Isobaric Vapor–Liquid Equilibrium Data for the Binary Systems of Dimethyl Carbonate with Xylene Isomers at 93.13 kPa

Satyajeet S. Yadav,‡ Nilesh A. Mali,* Satish M. Joshi,‡ and Prakash V. Chavan‡

* Chemical Engineering and Process Development Division, CSIR-National Chemical Laboratory, Dr. Homi Bhabha Road, Pune-08, Maharashtra, India
† Chemical Engineering Department, College of Engineering, Bharati Vidyapeeth Deemed University, Pune-08, Maharashtra, India
‡ Supporting Information

ABSTRACT: Isobaric binary vapor–liquid equilibrium (VLE) data for dimethyl carbonate with xylene isomers (p-xylene, m-xylene, o-xylene, and ethylbenzene) were measured at the local atmospheric pressure of 93.13 kPa by using a dynamic recirculation still. The experimental VLE data were tested and found to be thermodynamically consistent by Herington and Van Ness consistency test. The experimental VLE data were correlated using the Wilson, NRTL, and UNIQUAC activity coefficient models and binary interactions parameters were estimated using a suitable objective function. The absolute mean deviation between the experimental and the model predicted values of vapor phase composition and total pressure was well within acceptable limits. No azeotrope was observed in any of the binary pairs and appeared to be easy for separation using conventional distillation method.

INTRODUCTION

Petroleum product continues to dominate as a major source of energy among various available options worldwide. Ever increasing demands of petroleum products have promoted research on gasoline additives (oxygenated compound) in recent years. Because of high oxygen content and good blending property of dimethyl carbonate (DMC), it can be used directly as fuel additive and also a substitute for dimethyl sulfate, methyl halides, and phosgene for methylation reaction.1

It has been used as a single gasoline additive and coadditive with ethanol or butanol and found to show good results.2 DMC has a high solubility in gasoline that may decrease a gasoline mental data have been correlated with three activity coefficient models, Wilson, NRTL, and UNIQUAC, and the binary interaction parameters were estimated that can be used in process modeling.

EXPERIMENTAL SECTION

Materials. Detail specifications of various chemicals used for experimentation are listed in Table 1. The chemicals were used directly without any further purification. Table 2 contains the reported and experimental refractive index ($n_D$) and boiling points ($T_b$).

Apparatus and Procedure. In this study, the VLE experiments were carried out using a glass dynamic type recirculating still. The experimental setup, experimental procedure, and sample analyses were described in detail in previous work by Mali et al.10 Briefly, the apparatus is equipped with a boiling chamber, an insulated Cottrell tube, an insulated equilibrium chamber, a mixing chamber, and a condenser with suitable

Table 1. Component, Supplier, and Purity

<table>
<thead>
<tr>
<th>chemical name</th>
<th>CAS no.</th>
<th>source</th>
<th>purity (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl carbonate (DMC)</td>
<td>616-38-6</td>
<td>Loba chemicals</td>
<td>99</td>
</tr>
<tr>
<td>p-xylene</td>
<td>106-42-3</td>
<td>Loba chemicals</td>
<td>99</td>
</tr>
<tr>
<td>m-xylene</td>
<td>108-38-3</td>
<td>Loba chemicals</td>
<td>99</td>
</tr>
<tr>
<td>o-xylene</td>
<td>95-47-6</td>
<td>Merck chemicals</td>
<td>99</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>100-41-4</td>
<td>Spectrochem</td>
<td>99</td>
</tr>
</tbody>
</table>
coolant circulation. A Wika Hand-held thermometer (Model CTH7000) was used for measuring equilibrium temperature with an accuracy of ±0.01 K. In this apparatus, both liquid and vapor phases were continuously recirculated for faster attainment of equilibrium. The outlet of the vapor line in the condenser was kept open to atmosphere that ensures atmospheric pressure in the VLE still that was 93.13 kPa during experimental work. Sufficiently high cooling rate and condenser area were provided to ensure that there is no vapor escape. Once a constant temperature was reached, which indicates attainment of vapor−liquid equilibrium, both liquid and vapor samples were collected from two different sampling points in separate vials and analyzed for composition using a refractometer. A very small amount of samples (<0.5 mL) were withdrawn so that the equilibrium does not get disturbed. Once the composition of two consecutive samples was found to be same, which indicates vapor−liquid equilibrium, the experiment was stopped. A similar procedure was followed for all other binary compositions.

