# High-Pressure Vapor−Liquid Equilibria in the Systems Nitrogen + Dimethyl Ether, Methanol + Dimethyl Ether, Carbon Dioxide + Dimethyl Ether + Methanol, and Nitrogen + Dimethyl Ether + Methanol

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Isothermal ($P$, $T$, $x$, $y$) data have been measured for the binary and ternary systems nitrogen + dimethyl ether at 15, 35, and 45 °C, dimethyl ether + methanol at 80 °C, carbon dioxide + dimethyl ether + methanol at 40 and 60 °C, and nitrogen + dimethyl ether + methanol at 40 and 15 °C. The pressure range under investigation was up to 9.5 MPa. The experimental data for the binary systems were correlated with the SRK equation of state using the MHV2 mixing rule combined with the UNIFAC or UNIQUAC model for the expression of the excess Gibbs energy. The experimental data for the ternary systems have been compared with those predicted by means of the same models, and the results are discussed by comparison. The binary system of nitrogen + dimethyl ether as well as the two ternary systems have not previously been studied.

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## Introduction

Research in the field of alternative fuel technologies goes all the way from coal cleaning and gasification to methanol and dimethyl ether synthesis from syngas, followed by its subsequent conversion to value-added chemicals. The main advantage of using these fuels is that they give considerably less pollution than diesel oil. Haldor Topsoe A/S develops such technologies for which accurate experimental gas solubility data for systems containing dimethyl ether and/or methanol are desirable for the design of the separation unit in the plant. In addition, reliable models for phase equilibria calculation are needed for generalizations.

An apparatus for accurate determination of gas solubility in dimethyl ether has been constructed and validated previously.[1] High-pressure solubilities of carbon dioxide, carbon monoxide, and hydrogen in dimethyl ether have already been reported.[1,2] The present work is a continuation of the project and brings new information for the nitrogen solubility in dimethyl ether, and for the carbon dioxide and nitrogen solubility in dimethyl ether + methanol.

## Experimental Section

The measurements have been carried out using a 700 $cm^3$ cell made of steel and designed for temperatures from 0 to 200 °C and pressures up to 18 MPa. The details of the equipment and procedure used for high-pressure VLE determination have been described in detail elsewhere.[1] The temperature in the cell was measured by a S1220 Systemteknik AB digital thermometer equipped with a Pt-resistance probe calibrated by measuring the melting and boiling points of distilled water. The accuracy for the temperature instrument was ±0.01 K, but for temperature measurements it is ±0.05 K. The pressure was measured using a digital HBM Uberdruck Gage Pressure Meter calibrated against a Desgranges Et Huot 26000 dead weight tester. The accuracy of the pressure gage and of pressure measurements was ±0.01 MPa. The composition of the liquid and vapor phases was determined using a gas chromatograph Carlo Erba with hot wire detector (HWD) with estimated accuracy 1% in mole fraction. The sampling valve for the liquid phase was a Rheodyne Model 7410 with a 0.5 $\mu$L internal sample loop. The sampling valve for the gas phase was a Rheodyne Model 7013 with 500 $\mu$L external sample loop. The integrator used for the gas chromatograph was a Hewlett-Packard 3396 Series II. The characteristics of the gas chromatographic analysis were as follows: injector and detector temperatures were 200 °C; filament temperature was 250 °C; column was a 3 m Haysep T 80/100 mesh operating up to 160 °C; oven temperature was 150 °C. The flow rate of helium, used as carrier gas, was 18 $mL\cdot min^{-1}$. The chromatograph was calibrated by means of binary mixtures of known composition carefully prepared by weighing using a balance with a 0.001 g uncertainty. A mixture prepared in a 50 mL cylinder was expanded into a 1000 mL cylinder. Both cylinders were properly evacuated in advance, for 2−3 h. The two-cylinder system was connected to the gas sample line in the oven and warmed to about 100 to 150 °C to ensure that the entire mixture was gaseous before injection into the gas chromatograph. For each mixture of known composition at least four injections of 500 $\mu$L (vapor, at atmospheric pressure) were performed for all calibration points, and they were reproduced with <0.5% peak area difference. This proved that the synthetically prepared mixtures were homogeneous gas-phase mixtures. The composition versus area percentages thus determined have been correlated with a function of one parameter. The

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**Table 1. Calibration Results for the Gas Chromatograph**

| system | $f_{21}$[a] | mean deviation in composition | max. deviation in composition |
|---|---|---|---|
| nitrogen (1) + dimethyl ether (2) | 0.6856 | 0.010 | 0.026 |
| methanol (1) + dimethyl ether (2) | 0.7978 | 0.009 | 0.025 |
| carbon dioxide (1) + dimethyl ether (2) | 0.8059 | 0.003 | 0.012 |

[a] $f_{21}$ denotes the response factor for dimethyl ether relative to component 1.

