) and solid–fluid equilibrium (SFE) were performed in a high-pressure variable-volume view cell using the static synthetic method. The experimental apparatus used in this work is very similar to the one used in previous investigations.^{18,19} The experimental apparatus consisted basically of a view cell with two sapphire windows, one for visual observations and another for light entrance, an absolute pressure transducer (Smar LD 301) with a precision of 0.01 MPa, a portable programmer (Smar, HT 201) for the pressure data acquisition, and a syringe pump (ISCO 500D). The

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Table 2. VLE Experimental Data for CO₂ (1) + Chloroform (2)

x_1	P/bar	phase transition type	x_1	P/bar	phase transition type
$T = 303 \text{ K}$					
0.5600	39.3 ± 0.2	BP ^a	0.8635	58.0 ± 0.2	BP
0.6449	42.6 ± 0.2	BP	0.9155	62.5 ± 0.2	BP
0.7315	49.9 ± 0.2	BP	0.9479	64.5 ± 0.2	BP
0.7996	54.5 ± 0.2	BP	0.9649	65.0 ± 0.2	BP
0.8336	56.4 ± 0.2	BP			
$T = 313 \text{ K}$					
0.5600	47.7 ± 0.2	BP	0.8635	70.0 ± 0.2	BP
0.6449	51.6 ± 0.2	BP	0.9155	75.3 ± 0.2	BP
0.7315	59.7 ± 0.2	BP	0.9479	76.3 ± 0.2	BP
0.7996	64.4 ± 0.2	BP	0.9649	78.2 ± 0.2	BP
0.8336	67.9 ± 0.2	BP			
$T = 323 \text{ K}$					
0.5600	55.7 ± 0.2	BP	0.8336	80.1 ± 0.2	BP
0.6449	61.2 ± 0.2	BP	0.8635	81.9 ± 0.2	BP
0.7315	70.3 ± 0.2	BP	0.9155	88.1 ± 0.2	BP
0.7996	75.5 ± 0.2	BP	0.9479	85.9 ± 0.2	DP
$T = 333 \text{ K}$					
0.5600	63.7 ± 0.2	BP	0.8336	92.5 ± 0.2	BP
0.6449	71.6 ± 0.2	BP	0.8635	93.9 ± 0.2	BP
0.7315	81.1 ± 0.2	BP	0.9155	97.8 ± 0.2	DP ^b
0.7996	87.3 ± 0.2	BP	0.9479	93.2 ± 0.2	DP

^a BP - bubble point. ^b DP - dew point.

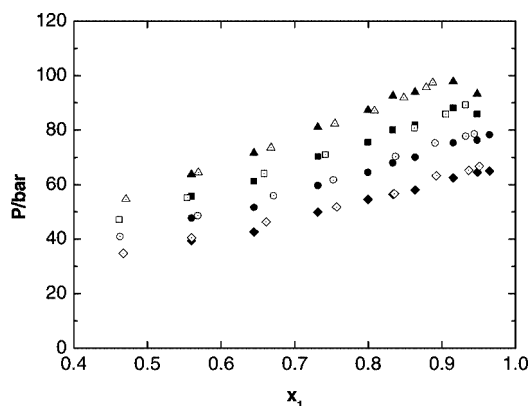


Figure 2. Comparison of the VLE measurement results for the CO₂ (1) + chloroform (2) system with the literature data: ◆, 303 K; ●, 313 K; ■, 323 K; ▲, 333 K. This work: ◇, 303 K; ○, 313 K; □, 323 K; △, 333 K Scurto et al.²³

pressure transducer used for pressure measurements was calibrated against a digital multimeter HP-34401A model. In the experimental apparatus, the pressure transducer is connected to the movable piston that permits the pressure control inside the cell. The equilibrium cell had a maximum internal volume of 25 cm³ and contained a movable piston, which permitted the pressure control inside the cell. The cell was equipped with a water bath and a PID controller (DIGI MEC mark, SHM 112 model). The controller was connected to a thermocouple (J type, with an accuracy of 1.0 K), which was in direct contact with the fluid mixture inside the equilibrium cell. The thermocouple was calibrated against a primary thermometer (Incoterm, 47342 model) at four fixed temperatures between (273 and 373) K. This arrangement provided a temperature control with a precision of 1.0 K. Initially, the cell and all lines were flushed with low-pressure CO₂ to remove residual air. Depending on the desired global composition, an amount of solute, acrylonitrile, or *p*-bromobenzaldehyde was weighed on a high-precision scale (Ohaus Analytical Standard, with 0.0001 g accuracy) and loaded into the cell. Afterward, the gas was pumped into the