Sample Analysis. For sample analysis, refractometer from Atago (model-RX-7000i) with an accuracy of ±0.0001 and resolution of 0.00001 was used. Calibration curves (refractive index (n_D) versus mole fraction) were generated before starting the VLE experiments by measuring n_D of the binary solution made of varying proportions of both components covering complete composition range. n_D was measured at 20 °C for all samples. The compositions of both samples (liquid and vapor) were obtained from respective n_D of samples and calibration

Table 2. Refractive Indices (n_D) and Boiling Points (T_b) of Pure Chemicals

<table>
<thead>
<tr>
<th>chemical</th>
<th>refractive index (n_D) at 25 °C</th>
<th>boiling point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>literature</td>
<td>measured</td>
</tr>
<tr>
<td>dimethyl carbonate</td>
<td>1.3666^5,6</td>
<td>1.3664</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-xylene</td>
<td>1.4932^8</td>
<td>1.4929</td>
</tr>
<tr>
<td></td>
<td>1.49286^9</td>
<td></td>
</tr>
<tr>
<td>m-xylene</td>
<td>1.4942^8</td>
<td>1.4943</td>
</tr>
<tr>
<td></td>
<td>1.49443^9</td>
<td></td>
</tr>
<tr>
<td>o-xylene</td>
<td>1.5028^8</td>
<td>1.5022</td>
</tr>
<tr>
<td></td>
<td>1.50177^9</td>
<td></td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>1.4930^8</td>
<td>1.4930</td>
</tr>
<tr>
<td></td>
<td>1.49298^9</td>
<td></td>
</tr>
</tbody>
</table>

“Standard uncertainties u are u(n_D) = 0.0001, u(T) = 0.1 K

Table 3. Antoine Constants

<table>
<thead>
<tr>
<th>chemical</th>
<th>Antoine constants^a</th>
<th>units</th>
<th>temperature range (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethyl carbonate^12</td>
<td>A 6.4338, B 1413.00</td>
<td>P = kPa, T = K</td>
<td>273.15−548.0</td>
</tr>
<tr>
<td>p-xylene^6,8</td>
<td>A 6.11543, B 1453.43</td>
<td>P = kPa, T = K</td>
<td>300.15−439.15</td>
</tr>
<tr>
<td>m-xylene^6,9</td>
<td>A 6.13399, B 1462.270</td>
<td>P = kPa, T = K</td>
<td>302.15−439.15</td>
</tr>
<tr>
<td>o-xylene^6,9</td>
<td>A 6.12644, B 1476.39</td>
<td>P = kPa, T = K</td>
<td>336.15−418.15</td>
</tr>
<tr>
<td>ethylbenzene^6,9</td>
<td>A 6.09070, B 1429.55</td>
<td>P = kPa, T = K</td>
<td>263.15−409.15</td>
</tr>
</tbody>
</table>

“Antoine equation no 2.

Figure 1. Calibration curve for p-xylene (1) + DMC (2) system. •, measured n_D at 293.15 K versus mole fraction of p-xylene (x_1); ---, third order polynomial.

Figure 2. Calibration curve for m-xylene (1) + DMC (2) system. •, measured n_D at 293.15 K versus mole fraction of m-xylene (x_1); ---, third order polynomial.
equation obtained by fitting appropriate polynomial equation to the calibration data.

Data Reduction. At experimental pressure of 93.13 kPa, the vapor phase could be assumed to be an ideal gas. Therefore, modified Raoult's law (eq 1) that takes into account only the liquid phase nonideality can be used for VLE calculations

\[ \gamma_i P = x_i P_{i}^{sat} \]  

where, \( x_i \) and \( \gamma_i \) are the liquid and vapor phase mole fraction of component \( i \) in equilibrium state, \( P \) is the total pressure, \( \gamma_i \) is the activity coefficient of component \( i \) in the liquid phase, and

\[ P_{i}^{sat} \]  

is pure component vapor pressure. The vapor pressure of the pure components used in the vapor–liquid equilibrium calculations are obtained through the Antoine equation (eq 2)

\[ \log(P_i^{sat}/\text{kPa}) = A - \left( \frac{B}{(T/K) + C} \right) \]  

Antoine constants required for calculating vapor pressure are given in Table 3.

