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# Articles

## VLE and VLLE Measurements of Dimethyl Ether Containing Systems. 2

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In total, 14 isotherms for systems composed of the components nitrogen, carbon dioxide, dimethyl ether (DME), water, ethanol, and 1-propanol were measured. Experimental data for all the phases present, vapor−liquid equilibria (VLE), or vapor−liquid−liquid equilibria (VLLE), in the temperature range (25 to 45) °C and in the pressure range (5 to 102) bar, are presented. The data were not correlated.

### Introduction

In a continuation of a research program involving measurements of VLE and VLLE data,[1,2] the systems nitrogen + DME + water + ethanol, carbon dioxide + DME + water + ethanol, carbon dioxide + DME + ethanol, carbon dioxide + 1-propanol, and carbon dioxide + DME + 1-propanol have been measured. No experimental data points for these systems have previously been published, except for the system carbon dioxide + 1-propanol.[3−5] All the systems have been measured as isotherms at the temperatures (25, 35, and 45) °C and in the pressure range (5 to102) bar. The mole fractions of both the liquid(s) and the vapor phase are given.

### Experimental Section

***Apparatus and Procedures.*** The measurements were previously described in detail.[1] The experimental apparatus is based on a high-pressure autoclave equipped with two windows, a movable sampling needle, and valves for performing on-line sampling from the cell. The equipment can be used to measure both VLE and VLLE, but not LLE, for safety reasons. In the methods applied, liquid samples are taken by recirculation of liquid through a liquid sampling valve, and gas samples are taken by flushing a vapor sampling valve with heated vapor from the cell.

The composition was measured using a Carlo Erba HRGC 5300 gas chromatograph based on pure component calibration. The uncertainty of the measured mole fractions is estimated to be 3%. The uncertainty of the temperature was found to be 0.2 K, while the uncertainty of the pressure was found to be 0.1 bar.

***Chemicals.*** The materials used are listed in Table 1. The purity of each material was checked using GC, and they were used without any further purification.

**Table 1. Materials Used, Supplier, and Purity**

| material | supplier | purity in % |
|---|---|---|
| carbon dioxide | Hede Nielsen | 99.995 |
| nitrogen | Hede Nielsen | 99.995 |
| dimethyl ether | Sigma Aldrich | 99.7 |
| water | J. T. Baker | 99.998 |
| ethanol | Danisco A/S | 99.9 |
| 1-propanol | Merck | 99.5 |

**Table 2. Composition of the Liquid ($x_i$) and Vapor ($y_i$) Phases at the Pressure *p* for the VLE System Nitrogen (1) + DME (2) + Water (3) + Ethanol (4)**