Table 3. VLE Experimental Data for CO₂ (1) + Acrylonitrile (2)

x_1	P/bar	phase transition type	x_1	P/bar	phase transition type
$T = 303 \text{ K}$					
0.6448	47.2 ± 0.2	BP ^a	0.8898	59.6 ± 0.2	BP
0.7396	53.5 ± 0.2	BP	0.9499	60.0 ± 0.2	BP
0.8282	57.9 ± 0.2	BP	0.9710	60.9 ± 0.2	BP
$T = 313 \text{ K}$					
0.6448	56.5 ± 0.2	BP	0.8898	73.2 ± 0.2	BP
0.7396	62.2 ± 0.2	BP	0.9499	74.1 ± 0.2	BP
0.8282	70.5 ± 0.2	BP	0.9710	75.0 ± 0.2	BP
$T = 323 \text{ K}$					
0.6448	69.3 ± 0.2	BP	0.8898	87.0 ± 0.2	BP
0.7396	73.2 ± 0.2	BP	0.9499	87.4 ± 0.2	BP
0.8282	83.2 ± 0.2	BP	0.9710	85.1 ± 0.2	DP ^b
$T = 333 \text{ K}$					
0.6448	75.8 ± 0.2	BP	0.8898	99.6 ± 0.2	BP
0.7396	85.8 ± 0.2	BP	0.9499	97.6 ± 0.2	DP
0.8282	96.5 ± 0.2	BP			

^a BP - bubble point. ^b DP - dew point.

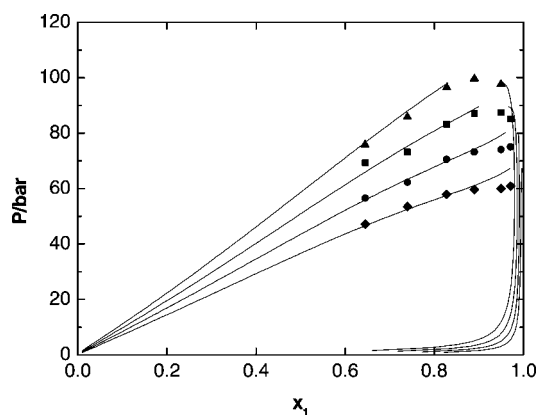


Figure 3. VLE P , x , y diagram for the CO₂ (1) + acrylonitrile (2) system: ◆, 303 K; ●, 313 K; ■, 333 K; and ▲, PR-EOS.

cell to reach the pre-established global composition. The amount of gas charged was monitored by the change in the total mass of the transfer vessel of the pump. Based on the uncertainties of the masses introduced, compositions are estimated to be accurate to within 1 % of the specified value. Then, the cell content was kept at continuous agitation with a magnetic stirrer and a Teflon-coated stirring bar. After reaching the desired temperature, the cell pressure was increased by applying pressure on the back of the piston with the syringe pump until observation of a single phase. At this point, the system was allowed to stabilize for at least 30 min. For transition, the cell pressure was decreased slowly until incipient formation of another phase. The equilibrium pressure was then recorded, after repetition of each experimental procedure at least three times, leading to 0.2 MPa experimental standard deviations. Phase transitions were recorded visually as bubble (BP), dew (DP), or melting points varying the pressure using the syringe pump and CO₂ as pressurizing fluid. In the BP transition, a small vapor bubble appears, while in the DP transition, a small amount of dew, or fog, is formed in the cell. In melting point transitions, precipitation of solid particles from the solution is observed.

Thermodynamic Modeling. The experimental data of the vapor–liquid equilibrium (VLE) were modeled using the isofugacity approach by the Peng–Robinson equation of state (PR-EOS)²⁰ with the van der Waals quadratic mixing rule (vdW2).