The liquid-phase activity coefficients \( \gamma_i \) were estimated using activity coefficient models such as Wilson, NRTL, and UNIQUAC. The experimental activity coefficient was calculated using eq 3 that is obtained by rearranging eq 1. Relative volatility and excess Gibbs energy were obtained by eq 4 and S, respectively.

| Table 5. Experimental VLE Data for p-Xylene (1) + DMC (2) at 93.13 kPa* |
|---|---|---|---|---|---|---|
| T/K | \( x_1 \) | \( y_1 \) | \( \gamma_1 \) | \( \gamma_2 \) | \( \alpha_{21} \) | \( \Delta G^e/RT \) |
| 360.73 | 0 | 0 | 1 | 0 | 0.001 |
| 361.49 | 0.0551 | 0.0284 | 2.250 | 1.003 | 1.995 | 0.048 |
| 362.26 | 0.1334 | 0.0609 | 1.940 | 1.031 | 2.372 | 0.115 |
| 363.55 | 0.2270 | 0.0852 | 1.522 | 1.011 | 3.013 | 0.155 |
| 364.62 | 0.3045 | 0.1089 | 1.397 | 1.130 | 3.580 | 0.187 |
| 365.49 | 0.3575 | 0.1236 | 1.309 | 1.172 | 3.945 | 0.198 |
| 367.65 | 0.4678 | 0.1598 | 1.199 | 1.267 | 4.620 | 0.211 |
| 369.75 | 0.5688 | 0.1857 | 1.065 | 1.421 | 5.785 | 0.187 |
| 370.83 | 0.7372 | 0.2935 | 1.040 | 1.658 | 6.752 | 0.161 |
| 384.79 | 0.8416 | 0.4386 | 1.038 | 1.715 | 6.802 | 0.117 |
| 396.71 | 0.9369 | 0.6856 | 1.017 | 1.744 | 6.806 | 0.051 |
| 403.24 | 0.9749 | 0.8466 | 1.001 | 1.806 | 7.026 | 0.016 |
| 408.37 | 1 | 1 | 1 | 1.000 |

*Standard uncertainties \( u(x_1) = 0.001, u(y_1) = 0.001, u(T) = 0.1 \text{ K}, u(P) = 0.1 \text{ kPa}. \)

| Table 6. Experimental VLE Data for m-Xylene (1) + DMC (2) at 93.13 kPa* |
|---|---|---|---|---|---|---|
| T/K | \( x_1 \) | \( y_1 \) | \( \gamma_1 \) | \( \gamma_2 \) | \( \alpha_{21} \) | \( \Delta G^e/RT \) |
| 360.73 | 0 | 0 | 1 | 0 | 0.001 |
| 361.20 | 0.0695 | 0.0229 | 1.446 | 1.001 | 3.189 | 0.027 |
| 363.10 | 0.1328 | 0.0439 | 1.404 | 1.021 | 3.338 | 0.063 |
| 363.66 | 0.1725 | 0.0571 | 1.378 | 1.037 | 3.446 | 0.085 |
| 364.16 | 0.1973 | 0.0642 | 1.331 | 1.044 | 3.583 | 0.091 |
| 369.96 | 0.3935 | 0.1425 | 1.208 | 1.056 | 3.903 | 0.108 |
| 373.53 | 0.5061 | 0.1853 | 1.080 | 1.106 | 4.507 | 0.089 |
| 377.03 | 0.5973 | 0.2386 | 1.048 | 1.143 | 4.735 | 0.082 |
| 383.50 | 0.7279 | 0.3487 | 1.020 | 1.201 | 4.997 | 0.064 |
| 389.23 | 0.8145 | 0.4618 | 1.009 | 1.241 | 5.118 | 0.047 |
| 394.72 | 0.8792 | 0.5869 | 1.006 | 1.261 | 5.121 | 0.034 |
| 399.19 | 0.9293 | 0.7064 | 1.005 | 1.362 | 5.460 | 0.027 |
| 409.13 | 1 | 1 | 1 | 1.000 |

