Barker method is often less sensitive to the shape of the *P* vs. $x_1$ curve near the end points than is the Mixon et al. method. The latter reflects the shapes of the splined fits in that specific region while the former reflects the values of the $G^E$ correlation constants obtained from a fit of all the data points across the entire composition range.

The activity coefficient values (as well as the $y_i$ and $G^E$ values) obtained are a function also of the equation of state used to estimate the vapor-phase fugacity coefficients. Table XI shows the effect of assuming ideal gases for the acetone + nitromethane system at 397.19 K where the pressure ranged from 195 to 665 kPa. The other three equations of state tested showed surprising agreement when the Tsonopoulos (*7*) correlation is used to estimate the *B* values for the virial equation.

**Registry No.** Ethyl acetate, 141-78-6; acetonitrile, 75-05-8; acetone, 67-64-1; nitromethane, 75-52-5.

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Received for review July 29, 1982. Accepted September 24, 1982. We gratefully acknowledge the financial support received from the National Science Foundation Grant CPE-80000534 and from the Industrial Participants in the Thermodynamic Research Laboratory.

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# Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of Nitromethane with Methanol and Ethanol

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**Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 388 K for methanol + nitromethane and at approximately 298, 348, and 398 K for ethanol + nitromethane. The experimental *PTx* data were reduced to $y_i$, $\gamma_i$, and $G^E$ values by both the Mixon–Gumowski–Carpenter and the Barker methods, but only the Mixon et al. results are reported in their entirety. Seven $G^E$ correlations were tested in the Barker data reduction; the five-constant Redlich–Kister equation gave the best results. The effect of the equation of state choice was investigated.**

## Introduction

This paper presents total-pressure vapor–liquid equilibrium (VLE) data for nitromethane with methanol and ethanol. Previous papers have reported data for nitromethane with 1-chlorobutane (*1*), with chlorobenzene (*2*), and with ethyl acetate, acetonitrile, and acetone (*3*). The apparatus and techniques used to measure all of these data have been described previously along with the defining equation for the activity coefficient and the standard states used (*4*).

## Chemicals Used

Table I. Chemicals Used

| component | vendor | stated purity, % |
|---|---|---|
| ethanol | U.S. Industrial Chemicals | 200 proof |
| methanol | Fisher Scientific | 99.9 |
| nitromethane | Mallinckrodt | 99.9 |

The sources and the purities of the chemicals used are listed in Table I. Activated molecular sieves (either 3A or 4A) were put into the chemical containers as they were received. Just prior to being loaded into the VLE cells, each chemical was poured into a distillation flask and distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of each distillate were discarded. The retained portions were caught in amber bottles and back-flushed with dry nitrogen for transfer to the cell-loading operation. The stated purities of the chemicals were verified with gas–liquid chromatography at this point.

None of the compounds exhibited any degradation during the VLE measurements. The cell pressures were stable with respect to time, and all liquids were perfectly clear when removed from the cells at the end of the last isotherm.

## Experimental Data

Tables II and III present the experimental *PTx* data. The "smooth" pressure values reported are from the least-squares cubic splined fits used to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*5*) for the reduction of *PTx* data.

Figures 1 and 2 show the experimental data in terms of the pressure deviation $P_D$ from Raoult's law

$$P_D = P - [P_2' + x_1(P_1' - P_2')]$$

where *P* is the experimental mixture pressure and the $P_i'$ values are the pure-component vapor pressures. The deviation pressure plot emphasizes the scatter more than the *P* vs. $x_1$ plot but does not show whether or not any azeotrope exists.

The point symbols in Figures 1 and 2 denote the experimental data points exactly. The curves approximate—in these cases quite closely—the splined fits of those data points. For an