**Table 2. Composition of the Liquid, $x_1$, and Vapor Phases, $y_1$, at the Pressure, $P$, and Temperature, $t$, for the Binary Nitrogen (1) + Dimethyl Ether (2) System**

| $x_1$ | $y_1$ | $P$/MPa | $x_1$ | $y_1$ | $P$/MPa |
|---|---|---|---|---|---|
| | | $t$ = 15.00 °C | | | |
| 0.000 | 0.000 | 0.44 | 0.035 | 0.845 | 4.83 |
| 0.004 | 0.473 | 1.00 | 0.039 | 0.857 | 5.37 |
| 0.008 | 0.664 | 1.53 | 0.043 | 0.858 | 5.89 |
| 0.014 | 0.743 | 2.24 | 0.046 | 0.868 | 6.41 |
| 0.017 | 0.783 | 2.77 | 0.049 | 0.870 | 6.93 |
| 0.021 | 0.807 | 3.27 | 0.054 | 0.876 | 7.44 |
| 0.025 | 0.825 | 3.80 | 0.059 | 0.881 | 7.96 |
| 0.030 | 0.839 | 4.33 | 0.060 | 0.882 | 8.48 |
| | | $t$ = 35.00 °C | | | |
| 0.000 | 0.000 | 0.78 | 0.039 | 0.771 | 5.36 |
| 0.008 | 0.393 | 1.60 | 0.044 | 0.780 | 5.81 |
| 0.012 | 0.536 | 2.17 | 0.050 | 0.788 | 6.34 |
| 0.017 | 0.615 | 2.71 | 0.054 | 0.796 | 6.84 |
| 0.021 | 0.666 | 3.16 | 0.059 | 0.805 | 7.34 |
| 0.026 | 0.718 | 3.72 | 0.063 | 0.806 | 7.89 |
| 0.030 | 0.743 | 4.25 | 0.067 | 0.808 | 8.43 |
| 0.034 | 0.756 | 4.72 | | | |
| | | $t$ = 45.00 °C | | | |
| 0.000 | 0.000 | 1.02 | 0.039 | 0.722 | 5.35 |
| 0.005 | 0.275 | 1.57 | 0.043 | 0.740 | 5.88 |
| 0.010 | 0.380 | 2.14 | 0.049 | 0.749 | 6.37 |
| 0.014 | 0.484 | 2.68 | 0.051 | 0.761 | 6.70 |
| 0.020 | 0.553 | 3.24 | 0.055 | 0.765 | 7.23 |
| 0.024 | 0.610 | 3.80 | 0.063 | 0.772 | 7.77 |
| 0.028 | 0.666 | 4.30 | 0.071 | 0.775 | 8.33 |
| 0.033 | 0.706 | 4.82 | | | |

theoretical background for adopting this type of correlation is based on the assumption that the detector output is linear in concentration. In a binary system 1−2, the function is given by

$$x_1 = \frac{a_1}{a_1 + (1 - a_1)\frac{R_{f2}}{R_{f1}}} \tag{1}$$

where $x_1$ is the mole fraction of component 1, $a_1 = A_1/(A_1 + A_2)$ denotes the area ratio, $R_{fi}$ is the proportionality factor between area $A_i$ and number of moles of component $i$, $R_{f2}/R_{f1} = f_{21}$ is the so-called relative response factor of the GC-detector for component 2 relative to component 1, and $f_{21}$ is the parameter obtained after correlation. Since the sample loop used for the liquid phase (0.5 $\mu$L) is $10^3$ times smaller than that used for the vapor phase, we assumed that we worked in the linear region of the detector for the liquid phase, too. This was verified further (for all systems investigated experimentally), since the total area for each sample at the GC-integrator for the liquid-phase analysis was smaller than that corresponding to the vapor phase. Therefore, the same calibration curve was used for liquid composition determination. For the ternary systems the procedure using the binary calibration curves has been used. The composition of the ternary systems has been calculated using the following formulas:

$$x_1 = \frac{f_{12}(a_1/a_2)}{S} \tag{2}$$

$$x_2 = \frac{1}{S} \tag{3}$$

$$x_3 = \frac{f_{32}(a_3/a_2)}{S} \tag{4}$$

where $S = 1 + f_{12}(a_1/a_2) + f_{32}(a_3/a_2)$, $a_i$ represents the area ratio of component $i$ from the ternary system analysis, and $f_{ij}$ is the relative response factor determined from the calibration data for the binary system ($j$) + ($i$), $f_{ij} = 1/f_{ji}$.

***Materials.*** The components used were of good purity, as follows: dimethyl ether, Fluka, min. 99.8%; nitrogen and carbon dioxide, AGA, min. 99.0%; and methanol, Riedel-de Haen, min. 99.8% with a maximum of 0.05% water content. The chemicals were used without further purification, and the liquid compounds were not degassed before their use. For dimethyl ether, nitrogen, and carbon dioxide, no impurity was detected by GC analyses.

## Results and Discussion

To determine the composition for the binary and ternary systems to be studied at equilibrium, the calibration curves for the gas chromatograph were needed. Following the procedure described above, three calibration curves have been determined for the following binary systems: nitrogen + dimethyl ether, dimethyl ether + methanol, and carbon dioxide + dimethyl ether. The relative response factors for dimethyl ether in each of the three binaries have been obtained, and they are shown in Table 1 together with the results of the correlation by means of eq 1. The mean deviation of the calibration curve can be used just as an estimate for the accuracy of the composition, since it includes the inaccuracy in the binary mixture preparation, which is difficult to evaluate. No point has been excluded from the experimental calibration data sets, since they were well distributed around the curve. The slightly higher value obtained for the nitrogen + dimethyl ether system may be due to some traces of air which could not be separated from the nitrogen signal to the GC-detector. However, no systematic errors have been found for this case. For the VLE measurements, the reproducibility in the liquid composition determination was 0.002 in mole fraction, and for the vapor phase, it was 0.005.