*Standard uncertainties \( u(x_1) = 0.001, u(y_1) = 0.001, u(T) = 0.1 \text{ K}, u(P) = 0.1 \text{ kPa}. \)

| Table 4. Polynomial Equation for Calibration Curves |
|---|---|---|
| binary pair | calibration curve | polynomial equation |
| p-xylene + DMC | Figure 1 | \( y = 0.0133x_1^3 - 0.0596x_1^2 + 0.1732x_1 + 1.3688 \) |
| m-xylene + DMC | Figure 2 | \( y = 0.0112x_1^3 - 0.0564x_1^2 + 0.1733x_1 + 1.3689 \) |
| o-xylene + DMC | Figure 3 | \( y = 0.0087x_1^3 - 0.0525x_1^2 + 0.1797x_1 + 1.369 \) |
| ethylbenzene + DMC | Figure 4 | \( y = 0.0013x_1^3 - 0.0419x_1^2 + 0.167x_1 + 1.369 \) |

DOI: 10.1021/jacs.9b00372

---

Figure 3. Calibration curve for p-xylene (1) + DMC (2) system. φ, measured \( n_0 \) at 293.15 K versus mole fraction of p-xylene (\( x_1 \)); −−, third order polynomial.

Figure 4. Calibration curve for ethylbenzene (1) + DMC (2) system. φ, measured \( n_0 \) at 293.15 K versus mole fraction of ethylbenzene (\( x_1 \)); −−, third order polynomial.
Ethylbenzene (1) + DMC (2) at 93.13 kPa

Table 8. Experimental VLE Data for the System Ethylbenzene (1) + DMC (2) at 93.13 kPa

<table>
<thead>
<tr>
<th>T/K</th>
<th>x₁</th>
<th>y₁</th>
<th>y₂</th>
<th>α₁₂</th>
<th>G⁺/RT</th>
</tr>
</thead>
<tbody>
<tr>
<td>360.73</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>361.48</td>
<td>0.0541</td>
<td>0.0173</td>
<td>1.708</td>
<td>1.014</td>
<td>3.253</td>
</tr>
<tr>
<td>362.09</td>
<td>0.0888</td>
<td>0.0281</td>
<td>1.657</td>
<td>1.021</td>
<td>3.365</td>
</tr>
<tr>
<td>363.52</td>
<td>0.1509</td>
<td>0.0492</td>
<td>1.617</td>
<td>1.023</td>
<td>3.432</td>
</tr>
<tr>
<td>365.18</td>
<td>0.2323</td>
<td>0.0763</td>
<td>1.532</td>
<td>1.043</td>
<td>3.664</td>
</tr>
<tr>
<td>367.71</td>
<td>0.3590</td>
<td>0.1159</td>
<td>1.375</td>
<td>1.105</td>
<td>4.273</td>
</tr>
<tr>
<td>368.68</td>
<td>0.4149</td>
<td>0.1249</td>
<td>1.239</td>
<td>1.163</td>
<td>4.699</td>
</tr>
<tr>
<td>374.88</td>
<td>0.5870</td>
<td>0.2097</td>
<td>1.185</td>
<td>1.232</td>
<td>5.357</td>
</tr>
<tr>
<td>382.02</td>
<td>0.7345</td>
<td>0.3305</td>
<td>1.176</td>
<td>1.319</td>
<td>5.602</td>
</tr>
<tr>
<td>390.84</td>
<td>0.8426</td>
<td>0.4525</td>
<td>1.060</td>
<td>1.424</td>
<td>6.478</td>
</tr>
<tr>
<td>397.46</td>
<td>0.9025</td>
<td>0.5665</td>
<td>1.014</td>
<td>1.527</td>
<td>7.086</td>
</tr>
<tr>
<td>404.50</td>
<td>0.9498</td>
<td>0.7269</td>
<td>1.007</td>
<td>1.560</td>
<td>7.107</td>
</tr>
<tr>
<td>414.41</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 9. Experimental and Calculated Relative Volatility Values for DMC + p-Xylene

