Supporting Information

Vapor-liquid equilibrium phase diagrams of the CO\textsubscript{2}/methanol, CO\textsubscript{2}/ethanol and CO\textsubscript{2}/water systems at 45 °C

1. Equations of State

In this work, the Stryjek and Vera modification of the Peng-Robinson equation of state (PRSV-EoS)\textsuperscript{[1]} are applied to represent the VLE of the binary systems involving carbon dioxide, methanol, ethanol and water at 45 °C and different pressures.

PR-EoS is of the form

\[ P = \frac{RT}{v-b} \left( \frac{a(T)}{v^2 + 2bv - b^2} \right) \]  \hspace{1cm} \text{(1)}

where \( T, P \) and \( v \) are the temperature, pressure and molar volume. Parameters \( a \) and \( b \) are given by

\[ a_i = 0.457235 \left( \frac{RT_{ci}}{P_{ci}} \right)^2 \left[ 1 + \kappa_i \left( 1 - \frac{T}{T_{ci}} \right) \right]^2 \]  \hspace{1cm} \text{(2)}

\[ b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \]  \hspace{1cm} \text{(3)}

For the PR-EoS, the \( \kappa_i \) term has the form

\[ \kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \]  \hspace{1cm} \text{(4)}

where \( \omega \) is Pitzer’s acentric factor. For the PRSV-EoS, \( \kappa_i \) is given by

\[ \kappa_i = \kappa_{0i} + \kappa_i \left( 1 + \sqrt{\frac{T}{T_{ci}}} \right) \left( 0.7 - \frac{T}{T_{ci}} \right) \]  \hspace{1cm} \text{(5)}

with

\[ \kappa_{0i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \]  \hspace{1cm} \text{(6)}
For mixtures, the Panagiotopoulous-Reid mixing rules are used,

\[ a = \sum_{i} \sum_{j} x_i x_j (a_i a_j)^{1/2} \left[ 1 - k_{ij} + (k_{ij} - k_{ji}) x_i \right] \]  

(7)

\[ b = \sum_{i} \sum_{j} x_i x_j \left( \frac{b_i + b_j}{2} \right) \]  

(8)

Table 1 gives the pure component parameters, \( T_c, P_c, \omega_i, \) and \( k_1. \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( T_c ) (K)</th>
<th>( P_c ) (MPa)</th>
<th>( \omega )</th>
<th>( k_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>304.21</td>
<td>7.382</td>
<td>0.225</td>
<td>0.04285</td>
</tr>
<tr>
<td>Methanol</td>
<td>512.64</td>
<td>8.097</td>
<td>0.565</td>
<td>-0.16816</td>
</tr>
<tr>
<td>Ethanol</td>
<td>513.92</td>
<td>6.148</td>
<td>0.644</td>
<td>-0.03374</td>
</tr>
<tr>
<td>Water</td>
<td>647.29</td>
<td>22.09</td>
<td>0.344</td>
<td>-0.06635</td>
</tr>
</tbody>
</table>

2. Calculation method

For a multicomponent system, the VLE is obtained equating the fugacities of each component in the vapor phase and in the liquid phases:

\[ f_i^V(P,T) = f_i^L(P,T) \]  

(9)

\[ \varphi_i^V y_i P = \varphi_i^L x_i P \]

where \( \varphi_i \) is the fugacity coefficient of component \( i \) (1=CO\(_2\)), that is easily obtained from the equation of state. For each phase,

\[ \sum_{i=1}^{N} y_i = 1; \sum_{i=1}^{N} x_i = 1 \]  

(10)

where \( N \) is the number of components. For the binary systems VLE data were used to correlate the cross interaction parameters \( k_{ij} \) and \( k_{ji}. \) The Simplex optimization method was used for the parameter regression using the objective function
\[ F = \sum_{j=1}^{n} \left[ 0.6 \times (x_{i,j}^{\text{exp}} - x_{i,j}^{\text{cal}})^2 + 0.4 \times (y_{i,j}^{\text{exp}} - y_{i,j}^{\text{cal}})^2 \right] \] (11)

where \( n \) is the number of the experimental data points. The temperature dependence of the interaction parameters was required because different experimental data were used under various temperatures; typically, they are expressed by linear relationships,

\[
k_{ij} = c_{ij} + d_{ij} T \quad k_{ji} = c_{ji} + d_{ji} T
\] (12)

3. Results of the three binaries

Figure 1 compares the calculated VLE data at 45 °C with the parameters listed in Table 2. Figure 1a shows a critical pressure of 10.8 MPa with the CO\(_2\) molar fraction of 0.882 for the CO\(_2\)(1)/methanol (2) mixture at 45 °C, therefore, the system is supercritical fluid when the pressure is larger than 10.8 MPa and CO\(_2\) molar fraction larger than 0.882. Figure 1b also indicates a critical pressure of 10.5 MPa with the CO\(_2\) molar fraction of 0.903 for the CO\(_2\)/ethanol system at 45 °C, suggesting the system is supercritical fluid when the pressure is larger than 10.5 MPa and CO\(_2\) molar fraction larger than 0.903. Yet Figure 1c reveals that the CO\(_2\)/water system does not appear supercritical fluid with vapor-liquid two phases at 45 °C and pressures up to 20 MPa.

<table>
<thead>
<tr>
<th>System</th>
<th>( k_{ij} )</th>
<th>( c_{ij} \times 10^4 )</th>
<th>( k_{ji} )</th>
<th>( c_{ji} \times 10^4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)(1)/methanol(2)</td>
<td>-0.1776</td>
<td>7.543</td>
<td>0.000002466</td>
<td>2.243</td>
</tr>
<tr>
<td>CO(_2)(1)/ethanol(2)</td>
<td>-0.02512</td>
<td>4.488</td>
<td>0.003956</td>
<td>2.714</td>
</tr>
<tr>
<td>CO(_2)(1)/water(2)</td>
<td>-0.4832</td>
<td>12.02</td>
<td>0.1729</td>
<td>1.098</td>
</tr>
</tbody>
</table>

† Binary interaction parameters obtained from [2]; †† Binary interaction parameters correlated with VLE data from [3] (290K-330K).

According to the added CO\(_2\), the estimated molar fractions of CO\(_2\) are 0.92 and 0.89, respectively, for 1ml ethanol and 1ml methanol in a high-pressure
visual vessel (the overall volume is about 12 ml), therefore, for the both cases, the mixtures are in supercritical state as watched by the visual vessel.

**Literature Cited**


Figure S1. Topographic images of PS-b-P4VP thin film spun-cast using toluene and subsequent thermal annealing at 130 °C for 60 h.

Figure S2. XPS core level scans for C1s and N1s of PS-b-P4VP films before (dotted line) and after (solid line) the CO2/methanol process.
Figure S3. Photographs of water droplets placed on the PS-b-P4VP films: (a) the as-cast film (the contact angle = 102.7°); (b) the processed film (the contact angle = 51.2°) at 20 MPa, 45 °C for 0.5 h.

Figure S4. The 638 nm excited Raman spectra of porous PPy film.

Figure S5. SEM image of a platinum replica of the nanoporous PS-b-P4VP film obtained by a CO₂/methanol
Figure S6. Reversible ammonia gas sensing performance of porous PPy film-1 (Sample 1).