***Binary Nitrogen + Dimethyl Ether System.*** The isothermal ($P$, $x$, $y$) experimental data for the binary nitrogen (1) + dimethyl ether (2) system at 15, 35, and 45 °C are shown in Table 2 and Figure 1. The SRK equation of state has been used to correlate the results. The mixing rules used were MHV2 (modified Huron Vidal second order) in combination with the modified UNIFAC and UNIQUAC models. The mixing rule combines the SRK equation of state with a model for the excess Gibbs energy.[3,4] The advantage of this mixing rule is its capability of predicting vapor−liquid compositions for mixtures of polar components. The first model is based on interactions between different groups. Only the corresponding interaction parameters between the ether group ($CH_2O$) and the nitrogen group ($N_2$) have been adjusted using the experimental data

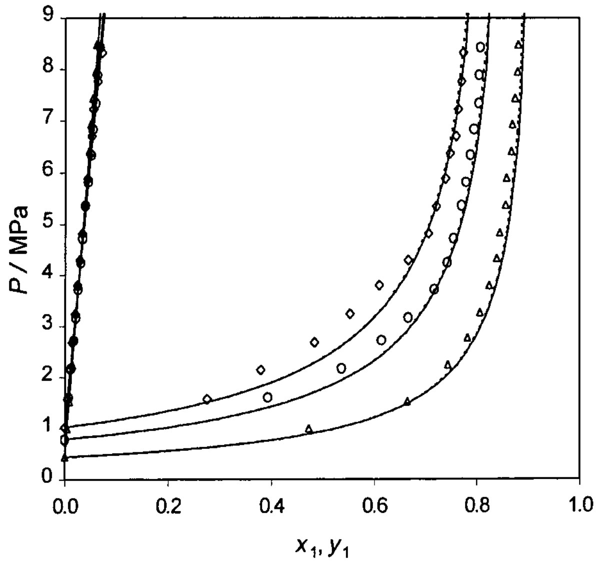

**Figure 1.** Isothermal pressure−composition data for nitrogen (1) + dimethyl ether (2): experimental data at 15 °C (△), 35 °C (○), and 45 °C (◇); (—) SRK/MHV2/UNIFAC; (- - -) SRK/MHV2/UNIQUAC.

for this system. The second model is based on interactions between the nitrogen molecule (1) and the dimethyl ether molecule (2). The objective function minimized by means of Marquardt's algorithm with a maximum of 100 iterations was of bubble pressure type in the form

$$F = \sum_i (R_{1i}^2 + R_{2i}^2) \tag{5}$$

where

$$R_{1i} = \left(\frac{P_c - P_e}{P_e}\right)_i \tag{6}$$

$$R_{2i} = (y_{1c} - y_{1e})_i \tag{7}$$

and the subscript c denotes calculated values, e denotes experimental values, and $i$ is the number of the experimental points. The estimated interaction parameters and relative absolute mean deviation in pressure and vapor-phase composition are shown in the cumulative Tables 7−9. As can be observed in Figure 1, the two mixing rules give practically identical and acceptable results in correlation.

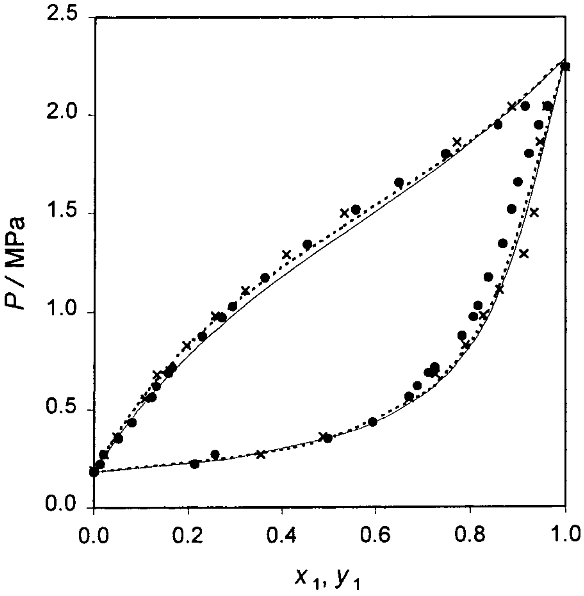

**Figure 2.** Comparison of experimental results with calculated values given by the Soave−Redlich−Kwong (SRK) equation of state for the dimethyl ether (1) + methanol (2) system at 80 °C: (×) experimental, this work; (●) experimental, Chang et al.;[5] (- - -) calculated with $k_{ij}$ adjusted with our data ($k_{ij}$ = 0.0064); (—) calculated with $k_{ij}$ adjusted with Chang et al. data ($k_{ij}$ = −0.0065).