Table 10. Experimental and Calculated Relative Volatility Values for DMC + m-Xylene

Table 11. Experimental and Calculated Relative Volatility Values for DMC + o-Xylene

\[ G^\pm = x_i \ln \gamma_i + x_2 n \gamma_2 \] (5)

RESULTS AND DISCUSSION

The calibration curves were generated by measuring \( n_D \) at 293.15 K for various different compositions of binary mixture (p-xylene + DMC, m-xylene + DMC, o-xylene + DMC, and ethylbenzene + DMC) covering complete composition range and are as given in Figures 1–4. The samples were prepared using an electronic weighing balance with an accuracy of ±0.1 mg. A suitable polynomial equation was fitted to the experimental \( n_D \) versus mole fraction data using Microsoft Excel to obtain polynomial constants of the equation. The polynomial equations used for composition measurement are given in Table 4. The experimental data of \( n_D \) for various different binary mixtures (mole fractions) used for generating calibration curve is given in the Supporting Information document.

The experimental VLE data along with experimental activity coefficient, relative volatility and excess Gibbs energy for p-xylene + DMC, m-xylene + DMC, o-xylene + DMC, and ethylbenzene + DMC pairs is listed in Tables 5–8, respectively. Uncertainty in \( n_D \) measurement (±0.0001) and the fitting accuracy of calibration curve contributes to the uncertainty of molar fraction measurement of the samples. In the present work, each sample was analyzed at least three times, and the average uncertainty in mole fraction was estimated, which turned out to be ±0.001.13

The experimental VLE data (see Tables 9–12) for all systems were regressed with Wilson, NRTL, and UNIQUAC activity...
coefficients for minimizing the objective function given by eq 6 to estimate the binary interaction parameters.

\[
\text{OF} = \sum_{i=1}^{N} \left( \frac{y_{1i}^{\text{exp}} - y_{1i}^{\text{cal}}}{y_{1i}^{\text{exp}}} \right) + \left( \frac{P_{i}^{\text{exp}} - P_{i}^{\text{cal}}}{P_{i}^{\text{exp}}} \right)
\]

where, \(N\) is the number of data points, \(y_{1i}^{\text{exp}}\) and \(P_{i}^{\text{exp}}\) are the experimental vapor mole fraction of component 1 and total pressure, respectively and \(y_{1i}^{\text{cal}}\) and \(P_{i}^{\text{cal}}\) are the calculated vapor mole fraction of component 1 and total pressure, respectively, using the activity coefficient model with estimated interaction parameters. While regressing NRTL model one of the three parameter of the model (\(\alpha\)) was kept constant at 0.3. The \(r\) and \(q\) parameters, which are structural volume and area parameter for the UNIQUAC model, respectively, used for regressing UNIQUAC model, are listed in Table 13. The binary interaction parameters (BIP) obtained through regression for Wilson, NRTL, and UNIQUAC are given in Table 17. The fitting of

---

**Table 12. Experimental and Calculated Relative Volatility Values for DMC + Ethylbenzene**

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(\alpha_{12}) exp</th>
<th>(\alpha_{12}) NRTL</th>
<th>(\alpha_{12}) UNIQUAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>361.24</td>
<td>1.822</td>
<td>1.754</td>
<td>1.954</td>
</tr>
<tr>
<td>361.55</td>
<td>1.947</td>
<td>1.901</td>
<td>2.057</td>
</tr>
<tr>
<td>362.91</td>
<td>2.539</td>
<td>2.534</td>
<td>2.518</td>
</tr>
<tr>
<td>364.85</td>
<td>3.139</td>
<td>3.266</td>
<td>3.137</td>
</tr>
<tr>
<td>367.04</td>
<td>3.781</td>
<td>3.931</td>
<td>3.750</td>
</tr>
<tr>
<td>368.97</td>
<td>4.219</td>
<td>4.373</td>
<td>4.196</td>
</tr>
<tr>
<td>373.77</td>
<td>5.033</td>
<td>5.088</td>
<td>4.992</td>
</tr>
<tr>
<td>377.14</td>
<td>5.376</td>
<td>5.388</td>
<td>5.362</td>
</tr>
<tr>
<td>383.26</td>
<td>5.816</td>
<td>5.710</td>
<td>5.802</td>
</tr>
<tr>
<td>390.65</td>
<td>6.010</td>
<td>5.884</td>
<td>6.089</td>
</tr>
<tr>
<td>395.26</td>
<td>6.172</td>
<td>5.935</td>
<td>6.200</td>
</tr>
</tbody>
</table>