| liquid | | | vapor | | | |
|---|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $y_1$ | $y_2$ | $y_3$ | $p$/bar |
| | | | $T$ = 25.0 °C | | | |
| 0.0000 | 0.2854 | 0.6271 | 0.0000 | 0.9975 | 0.0000 | 4.9 |
| 0.0005 | 0.2860 | 0.6265 | 0.4448 | 0.5541 | 0.0000 | 14.3 |
| 0.0009 | 0.2956 | 0.6162 | 0.5756 | 0.4233 | 0.0000 | 21.7 |
| 0.0018 | 0.2929 | 0.6162 | 0.6877 | 0.3114 | 0.0000 | 36.1 |
| 0.0026 | 0.2945 | 0.6121 | 0.7435 | 0.2553 | 0.0000 | 50.7 |
| 0.0035 | 0.2923 | 0.6151 | 0.7719 | 0.2273 | 0.0000 | 66.7 |
| 0.0043 | 0.2871 | 0.6183 | 0.7878 | 0.2113 | 0.0000 | 80.0 |
| 0.0054 | 0.2883 | 0.6177 | 0.7980 | 0.2011 | 0.0000 | 102.1 |
| | | | $T$ = 35.0 °C | | | |
| 0.0000 | 0.2921 | 0.6188 | 0.0000 | 0.9978 | 0.0000 | 6.2 |
| 0.0005 | 0.2948 | 0.6147 | 0.3422 | 0.6560 | 0.0000 | 14.3 |
| 0.0010 | 0.2945 | 0.6153 | 0.5090 | 0.4900 | 0.0000 | 23.2 |
| 0.0018 | 0.2902 | 0.6171 | 0.6270 | 0.3717 | 0.0000 | 37.1 |
| 0.0026 | 0.2882 | 0.6197 | 0.6834 | 0.3152 | 0.0000 | 50.9 |
| 0.0038 | 0.2905 | 0.6174 | 0.7283 | 0.2708 | 0.0000 | 66.7 |
| 0.0043 | 0.2836 | 0.6213 | 0.7468 | 0.2524 | 0.0000 | 81.7 |
| 0.0055 | 0.2806 | 0.6231 | 0.7652 | 0.2340 | 0.0000 | 101.9 |
| | | | $T$ = 45.0 °C | | | |
| 0.0000 | 0.2416 | 0.6555 | 0.0000 | 0.9966 | 0.0000 | 7.3 |
| 0.0002 | 0.2376 | 0.6513 | 0.2023 | 0.7952 | 0.0000 | 11.7 |
| 0.0006 | 0.2474 | 0.6395 | 0.4163 | 0.5750 | 0.0000 | 21.0 |
| 0.0012 | 0.2403 | 0.6447 | 0.5609 | 0.4371 | 0.0000 | 33.8 |
| 0.0019 | 0.2387 | 0.6460 | 0.6477 | 0.3511 | 0.0000 | 47.7 |
| 0.0028 | 0.2347 | 0.6475 | 0.6995 | 0.2992 | 0.0000 | 66.5 |
| 0.0035 | 0.2296 | 0.6525 | 0.7267 | 0.2721 | 0.0000 | 80.1 |
| 0.0043 | 0.2293 | 0.6508 | 0.7456 | 0.2529 | 0.0000 | 101.4 |

### Results and Discussion

Vapor−liquid equilibrium data for nitrogen + DME + water + ethanol at (25, 35, and 45) °C are presented in Table 2. The system was measured by first adding water + ethanol to the cell followed by DME. The pressure was thereafter increased by adding nitrogen to the cell. The

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**Table 3. Composition of the Liquid ($x_i$) and Vapor ($y_i$) Phases at Pressure *p* for the VLLE System Carbon Dioxide (1) + DME (2) + Water (3) + Ethanol (4)**