**Table 3. Composition of the Liquid, $x_1$, and Vapor Phases, $y_1$, at the Pressure, $P$, and 80.00 °C for the Binary Dimethyl Ether (1) + Methanol (2) System**

| $x_1$ | $y_1$ | $P$/MPa | $x_1$ | $y_1$ | $P$/MPa |
|---|---|---|---|---|---|
| 0.000 | 0.000 | 0.19 | 0.321 | 0.862 | 1.11 |
| 0.022 | 0.354 | 0.27 | 0.409 | 0.913 | 1.29 |
| 0.047 | 0.487 | 0.36 | 0.532 | 0.934 | 1.50 |
| 0.108 | 0.672 | 0.56 | 0.772 | 0.947 | 1.86 |
| 0.133 | 0.727 | 0.68 | 0.888 | 0.961 | 2.04 |
| 0.195 | 0.790 | 0.83 | 1.000 | 1.000 | 2.24 |
| 0.255 | 0.827 | 0.98 | | | |

**Table 4. Absolute Relative Mean Deviation in Pressure, Δ$P$, and Vapor Composition, Δ$y_1$, for the Dimethyl Ether (1) + Methanol (2) System at 80.00 °C from Correlation with Different EOS Models**

| EOS/source of data | Δ$P$/% | Δ$y_1$/% |
|---|---|---|
| SRK/MHV2/UNIFAC | | |
| Chang et al.[5] | 1.93 | 3.32 |
| this work | 2.17 | 3.31 |
| SRK/MHV2/UNIQUAC | | |
| Chang et al.[5] | 1.85 | 3.45 |
| this work | 2.30 | 3.32 |
| PR | | |
| Chang et al.[5] ($k_{ij}$ = −0.0015) | 3.55 | 3.48 |
| this work ($k_{ij}$ = 0.0109) | 2.90 | 1.89 |
| SRK | | |
| Chang et al.[5] ($k_{ij}$ = −0.0065) | 3.41 | 4.11 |
| this work ($k_{ij}$ = 0.0064) | 2.63 | 1.95 |

***Binary Dimethyl Ether + Methanol System.*** The second binary system of practical interest was dimethyl ether + methanol. Experimental VLE data for this system have already been reported in the literature.[5,6] In the present work we measured this system just at one temperature in order to compare with literature data and to verify our experimental methodology. The isothermal ($P$, $x$, $y$) experimental data measured for the binary dimethyl ether (1) + methanol (2) system at 80 °C are shown in Table 3. They have been compared with Chang et al. data[5] at the same temperature. The results of correlation with different EOS models (SRK/MHV2/UNIFAC or UNIQUAC, Peng−Robinson (PR), and Soave−Redlich−Kwong (SRK) equations of state with quadratic mixing rules with one $k_{ij}$ parameter) are shown in Table 4. For the UNIFAC model just the interaction parameters corresponding to $CH_2O$/$CH_3OH$ were adjusted, all others being from the database for UNIFAC.[7] In Figure 2 both sets of experimental data are shown, and results of correlation by using the SRK equation of state are given as an example. It can be seen that, despite excellent agreement between the two sets of data for the bubble curve, there is a small discrepancy in the vapor phase especially at the higher composition of dimethyl ether. The same discrepancy to the Chang et al. data[5] appears in the Holldorff and Knapp paper[6] when the same type of comparison was made for the 20 °C isotherm.

***Ternary Carbon Dioxide + Dimethyl Ether + Methanol System.*** For the ternary carbon dioxide (1) + dimethyl

**Table 5. Composition of the Liquid, $x_1$, $x_2$, and Vapor Phases, $y_1$, $y_2$, at the Pressure, $P$, and Temperature, $t$, for the Ternary Carbon Dioxide (1) + Dimethyl Ether (2) + Methanol (3) System**

| $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P$/MPa | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P$/MPa |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $t$ = 40.00 °C (Set I) | | | | | |
| 0.000 | 0.543 | 0.000 | 0.933 | 0.62 | 0.238 | 0.422 | 0.766 | 0.225 | 2.57 |
| 0.024 | 0.528 | 0.213 | 0.722 | 0.82 | 0.281 | 0.396 | 0.799 | 0.198 | 2.94 |
| 0.062 | 0.507 | 0.461 | 0.523 | 1.12 | 0.331 | 0.372 | 0.832 | 0.168 | 3.35 |
| 0.089 | 0.492 | 0.543 | 0.435 | 1.36 | 0.389 | 0.342 | 0.855 | 0.143 | 3.81 |
| 0.119 | 0.475 | 0.615 | 0.368 | 1.61 | 0.506 | 0.283 | 0.881 | 0.118 | 4.43 |
| 0.161 | 0.460 | 0.682 | 0.306 | 1.94 | 0.559 | 0.252 | 0.881 | 0.118 | 4.88 |
| | | | | $t$ = 40.00 °C (Set II) | | | | | |
| 0.000 | 0.055 | 0.000 | 0.692 | 0.16 | 0.163 | 0.046 | 0.965 | 0.034 | 2.94 |
| 0.010 | 0.054 | 0.578 | 0.296 | 0.34 | 0.196 | 0.044 | 0.970 | 0.028 | 3.43 |
| 0.030 | 0.053 | 0.797 | 0.146 | 0.68 | 0.236 | 0.042 | 0.974 | 0.024 | 4.01 |
| 0.046 | 0.053 | 0.866 | 0.100 | 1.00 | 0.278 | 0.040 | 0.978 | 0.021 | 4.59 |
| 0.061 | 0.050 | 0.900 | 0.076 | 1.34 | 0.327 | 0.039 | 0.979 | 0.019 | 5.17 |
| 0.085 | 0.050 | 0.929 | 0.057 | 1.74 | 0.410 | 0.034 | 0.983 | 0.016 | 5.69 |
| 0.134 | 0.047 | 0.958 | 0.040 | 2.50 | 0.480 | 0.029 | 0.986 | 0.013 | 6.48 |
| | | | | $t$ = 60.00 °C | | | | | |
| 0.000 | 0.522 | 0.000 | 0.967 | 1.00 | 0.207 | 0.416 | 0.709 | 0.280 | 3.39 |
| 0.030 | 0.503 | 0.245 | 0.728 | 1.33 | 0.280 | 0.382 | 0.746 | 0.245 | 4.19 |
| 0.066 | 0.489 | 0.448 | 0.533 | 1.74 | 0.366 | 0.339 | 0.815 | 0.177 | 5.15 |
| 0.104 | 0.466 | 0.557 | 0.427 | 2.18 | 0.497 | 0.274 | 0.847 | 0.146 | 6.14 |
| 0.150 | 0.444 | 0.642 | 0.346 | 2.72 | | | | | |