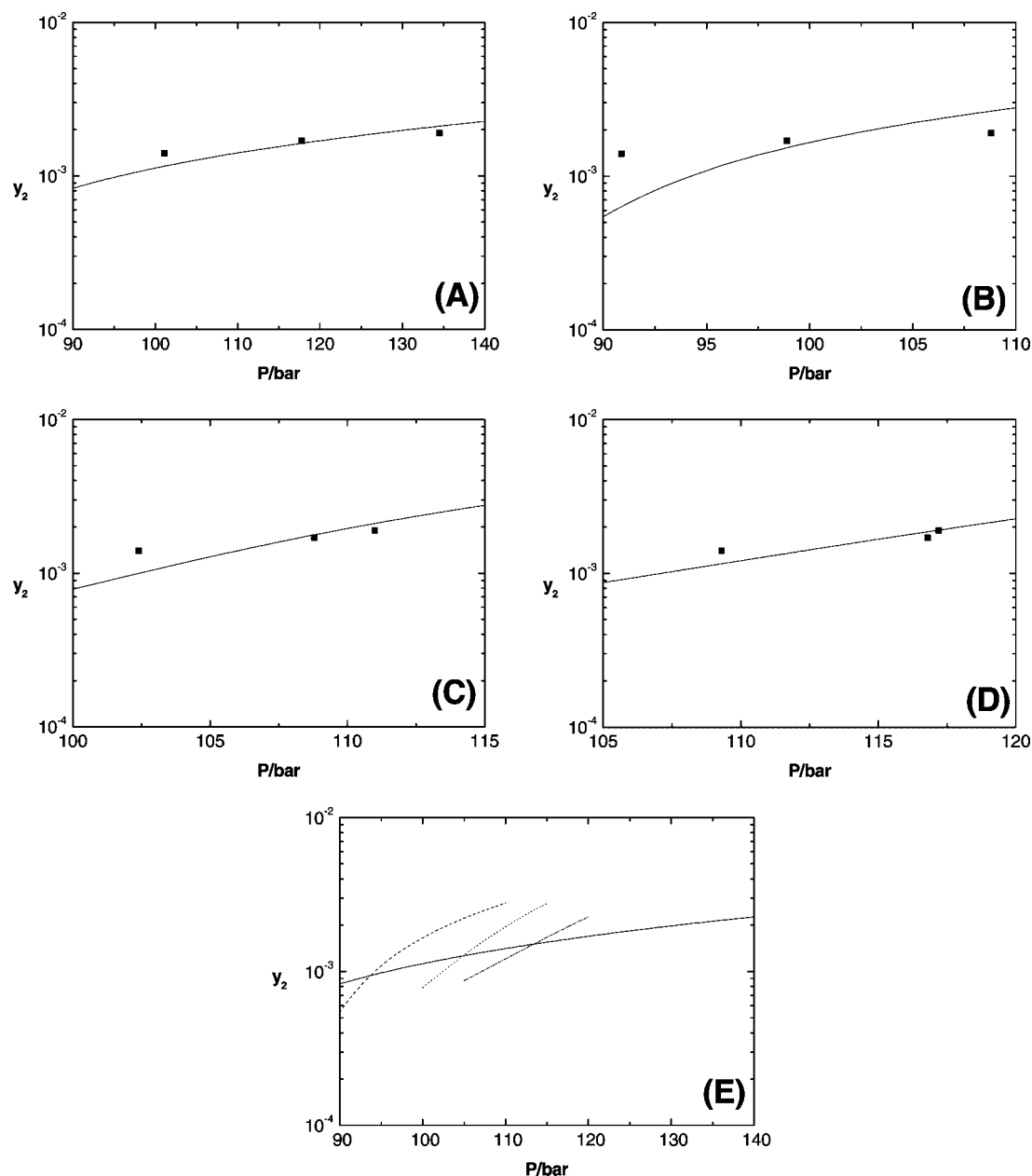


Figure 4. Solubility of the *p*-bromobenzaldehyde in CO₂ as a function of the pressure and temperature: A, 303 K; B, 313 K; C, 323 K; D, 333 K. ■, Experimental data; — PR-EOS, E, all isotherms; bold —, 303 K; — —, 313 K; ···, 323 K; -·-·, 333 K.

Table 4. Solubility Experimental Data for CO₂ (1) + *p*-Bromobenzaldehyde (2)

$10^3 y_2$	<i>P</i> /bar	$10^3 y_2$	<i>P</i> /bar
<i>T</i> = 303 K		<i>T</i> = 313 K	
1.4	101.1 ± 0.2	1.4	90.6 ± 0.2
1.7	117.8 ± 0.2	1.7	98.9 ± 0.2
1.9	134.5 ± 0.2	1.9	108.8 ± 0.2
<i>T</i> = 323 K		<i>T</i> = 333 K	
1.4	102.4 ± 0.2	1.4	109.3 ± 0.2
1.7	108.8 ± 0.2	1.7	116.8 ± 0.2
1.9	111.0 ± 0.2	1.9	117.2 ± 0.2

To correlate the solubility of *p*-bromobenzaldehyde (2) in CO₂ at high pressures, we used the following equation²¹

$$y_2 = \frac{P_2^{\text{sat}}}{\hat{\phi}_2^\infty P} \exp\left(\frac{PV_2^s}{RT}\right) \quad (1)$$

where y_2 is the mole fraction of solute; P_2^{sat} is the solid/vapor saturation pressure at temperature T ; V_2^s is the molar volume

Table 5. Solid/Vapor Saturation Pressure for Pure *p*-Bromobenzaldehyde Fitted Using Equation 1, from SFE Data of the System CO₂ (1) + *p*-Bromobenzaldehyde (2)

<i>T</i> /K	P_2^{sat} /bar
303	$2.93 \cdot 10^{-6}$
313	$2.81 \cdot 10^{-5}$
323	$1.31 \cdot 10^{-4}$
333	$3.69 \cdot 10^{-4}$

of the solid; and $\hat{\phi}_2^\infty$ is the vapor-phase fugacity coefficient of the solute at infinite dilution.