**Table 13. \(r\) and \(q\) Values for UNIQUAC Model**

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>chemical</th>
<th>(r)</th>
<th>(q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMC</td>
<td>3.048</td>
<td>2.816</td>
</tr>
<tr>
<td>2</td>
<td>p-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>3</td>
<td>m-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>4</td>
<td>o-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>5</td>
<td>ethylbenzene</td>
<td>4.60</td>
<td>3.51</td>
</tr>
</tbody>
</table>

---

Figure 5. \(T-x,y\) plot for the p-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 6. \(T-x,y\) plot for the m-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 7. \(T-x,y\) plot for the o-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 8. \(T-x,y\) plot for the ethylbenzene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

---

**Table 12. Experimental and Calculated Relative Volatility Values for DMC + Ethylbenzene**

<table>
<thead>
<tr>
<th>(T) (K)</th>
<th>(\alpha_{12}) exp</th>
<th>(\alpha_{12}) NRTL</th>
<th>(\alpha_{12}) UNIQUAC</th>
</tr>
</thead>
<tbody>
<tr>
<td>361.24</td>
<td>1.822</td>
<td>1.754</td>
<td>1.954</td>
</tr>
<tr>
<td>361.55</td>
<td>1.947</td>
<td>1.901</td>
<td>2.057</td>
</tr>
<tr>
<td>362.91</td>
<td>2.539</td>
<td>2.534</td>
<td>2.518</td>
</tr>
<tr>
<td>364.85</td>
<td>3.139</td>
<td>3.266</td>
<td>3.137</td>
</tr>
<tr>
<td>367.04</td>
<td>3.781</td>
<td>3.931</td>
<td>3.750</td>
</tr>
<tr>
<td>368.97</td>
<td>4.219</td>
<td>4.373</td>
<td>4.196</td>
</tr>
<tr>
<td>373.77</td>
<td>5.033</td>
<td>5.088</td>
<td>4.992</td>
</tr>
<tr>
<td>377.14</td>
<td>5.376</td>
<td>5.388</td>
<td>5.362</td>
</tr>
<tr>
<td>383.26</td>
<td>5.816</td>
<td>5.710</td>
<td>5.802</td>
</tr>
<tr>
<td>390.65</td>
<td>6.010</td>
<td>5.884</td>
<td>6.089</td>
</tr>
<tr>
<td>395.26</td>
<td>6.172</td>
<td>5.935</td>
<td>6.200</td>
</tr>
</tbody>
</table>

**Table 13. \(r\) and \(q\) Values for UNIQUAC Model**

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>chemical</th>
<th>(r)</th>
<th>(q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DMC</td>
<td>3.048</td>
<td>2.816</td>
</tr>
<tr>
<td>2</td>
<td>p-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>3</td>
<td>m-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>4</td>
<td>o-xylene</td>
<td>4.66</td>
<td>3.54</td>
</tr>
<tr>
<td>5</td>
<td>ethylbenzene</td>
<td>4.60</td>
<td>3.51</td>
</tr>
</tbody>
</table>

---

Figure 5. \(T-x,y\) plot for the p-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 6. \(T-x,y\) plot for the m-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 7. \(T-x,y\) plot for the o-xylene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.

Figure 8. \(T-x,y\) plot for the ethylbenzene (1) + DMC (2); ■, \(T-y\) (experimental at 93.13 kPa); ●, \(T-x\) (experimental at 93.13 kPa); - - -, NRTL model; ••••, Wilson model; ......, UNIQUAC model.
various different activity coefficient models to the experimental data is shown in Figures 5–8. No azeotropic behavior was seen for any of the pair. In fact, vapor and liquid composition curves are quite apart and no pinch was observed for all systems, which indicate an easy separation using conventional distillation column with less number of equilibrium stages.