**Table 6. Pure Component Data:[10] Critical Temperature, $T_c$, Critical Pressure, $P_c$, Acentric Factor, $\omega$, Volume, $R$, and Surface Area, $Q$**

| component | $T_c$/K | $P_c$/MPa | $w$ | $R$ | $Q$ |
|---|---|---|---|---|---|
| carbon dioxide | 304.21 | 7.3830 | 0.2236 | 1.2986 | 1.2920 |
| nitrogen | 126.20 | 3.4000 | 0.0377 | 1.0415 | 1.0880 |
| dimethyl ether | 400.10 | 5.3700 | 0.2002 | 2.0461 | 1.9360 |
| methanol | 512.64 | 8.0970 | 0.5640 | 1.4311 | 1.4320 |

**Table 7. Interaction Parameters $a_{ij}^0$, $a_{ij}^1$, and $a_{ij}^2$ Adjusted[a] for the UNIFAC Model $(a_{ij}) = a_{ij}^0 + a_{ij}^1(T - 298.15) + a_{ij}^2(T \ln(298.15/T) + T - 298.15)$[b]**

| group | $a_{ij}^0$/K | | | | |
|---|---|---|---|---|---|
| $i/j$ | $CH_2$ | $CH_3OH$ | $CH_2O$ | $CO_2$ | $N_2$ |
| $CH_2$ | 0.0000 | 1318.0000 | 230.5000 | 123.9000 | 279.8000 |
| $CH_3OH$ | 16.2500 | 0.0000 | 149.2974 | −111.4800 | 48.5238 |
| $CH_2O$ | 369.9000 | 172.4121 | 0.0000 | 20192.9384 | 391.3900 |
| $CO_2$ | −55.6900 | 715.8055 | −213.0262 | 0.0000 | |
| $N_2$ | −152.5000 | 1734.0976 | 346.5200 | | 0.0000 |

| group | $a_{ij}^1$ | | | | |
|---|---|---|---|---|---|
| $i/j$ | $CH_2$ | $CH_3OH$ | $CH_2O$ | $CO_2$ | $N_2$ |
| $CH_2$ | 0.0000 | −0.0126 | −1.3280 | −0.4065 | 1.1190 |
| $CH_3OH$ | −0.3005 | 0.0000 | −1.8770 | −0.6264 | −2.6619 |
| $CH_2O$ | −1.5420 | −0.0520 | 0.0000 | 76.2072 | −0.1745 |
| $CO_2$ | −0.4904 | −2.0388 | −0.3011 | 0.0000 | |
| $N_2$ | −1.2410 | 4.1629 | −1.1268 | | 0.0000 |

| group | $a_{ij}^2$ | | | | |
|---|---|---|---|---|---|
| $i/j$ | $CH_2$ | $CH_3OH$ | $CH_2O$ | $CO_2$ | $N_2$ |
| $CH_2$ | 0.0000 | 9.0000 | −2.4760 | 0.0000 | 0.0000 |
| $CH_3OH$ | 0.6924 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| $CH_2O$ | −3.2280 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| $CO_2$ | 0.0000 | 0.0000 | 0.0000 | 0.0000 | |
| $N_2$ | 0.0000 | 0.0000 | 0.0000 | | 0.0000 |

[a] Except the corresponding interaction parameters for the $CH_2$ group, which are those from the UNIFAC database. [b] $i$ and $j$ denote the groups.