| lower liquid | | | upper liquid | | | vapor | | | |
|---|---|---|---|---|---|---|---|---|---|
| $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ | $y_1$ | $y_2$ | $y_3$ | $p$/bar |
| | | | | $T = 25.0$ °C | | | | | |
| 0.0000 | 0.2396 | 0.7164 | | | | 0.0000 | 0.9985 | 0.0000 | 5.1 |
| 0.0152 | 0.1549 | 0.7869 | 0.1305 | 0.5200 | 0.3002 | 0.6413 | 0.3583 | 0.0000 | 14.1 |
| 0.0174 | 0.1163 | 0.8249 | 0.2491 | 0.5260 | 0.1813 | 0.7572 | 0.2425 | 0.0000 | 19.6 |
| 0.0205 | 0.0668 | 0.8730 | 0.3909 | 0.4277 | 0.1473 | 0.8385 | 0.1609 | 0.0000 | 26.7 |
| 0.0180 | 0.0394 | 0.9040 | 0.5480 | 0.3525 | 0.0734 | 0.8900 | 0.1092 | 0.0000 | 34.8 |
| 0.0214 | 0.0334 | 0.9082 | 0.5803 | 0.2907 | 0.1057 | 0.9044 | 0.0946 | 0.0000 | 37.9 |
| | | | | $T = 35.0$ °C | | | | | |
| 0.0000 | 0.2577 | 0.6178 | | | | 0.0000 | 0.9938 | 0.0000 | 5.3 |
| 0.0227 | 0.2250 | 0.6310 | | | | 0.5811 | 0.4179 | 0.0000 | 13.9 |
| 0.0525 | 0.2031 | 0.6292 | | | | 0.7381 | 0.2607 | 0.0000 | 22.0 |
| 0.0521 | 0.1427 | 0.6993 | 0.1925 | 0.3109 | 0.3764 | 0.8174 | 0.1819 | 0.0000 | 29.5 |
| 0.0420 | 0.0946 | 0.7683 | 0.3241 | 0.3230 | 0.2452 | 0.8532 | 0.1456 | 0.0000 | 35.6 |
| 0.0380 | 0.0664 | 0.7978 | 0.4279 | 0.3023 | 0.1773 | 0.8789 | 0.1199 | 0.0000 | 40.4 |
| | | | | $T = 45.0$ °C | | | | | |
| 0.0000 | 0.2412 | 0.6568 | | | | 0.0000 | 0.9972 | 0.0000 | 7.4 |
| 0.0242 | 0.2408 | 0.6348 | | | | 0.5319 | 0.4668 | 0.0000 | 16.2 |
| 0.0416 | 0.2380 | 0.6220 | | | | 0.6440 | 0.3548 | 0.0000 | 21.3 |
| 0.0682 | 0.2281 | 0.6072 | | | | 0.7214 | 0.2771 | 0.0000 | 27.7 |
| 0.0399 | 0.1408 | 0.7320 | 0.1673 | 0.3408 | 0.3893 | 0.7474 | 0.2515 | 0.0000 | 31.3 |
| 0.0345 | 0.1035 | 0.7786 | 0.2525 | 0.3571 | 0.2931 | 0.7906 | 0.2081 | 0.0000 | 36.2 |
| 0.0336 | 0.0756 | 0.8101 | 0.3529 | 0.3375 | 0.2226 | 0.8344 | 0.1642 | 0.0000 | 42.4 |

**Table 4. Composition of the Liquid ($x_i$) and Vapor ($y_i$) Phases at Pressure *p* for the VLE System Carbon Dioxide (1) + DME (2) + Ethanol (3)**

| $x_1$ | $x_2$ | $y_1$ | $y_2$ | $p$/bar | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $p$/bar |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $T = 25.0$ °C | | | | | |
| 0.0000 | 0.5601 | 0.0000 | 0.9883 | 4.2 | 0.2915 | 0.3974 | 0.8269 | 0.1701 | 21.7 |
| 0.1153 | 0.4991 | 0.6411 | 0.3542 | 11.2 | 0.3521 | 0.3698 | 0.8591 | 0.1381 | 25.5 |
| 0.2242 | 0.4387 | 0.7846 | 0.2120 | 17.6 | 0.4538 | 0.3132 | 0.8904 | 0.1068 | 31.8 |
| | | | | $T = 35.0$ °C | | | | | |
| 0.0000 | 0.5319 | 0.0000 | 0.9846 | 5.3 | 0.2876 | 0.3832 | 0.8202 | 0.1761 | 26.5 |
| 0.0722 | 0.4921 | 0.5100 | 0.4811 | 10.7 | 0.3509 | 0.3504 | 0.8517 | 0.1452 | 31.1 |
| 0.1490 | 0.4558 | 0.6901 | 0.3050 | 16.2 | 0.4103 | 0.3181 | 0.8711 | 0.1256 | 35.7 |
| 0.2235 | 0.4162 | 0.7712 | 0.2239 | 21.7 | | | | | |
| | | | | $T = 45.0$ °C | | | | | |
| 0.0000 | 0.4715 | 0.0000 | 0.9863 | 6.1 | 0.2168 | 0.3700 | 0.7755 | 0.2198 | 26.3 |
| 0.0551 | 0.4435 | 0.4675 | 0.5243 | 11.5 | 0.2708 | 0.3473 | 0.8168 | 0.1793 | 31.3 |
| 0.1032 | 0.4231 | 0.6197 | 0.3744 | 15.8 | 0.3486 | 0.3133 | 0.8521 | 0.1441 | 38.0 |
| 0.1638 | 0.3965 | 0.7226 | 0.2719 | 21.4 | | | | | |