**Thermodynamic Consistency Test of the Experimental Data.** The thermodynamic consistency of experimental VLE data was checked through the Herington area test and Van Ness test. Parameters to be estimated for Herington method are expressed as follows

\[
D = 100 \times \left[ \int_{x_1=0}^{x_1=1} \frac{1}{T_2} \ln \gamma_1 \, dx_1 \right]
\]

\[
J = 150 \times \left( \frac{T_{\text{max}} - T_{\text{min}}}{T_{\text{min}}} \right)
\]

where the values of \(D\) can be obtained from the ln(\(\gamma_1/\gamma_2\)) versus \(x_1\) plot, and \(T_{\text{max}}\) and \(T_{\text{min}}\) are the maximum and minimum temperatures of the measurement system. The value of \(|D - J|\) should be less than 10 for the isobaric VLE data to be thermodynamically consistent. Van Ness test was also carried for all binary systems. In this method, the experimental data would pass the test if \(\Delta y\) and \(\Delta p\), as calculated using eqs 9 and 10, respectively, are less than or equal to 1.5

\[
\Delta y = \frac{1}{n} \sum_{i=1}^{n} 100 \left| \frac{y_i^{\text{cal}} - y_i^{\text{exp}}}{y_i^{\text{exp}}} \right|
\]

\[
\Delta p = \frac{1}{n} \sum_{i=1}^{n} 100 \left| \frac{P_i^{\text{cal}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right|
\]

**Table 14. Results of Thermodynamic Consistency Tests**

| systems | Herington test | | Wilson | | NRTL | | UNIQUAC | | results |
|---------|---------------|----------------|---------|----------------|----------------|----------------|----------------|--------|
| DMC + p-xylene | 3.02 | 0.78 | 0.60 | 0.47 | 0.78 | 0.57 | 0.94 | passed |
| DMC + m-xylene | 3.56 | 0.21 | 0.64 | 0.36 | 0.85 | 0.29 | 0.76 | passed |
| DMC + o-xylene | 7.69 | 0.84 | 0.43 | 0.90 | 0.39 | 0.91 | 0.75 | passed |
| DMC + ethylbenzene | 8.75 | 0.28 | 0.65 | 0.10 | 0.19 | 0.10 | 0.21 | passed |

**Table 15. Criteria of the Data Consistency Based on Absolute Mean Deviation**

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>parameter</th>
<th>formula</th>
<th>criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>absolute mean deviation in vapor composition</td>
<td>(\delta y = \frac{1}{N} \sum_{i=1}^{n} (y_i^{\text{cal}} - y_i^{\text{exp}}))</td>
<td>(\Delta y \leq 0.01)</td>
</tr>
<tr>
<td>2</td>
<td>absolute mean deviation in total system pressure</td>
<td>(\delta p = \frac{1}{N} \sum_{i=1}^{n} (p_i^{\text{cal}} - p_i^{\text{exp}}))</td>
<td>(\Delta p \leq 1.33)</td>
</tr>
</tbody>
</table>

**Table 16. Absolute Mean Deviations Results**

| systems | absolute mean deviations | Wilson | | NRTL | | UNIQUAC |
|---------|--------------------------|---------|----------------|----------------|----------------|
| DMC + p-xylene | | 0.008 | 0.56 | 0.005 | 0.72 | 0.006 | 0.88 |
| DMC + m-xylene | | 0.002 | 0.59 | 0.004 | 0.79 | 0.003 | 0.71 |
| DMC + o-xylene | | 0.008 | 0.40 | 0.009 | 0.36 | 0.009 | 0.70 |
| DMC + ethylbenzene | | 0.003 | 0.61 | 0.001 | 0.18 | 0.001 | 0.19 |