**Table 8. Interaction Parameters $a_{ij}^0$ and $a_{ij}^1$ for the UNIQUAC Model $(a_{ij}) = a_{ij}^0 + a_{ij}^1(T - 298.15)$[a]**

| | $a_{ij}^0$/K | | | |
|---|---|---|---|---|
| component $i/j$ | nitrogen | carbon dioxide | dimethyl ether | methanol |
| nitrogen | 0.0000 | | −65.7760 | 4870.3658 |
| carbon dioxide | | 0.0000 | 12.6400 | 290.9300 |
| dimethyl ether | 430.1369 | −78.9730 | 0.0000 | 197.4000 |
| methanol | 296.7256 | 66.4280 | 4.4561 | 0.0000 |

| | $a_{ij}^1$ | | | |
|---|---|---|---|---|
| component $i/j$ | nitrogen | carbon dioxide | dimethyl ether | methanol |
| nitrogen | 0.0000 | | −0.6661 | 14.4258 |
| carbon dioxide | | 0.0000 | 0.6638 | −1.7555 |
| dimethyl ether | 0.2374 | −0.2760 | 0.0000 | 0.8489 |
| methanol | −4.2898 | 0.1086 | −1.0315 | 0.0000 |

[a] $i$ and $j$ denote the components.

ether (2) + methanol (3) system three sets of experiments were carried out. Set I, at 40 °C, started with an approximately equimolar composition in the binary dimethyl ether (2) + methanol (3) system and increased the pressure in the system by adding carbon dioxide (1). Similarly, Set II experiments, at the same temperature, were carried out starting with a high content of methanol in the binary system of dimethyl ether (2) + methanol (3). To see the effect of temperature for the carbon dioxide solubility, the third set of experiments was carried out at 60 °C starting with an approximately equimolar composition of the binary dimethyl ether (2) + methanol (3) system. The composition at equilibrium has been determined using two calibration curves for constituent binary subsystems: carbon dioxide (1) + dimethyl ether (2) and dimethyl ether (2) + methanol (3). The experimental ($P$, $x$, $y$) data at 40 and 60 °C are presented in Table 5. The experimental data have been compared with those predicted by the SRK equation of state using the MHV2 mixing rule combined with modified UNIFAC or UNIQUAC. For the models two sets of parameters have been used [for UNIFAC, parameters already existing in the database;[7] for UNIFAC and UNIQUAC, parameters estimated from different sources as follows: for carbon dioxide (1) + dimethyl ether (2), the data of Tsang and Street;[8] for carbon dioxide (1) + methanol (3), the data of Hong and Kobayashi;[9] and, for dimethyl ether (2) + methanol (3), the data of Chang et al.[5]] For UNIFAC, the parameters adjusted were those for the group interactions $CO_2/CH_2O$, $CO_2/CH_3OH$, and $CH_2O/CH_3OH$. The pure component data used for calculation[10] are presented in Table 6. The adjusted parameters for UNIFAC are presented in Table 7 and those determined for UNIQUAC in Table 8. The results obtained after correlation and or prediction for all constituent binary subsystems and the

**Table 9. Results of Comparison of the Experimental Data with Those Predicted by Means of SRK/MHV2/UNIFAC or UNIQUAC for Constituent Binary Subsystems in the Ternary Carbon Dioxide (1) + Dimethyl Ether (2) + Methanol (3) and Nitrogen (1) + Dimethyl Ether (2) + Methanol (3) Systems (Bubble Pressure Predictions)**

| | UNIFAC (param database) | UNIFAC (param adj on data) | UNIQUAC (param adj on data) |
|---|---|---|---|
| | Carbon Dioxide (1) + Dimethyl Ether (2) 10 Isotherms[8] from 0 to 113.41 °C | | |
| $\%\Delta y_1$ | 4.39 | 3.23 | 2.81 |
| $\%\Delta P$ | 5.98 | 2.07 | 2.21 |
| | Carbon Dioxide (1) + Methanol (3) 6 Isotherms[9] from −43.15 to 56.85 °C | | |
| $\%\Delta y_1$ | 1.00 | 0.83 | 0.85 |
| $\%\Delta P$ | 5.53 | 2.36 | 2.13 |
| | Dimethyl Ether (2) + Methanol (3) 10 Isotherms[5] from 0 to 180 °C | | |
| $\%\Delta y_2$ | 5.3 (2.56[a]) | 4.65 (3.21[a]) | 4.28 (3.14[a]) |
| $\%\Delta P$ | 19.77 (10.02[a]) | 16.34 (2.25[a]) | 15.26 (2.37[a]) |
| | Nitrogen (1) + Dimethyl Ether (2) 3 Isotherms (This Work) from 15 to 45 °C | | |
| $\%\Delta y_1$ | 9.36 | 3.15 | 3.02 |
| $\%\Delta P$ | 30.33 | 2.11 | 2.08 |
| | Nitrogen (1) + Methanol (3) 4 Isotherms[11] from −48.15 to 26.85 °C | | |
| $\%\Delta P$ | 21.04 | 6.63 | 7.69 |

[a] Values for the isotherms of 40 and 60 °C.

ternary systems are shown in Tables 9 and 10. The experimental results seem to be better described (on the average) by SRK/MHV2/UNIQUAC. Both UNIFAC and UNIQUAC give a deviation in pressure about 8%, but UNIQUAC gives better results in composition prediction, 4.2% on average, compared with UNIFAC, which gives 9.3%. By using UNIFAC with adjusted parameters, no significant improvement in the ternary prediction can be seen in Table 10. Taking into account the predictions for the binary subsystems presented in Table 9, we may conclude that the predictions for ternary systems are in agreement with the capability for prediction of SRK/MHV2/UNIFAC and SRK/MHV2/UNIQUAC. Even if we try to readjust the remaining parameters for UNIFAC, no better prediction is expected compared with UNIQUAC, since the binaries are represented equally well by both models.