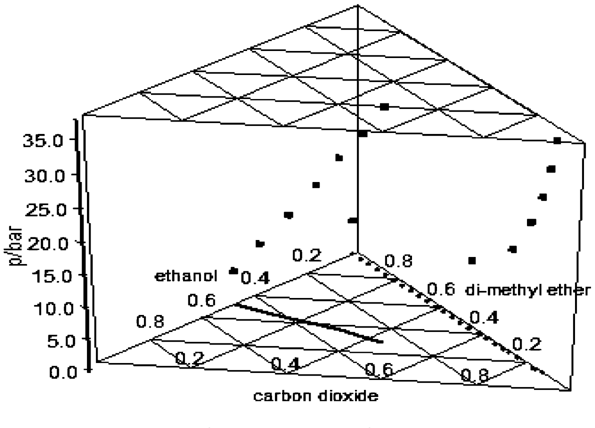

**Figure 1.** 3D plot of the isotherms for the VLE system carbon dioxide + DME + ethanol at $T = 35.0$ °C: liquid phase (—); vapor phase (- - -).

**Table 5. Composition of the Liquid ($x_1$) and Vapor ($y_1$) Phases at the Pressure *p* for the System Carbon Dioxide (1) + 1-Propanol (2)**

| $x_1$ | $y_1$ | $p$/bar | $x_1$ | $y_1$ | $p$/bar |
|---|---|---|---|---|---|
| | | $T = 35.0$ °C | | | |
| 0.0185 | 0.9864 | 4.7 | 0.3385 | 0.9970 | 48.5 |
| 0.0359 | 0.9924 | 8.2 | 0.4068 | 0.9943 | 54.7 |
| 0.0848 | 0.9964 | 16.3 | 0.4142 | 0.9961 | 55.7 |
| 0.1508 | 0.9968 | 25.6 | 0.5281 | 0.9957 | 64.3 |
| 0.2202 | 0.9964 | 35.7 | 0.6765 | 0.9952 | 69.1 |
| | | $T = 45.0$ °C | | | |
| 0.0200 | 0.9855 | 5.4 | 0.2892 | 0.9966 | 49.2 |
| 0.0534 | 0.9934 | 12.1 | 0.3502 | 0.9964 | 56.7 |
| 0.0836 | 0.9958 | 18.4 | 0.4428 | 0.9949 | 66.6 |
| 0.1276 | 0.9964 | 25.0 | 0.5269 | 0.9923 | 73.7 |
| 0.1657 | 0.9965 | 32.2 | 0.7001 | 0.9876 | 83.3 |
| 0.2276 | 0.9971 | 40.5 | | | |

system showed no sign of any second liquid phase, and the solubility of nitrogen in the liquid phase was small. The solubility of water in the vapor phase was so small that it could not be detected properly with the GC used in this work.

Vapor−liquid−liquid equilibrium data for carbon dioxide + DME + water + ethanol at (25, 35, and 45) °C are presented in Table 3. The experimental procedure was the same as that for the previous system. A second liquid phase would form after raising the pressure, and this second phase would expand while the vapor phase would shrink as the pressure was raised. The measurements were stopped when the system was close to becoming an LLE system. The solubility of water in the vapor phase was so small that it could not be detected on the used GC.