**Table 17. Binary Interaction Parameters for Different Models**

<table>
<thead>
<tr>
<th>binary system</th>
<th>interaction parameter</th>
<th>NRTL (^a)</th>
<th>Wilson (^b)</th>
<th>UNIQUAC (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-xylene + DMC</td>
<td>(A_{12})</td>
<td>(-789.779)</td>
<td>(1847.663)</td>
<td>(-611.307)</td>
</tr>
<tr>
<td></td>
<td>(A_{11})</td>
<td>(4192.038)</td>
<td>(1551.915)</td>
<td>(1428.215)</td>
</tr>
<tr>
<td></td>
<td>(a)</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-xylene + DMC</td>
<td>(A_{12})</td>
<td>(-1757.749)</td>
<td>(271.185)</td>
<td>(19.398)</td>
</tr>
<tr>
<td></td>
<td>(A_{11})</td>
<td>(3615.399)</td>
<td>(993.026)</td>
<td>(119.711)</td>
</tr>
<tr>
<td></td>
<td>(a)</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>o-xylene + DMC</td>
<td>(A_{12})</td>
<td>(-750.773)</td>
<td>(1109.133)</td>
<td>(-235.438)</td>
</tr>
<tr>
<td></td>
<td>(A_{11})</td>
<td>(3178.326)</td>
<td>(1218.154)</td>
<td>(661.903)</td>
</tr>
<tr>
<td></td>
<td>(A)</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ethylbenzene + DMC</td>
<td>(A_{12})</td>
<td>(-463.773)</td>
<td>(2442.402)</td>
<td>(-191.845)</td>
</tr>
<tr>
<td></td>
<td>(A_{11})</td>
<td>(2995.651)</td>
<td>(665.908)</td>
<td>(723.018)</td>
</tr>
<tr>
<td></td>
<td>(a)</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)The interaction parameters for the NRTL model: \(A_{12}\) (J mol\(^{-1}\)) = \((g_{ij} - g_{ii})/R\). \(^b\)The interaction parameters for the Wilson model: \(A_{12}\) (J mol\(^{-1}\)) = \((\lambda_{ij} - \lambda_{ii})/R\). \(^c\)The interaction parameters for the UNIQUAC model: \(A_{12}\) (J mol\(^{-1}\)) = \((U_{ij} - U_{ii})/R\).
where \( n \) is the total number of experimental data; \( \exp \) are measured values; \( \text{cal} \) are the calculated results that were obtained from the Wilson, NRTL, and UNIQUAC models. The result of the Herington and Van Ness tests are summarized in Table 14. All models fitted well to the experimental VLE data and passed both thermodynamic consistency tests.

Absolute mean deviation between experimental and calculated vapor phase composition \((\delta y)\) and total pressure \((\delta P)\) was also calculated. According to Zhu et al.,\(^{16}\) for isobaric experimental VLE data, both absolute mean deviations should meet the criteria mentioned in Table 15. For all four binary systems, the experimental VLE data satisfies the criteria as given in Table 16.

## CONCLUSIONS

The isobaric VLE data for binary systems of dimethyl carbonate + p-xylene, dimethyl carbonate + m-xylene, dimethyl carbonate + o-xylene, and dimethyl carbonate + ethylbenzene were measured using a dynamic recirculation still at local atmospheric pressure of 93.13 kPa. The VLE data were found thermodynamically consistent according to the Herington and Van Ness test. The experimental VLE data were correlated by the Wilson, NRTL, and UNIQUAC activity coefficient models and all models fitted well for all binary pairs. Absolute mean deviation between experimental and model predicted values for vapor phase composition and total pressure was also found in acceptable limits for a consistent data. As no azeotrope was observed in any system, conventional distillation can be employed for separation of these mixtures. VLE plots also indicate that separation of these systems with conventional distillation column would be easy with significantly less number of stages.

## ASSOCIATED CONTENT

1. Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jced.7b00372.

Additional tables (PDF)

## AUTHOR INFORMATION

### Corresponding Author

*Tel.: +91 20 25902176. Fax: +91 20 21762621. E-mail: na.mali@ncl.res.in.*

**ORCID**

Nilesh A. Mali: 0000-0001-6832-9230

**Notes**

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The Authors are thankful to CSIR-National Chemical Laboratory, Pune (Maharashtra), India for supporting the present work.

## REFERENCES