***Ternary Nitrogen (1) + Dimethyl Ether (2) + Methanol (3) System.*** New isothermal ($P$, $T$, $x$, $y$) data have been measured for the ternary system of nitrogen (1) + dimethyl ether (2) + methanol (3) at 40 and 15 °C. At 40 °C two sets of experiments have been carried out in the same manner as for the previous ternary system. For practical reasons it was interesting to see what is the behavior of the ternary at a lower temperature. Therefore, a new set of experiments has been carried out at 15 °C starting with approximately equimolar composition. The composition at equilibrium has been determined using two calibration curves for constituent binary subsystems: nitrogen (1) + methanol (2) and dimethyl ether (2) + methanol (3). The experimental data ($P$, $T$, $x$, $y$) for nitrogen (1) + dimethyl ether (2) + methanol (3) are presented in Table 11. They have been compared with those predicted by the SRK equation of state with the MHV2 mixing rule combined with modified UNIFAC or UNIQUAC using an identical procedure as for the previously described ternary system. There are just two differences: (1) the adjusted parameters used for UNIFAC were those corresponding to the $CH_2O/N_2$, $CH_3OH/N_2$, and $CH_2O/CH_3OH$ group interactions; (2) the adjustment of the additional parameters for UNIFAC and UNIQUAC was made by using experimental data for binary systems as follows. For nitrogen (1) + dimethyl ether (2), our data were used, and for

**Table 10. Results of Comparison of the Experimental Data with Those Predicted by Means of SRK/MHV2/UNIFAC or UNIQUAC for the Ternary Carbon Dioxide (1) + Dimethyl Ether (2) + Methanol (3) and Nitrogen (1) + Dimethyl Ether (2) + Methanol (3) Systems**

| | UNIFAC (param database) | | UNIFAC (param adjusted on binary exp data) | | UNIQUAC (param adjusted on binary exp data) | |
|---|---|---|---|---|---|---|
| | | | Carbon Dioxide (1) + Dimethyl Ether (2) + Methanol (3) 40.00 °C (Set I) | | | |
| $\Delta y_1$ | 0.032 | (6.90%)[a] | 0.027 | (5.81%) | 0.008 | (1.58%) |
| $\Delta y_2$ | 0.034 | (12.26%) | 0.035 | (13.06%) | 0.014 | (6.90%) |
| $\Delta P$/MPa | 0.20 | (7.8%) | 0.16 | (9.1%) | 0.17 | (6.8%) |
| | | | 40.00 °C (Set II) | | | |
| $\Delta y_1$ | 0.013 | (1.77%) | 0.009 | (1.14%) | 0.009 | (0.98%) |
| $\Delta y_2$ | 0.013 | (18.91%) | 0.013 | (17.13%) | 0.009 | (8.60%) |
| $\Delta P$/MPa | 0.13 | (9.3%) | 0.18 | (10.7%) | 0.15 | (8.3%) |
| | | | 60.00 °C | | | |
| $\Delta y_1$ | 0.024 | (5.41%) | 0.032 | (7.41%) | 0.014 | (2.49%) |
| $\Delta y_2$ | 0.038 | (10.48%) | 0.031 | (9.32%) | 0.015 | (4.92%) |
| $\Delta P$/MPa | 0.21 | (6.4%) | 0.27 | (10.7%) | 0.26 | (8.3%) |
| | | | Nitrogen (1) + Dimethyl Ether (2) + Methanol (3) 40.00 °C (Set I) | | | |
| $\Delta y_1$ | 0.011 | (1.79%) | 0.028 | (4.39%) | 0.029 | (4.56%) |
| $\Delta y_2$ | 0.017 | (6.72%) | 0.036 | (14.35%) | 0.036 | (14.16%) |
| $\Delta P$/MPa | 0.11 | (3.4%) | 0.75 | (16.1%) | 0.82 | (17.6%) |
| | | | 40.00 °C (Set II) | | | |
| $\Delta y_1$ | 0.006 | (0.75%) | 0.012 | (1.20%) | 0.012 | (1.30%) |
| $\Delta y_2$ | 0.017 | (26.78%) | 0.012 | (7.83%) | 0.013 | (10.97%) |
| $\Delta P$/MPa | 0.09 | (6.9%) | 0.38 | (8.8%) | 0.45 | (10.1%) |
| | | | 15.00 °C | | | |
| $\Delta y_1$ | 0.029 | (4.00%) | 0.041 | (5.65%) | 0.038 | (5.26%) |
| $\Delta y_2$ | 0.031 | (17.16%) | 0.043 | (24.4%) | 0.040 | (22.04%) |
| $\Delta P$/MPa | 0.63 | (16.1%) | 1.57 | (35.6%) | 1.41 | (32.2%) |

[a] Values in parentheses are absolute mean relative deviations.