**Table 6. Composition of the Liquid ($x_i$) and Vapor ($y_i$) Phases at Pressure *p* for the VLE System Carbon Dioxide (1) + DME (2) + 1-Propanol (3)**

| $x_1$ | $x_2$ | $y_1$ | $y_2$ | $p$/bar | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $p$/bar |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $T = 25.0$ °C | | | | | |
| 0.0000 | 0.5901 | 0.0000 | 0.9950 | 4.3 | 0.2792 | 0.4459 | 0.8120 | 0.1865 | 21.6 |
| 0.1024 | 0.5518 | 0.5998 | 0.3980 | 10.8 | 0.3597 | 0.3953 | 0.8577 | 0.1409 | 27.2 |
| 0.2118 | 0.4872 | 0.7564 | 0.2420 | 17.2 | 0.3734 | 0.3827 | 0.8790 | 0.1197 | 31.3 |
| | | | | $T = 35.0$ °C | | | | | |
| 0.0000 | 0.1741 | 0.0000 | 0.9949 | 5.2 | 0.2232 | 0.4294 | 0.7695 | 0.2288 | 22.6 |
| 0.0836 | 0.4987 | 0.5623 | 0.4345 | 11.9 | 0.2810 | 0.4012 | 0.8128 | 0.1852 | 27.0 |
| 0.1429 | 0.4842 | 0.6840 | 0.3136 | 16.3 | 0.3523 | 0.3624 | 0.8474 | 0.1509 | 32.3 |
| | | | | $T = 45.0$ °C | | | | | |
| 0.0000 | 0.5707 | 0.0000 | 0.9937 | 6.3 | 0.1813 | 0.4552 | 0.7219 | 0.2756 | 22.7 |
| 0.0600 | 0.5037 | 0.4304 | 0.5615 | 12.2 | 0.2480 | 0.4160 | 0.7774 | 0.2203 | 29.2 |
| 0.1246 | 0.4763 | 0.6367 | 0.3599 | 18.0 | 0.3160 | 0.3770 | 0.8176 | 0.1801 | 35.1 |

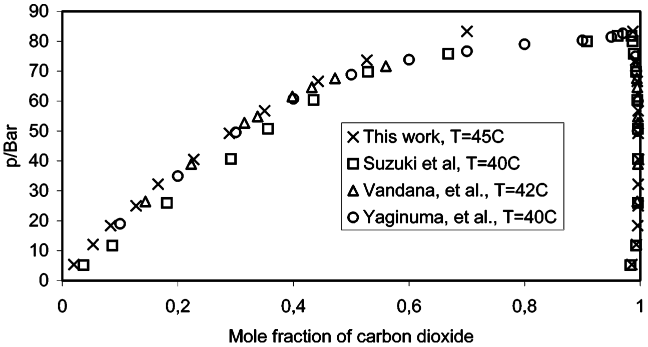

**Figure 2.** VLE curves for the system carbon dioxide (1) + 1-propanol (2) taken from different sources.

Vapor−liquid equilibrium data for carbon dioxide + DME + ethanol at (25, 35, and 45) °C are presented in Table 4. No second liquid phase was found. As the pressure was increased, the liquid phase would expand, and the measurements were stopped when the system was close to becoming a one-phase system. Figure 1 shows a 3D plot of one of the isotherms in Table 4. The figure shows the two phases both as 2D projection lines onto the composition space and as 3D points in the composition, pressure space.

Vapor−liquid equilibrium data for carbon dioxide + 1-propanol at (35 and 45) °C are presented in Table 5. No second liquid phase was found. As the pressure was raised, the liquid phase would expand, and the measurements were stopped when the system was close to becoming a one-phase system. A comparison between literature data and the data in Table 5 is shown in Figure 2. As can be seen, some minor deviations between data sets are observed. Only one data point is reported herein for the $CO_2$ mole fraction range 0.6 to 0.95, which is approximately 5% higher than the literature values. However, this deviation is apparently less than that seen between the literature data from refs 4 and 5 both measured at 40 °C.

Vapor−liquid equilibrium data for carbon dioxide + DME + 1-propanol at (25, 35, and 45) °C are presented in Table 6. No second liquid phase was found. As the pressure was increased, the liquid phase would expand, and the measurements were stopped when the system was close to becoming a one-phase system.

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