The fugacity coefficient of the solute at infinite dilution was determined using the Peng–Robinson equation of state (PR-EOS) with zero interaction parameters at the limit of infinite dilution of component 2 in CO₂.²¹

The equation proposed by Rackett²² was used for the estimation of the molar volume V_2^s . This approach was used because we admitted that the saturated liquid volume is very close to the solid volume at the same temperature. The

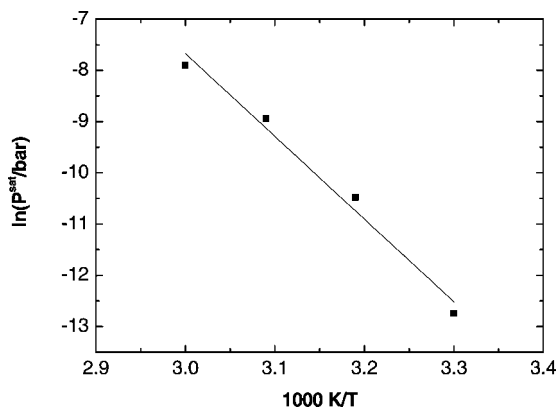


Figure 5. Temperature dependency of the solid/vapor saturation pressure (P_2^{sat}). ■, Calculated saturation pressure data and —, Clausius/Clapeyron equation.

melting temperature ($T_m = 334.15$ K) was employed at the calculation of the molar volume. The value calculated for V_2^s was equal to $149.2 \text{ cm}^3 \cdot \text{mol}^{-1}$.

The solid/vapor saturation pressure P_2^{sat} is the only parameter unknown in eq 1. To fit this parameter, the SFE data of system CO_2 (1) + p -bromobenzaldehyde (2) were used.

Results and Discussion

To test the reliability of the apparatus and experimental procedure, VLE data for the binary CO_2 (1) + chloroform (2) system were measured and compared with the values available in the literature.²³ Numerical values of VLE data for CO_2 (1) + chloroform (2) are reported in Table 2. As shown in Figure 2, the data reported in this work were in agreement with data obtained by Scurto et al.²³

The VLE experimental data of the system CO_2 (1) + acrylonitrile (2) at the temperature range from (303 to 333) K are reported in Table 3. The results obtained were presented in Figure 3. In this figure, it can be verified that for pressures higher than 100 bar the system is composed of a single phase at the studied temperatures. The p -bromobenzaldehyde solubility in CO_2 is presented in Figure 4, and the experimental data are presented in Table 4. Figure 4E presents all isotherms plotted together on the same chart. This figure shows the existence of intersection points for pairs of isotherms. Such behavior is normal as shown by Tester and Model.²⁴ Table 5 shows the values of solid/vapor saturation pressure fitted at each temperature. The logarithm of solid/vapor saturation pressure has a linear dependency on the inverse temperature; i.e., this property can be represented by the Clausius/Clapeyron equation. To verify this dependence and validate our estimation, $\ln P^{\text{sat}}$ was plotted as a function of inverse temperature. Figure 5 shows the linear fit with the parameters obtained on the fit.

The VLE experimental data of the system CO_2 (1) + acrylonitrile (2) obtained here were modeled with the Peng–Robinson equation of state (PR-EOS) and the classical quadratic mixing rule providing a satisfactory agreement between experimental and calculated values. The parameters fitted were $k_{12} = 4.61 \cdot 10^{-2}$ and $l_{12} = 3.46 \cdot 10^{-2}$.

Conclusions

In this work, the phase equilibrium data of CO_2 with acrylonitrile and p -bromobenzaldehyde binary mixtures are reported at the temperature range from (303 to 333) K. For

the CO_2 + acrylonitrile system, bubble and dew points up to 100 bar were observed, and for the CO_2 + p -bromobenzaldehyde system, solid–fluid transitions were noticed. The experimental data were modeled with the PR-EOS using the classical quadratic mixing rule providing a good representation of the experimental information. The knowledge of the phase behavior of components in scCO_2 (used as the reaction medium) can be useful to minimize the restrictions of mass-transfer between the regions of split phases and for a possible fractionation step of the reaction products.

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