**Table 11. Composition of the Liquid, $x_1$, $x_2$, and Vapor Phases, $y_1$, $y_2$, at the Pressure, *P*, and Temperature, *t*, for the Ternary Nitrogen (1) + Dimethyl Ether (2) + Methanol (3) System**

| $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P$/MPa | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $P$/MPa |
|---|---|---|---|---|---|---|---|---|---|
| $t = 15.00$ °C | | | | | | | | | |
| 0.000 | 0.569 | 0.000 | 0.980 | 0.32 | 0.025 | 0.546 | 0.889 | 0.111 | 4.68 |
| 0.004 | 0.567 | 0.574 | 0.425 | 0.77[a] | 0.031 | 0.543 | 0.905 | 0.095 | 5.79 |
| 0.008 | 0.562 | 0.744 | 0.256 | 1.44 | 0.037 | 0.537 | 0.913 | 0.087 | 6.97 |
| 0.012 | 0.551 | 0.823 | 0.177 | 2.32 | 0.043 | 0.531 | 0.915 | 0.085 | 8.22 |
| 0.019 | 0.552 | 0.868 | 0.132 | 3.50 | 0.048 | 0.528 | 0.922 | 0.078 | 9.28 |
| $t = 40.00$ °C (Set I) | | | | | | | | | |
| 0.000 | 0.567 | 0.000 | 0.971 | 0.65 | 0.028 | 0.537 | 0.834 | 0.166 | 5.20 |
| 0.005 | 0.561 | 0.467 | 0.533 | 1.28 | 0.034 | 0.531 | 0.844 | 0.156 | 6.27 |
| 0.008 | 0.552 | 0.648 | 0.352 | 1.91 | 0.040 | 0.525 | 0.857 | 0.143 | 7.39 |
| 0.015 | 0.548 | 0.747 | 0.253 | 3.05 | 0.046 | 0.518 | 0.861 | 0.140 | 8.60 |
| 0.021 | 0.543 | 0.799 | 0.201 | 4.04 | | | | | |
| $t = 40.00$ °C (Set II) | | | | | | | | | |
| 0.000 | 0.063 | 0.000 | 0.685 | 0.17 | 0.012 | 0.062 | 0.968 | 0.032 | 4.33 |
| 0.002 | 0.064 | 0.820 | 0.145 | 0.81[a] | 0.015 | 0.062 | 0.972 | 0.028 | 5.49 |
| 0.004 | 0.063 | 0.921 | 0.079 | 1.55 | 0.018 | 0.060 | 0.976 | 0.024 | 6.59 |
| 0.006 | 0.062 | 0.944 | 0.056 | 2.33 | 0.020 | 0.060 | 0.977 | 0.023 | 7.76 |
| 0.009 | 0.062 | 0.959 | 0.041 | 3.24 | 0.023 | 0.060 | 0.979 | 0.021 | 8.85 |

[a] Points for the ternary systems where the methanol was detected in the vapor phase.

nitrogen (1) + methanol (3), the data of Weber et al.[11] were used. The parameters are shown in Tables 7 and 8, and the results of correlation and or prediction are presented in Tables 9 and 10. As can be seen in Table 10, the SRK/MHV2/UNIFAC model with the parameters from the database reproduces quite well the data for this ternary system. This is unexpected since the same parameters give unsatisfactory results for the prediction of the VLE data of the binary constituent subsystems (especially for nitrogen + dimethyl ether and nitrogen + methanol). An adjustment of the UNIFAC parameters using the binary experimental data leads to a similar representation of both binary and ternary systems as the UNIQUAC model. It is worth mentioning that, during experiments for both the binary nitrogen + dimethyl ether and the ternary nitrogen + dimethyl ether + methanol systems, there was a small pressure drop (0.02 MPa) in the system produced by taking three to four samples from the vapor phase. However, average pressure values have been taken as good and they were within the limits of the pressure measurement accuracy of 0.01 MPa. In addition, for the ternary system, all but two experimental points measured at lower pressure (see footnote *a* in Table 11) had no vapor-phase methanol detected by the gas chromatograph.

## Conclusions

New VLE experimental data (*P*, *T*, *x*, *y*) have been measured for one binary system (nitrogen + dimethyl ether at 15, 35, and 45 °C) and two ternary systems (carbon dioxide + dimethyl ether + methanol at 40 and 60 °C and nitrogen + dimethyl ether + methanol at 15 and 40 °C) at pressures up to 9.5 MPa. The quality of the experimental methodology used was shown by measuring an isotherm (at 80 °C) for the binary dimethyl ether + methanol system and by comparison of our experimental data with literature data and the results with four different EOS models. The new experimental data reported for the binary nitrogen + dimethyl ether system are well correlated with both SRK/MHV2/UNIFAC and UNIQUAC models. For the ternary systems, a qualitatively good representation has been found by the same two predictive models within their limitations and the accuracy of VLE measurements. However, some precautions have to be taken in using a unique set of parameters for UNIFAC (as given in the existing database) in predicting all the binary and multicomponent systems with the same good results. The group contribution concept is not able to account for proximity effects which are significant, for example, when intermolecular hydrogen bonds or conjugation effects are present. This might be the case for methanol and dimethyl ether in the binary systems with nitrogen. Due to the small solubility of nitrogen in these liquids, the association between molecules may be significant. This could be the reason the UNIQUAC model for the nitrogen + methanol and nitrogen + dimethyl ether + methanol systems is not very accurate. The main purpose of this paper was to produce the experimental data and correlate them with a reasonable model. To obtain a better prediction using a single set of parameters for these systems, other possible models which probably consider association should be investigated in the future.

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