Table II. Experimental $P$ vs. $x_1$ Values for the Methanol (1) + Nitromethane (2) System

| | 298.16 K | | | 348.17 K | | | 388.24 K | |
|---|---|---|---|---|---|---|---|---|
| | PRESSURE, KPA | | | PRESSURE, KPA | | | PRESSURE, KPA | |
| X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH |
| .0000 | 4.775 | 4.775 | .0000 | 41.98 | 41.98 | .0000 | 151.57 | 151.58 |
| .0431 | 8.624 | 8.623 | .0429 | 62.20 | 62.22 | .0425 | 205.46 | 205.36 |
| .0807 | 10.775 | 10.779 | .0804 | 76.39 | 76.34 | .0799 | 244.35 | 244.59 |
| .1404 | 12.811 | 12.802 | .1400 | 93.18 | 93.26 | .1394 | 297.6 | 297.2 |
| .2107 | 14.192 | 14.202 | .2103 | 107.12 | 107.04 | .2094 | 346.5 | 347.0 |
| .3122 | 15.310 | 15.301 | .3118 | 120.37 | 120.43 | .3109 | 401.0 | 400.7 |
| .4159 | 15.952 | 15.960 | .4155 | 129.41 | 129.40 | .4146 | 440.6 | 440.4 |
| .5111 | 16.398 | 16.394 | .5108 | 135.59 | 135.57 | .5100 | 469.2 | 469.5 |
| .6154 | 16.799 | 16.799 | .6151 | 141.04 | 141.03 | .6145 | 496.1 | 496.0 |
| .7201 | 17.137 | 17.140 | .7199 | 145.58 | 145.64 | .7195 | 518.8 | 518.6 |
| .7855 | 17.314 | 17.310 | .7854 | 148.13 | 148.09 | .7852 | 531.0 | 531.2 |
| .8592 | 17.433 | 17.436 | .8591 | 150.43 | 150.37 | .8590 | 543.6 | 543.6 |
| .9053 | 17.435 | 17.434 | .9053 | 151.45 | 151.53 | .9052 | 550.0 | 550.0 |
| .9549 | 17.305 | 17.305 | .9549 | 152.29 | 152.26 | .9549 | 555.4 | 555.4 |
| 1.0000 | 16.974 | 16.973 | 1.0000 | 151.27 | 151.28 | 1.0000 | 557.9 | 557.9 |

Table III. Experimental $P$ vs. $x_1$ Values for the Ethanol (1) + Nitromethane (2) System

| | 298.18 K | | | 348.15 K | | | 398.17 K | |
|---|---|---|---|---|---|---|---|---|
| | PRESSURE, KPA | | | PRESSURE, KPA | | | PRESSURE, KPA | |
| X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH |
| .0000 | 4.790 | 4.790 | .0000 | 42.13 | 42.13 | .0000 | 200.83 | 200.83 |
| .0478 | 7.092 | 7.092 | .0477 | 55.95 | 55.95 | .0475 | 247.78 | 247.79 |
| .0939 | 8.292 | 8.294 | .0937 | 65.74 | 65.74 | .0935 | 285.6 | 285.6 |
| .1484 | 9.058 | 9.054 | .1483 | 74.06 | 74.06 | .1479 | 322.9 | 323.0 |
| .2208 | 9.592 | 9.596 | .2206 | 81.59 | 81.60 | .2201 | 362.7 | 362.6 |
| .3051 | 9.902 | 9.899 | .3049 | 87.25 | 87.21 | .3044 | 398.4 | 398.2 |
| .4008 | 10.071 | 10.077 | .4006 | 91.36 | 91.40 | .4001 | 428.9 | 429.1 |
| .4991 | 10.172 | 10.167 | .4990 | 94.18 | 94.18 | .4985 | 453.3 | 453.3 |
| .6063 | 10.218 | 10.211 | .6062 | 96.18 | 96.14 | .6058 | 473.5 | 473.5 |
| .6998 | 10.210 | 10.216 | .6998 | 97.31 | 97.32 | .6995 | 487.7 | 487.6 |
| .7505 | 10.158 | 10.168 | .7504 | 97.55 | 97.60 | .7502 | 493.7 | 493.8 |
| .8651 | 9.800 | 9.783 | .8651 | 96.72 | 96.66 | .8650 | 503.0 | 502.9 |
| .9234 | 9.318 | 9.324 | .9235 | 94.80 | 94.85 | .9234 | 504.0 | 504.1 |
| .9618 | 8.771 | 8.775 | .9618 | 92.59 | 92.57 | .9618 | 502.7 | 502.6 |
| 1.0000 | 7.924 | 7.922 | 1.0000 | 89.00 | 89.01 | 1.0000 | 498.4 | 498.4 |

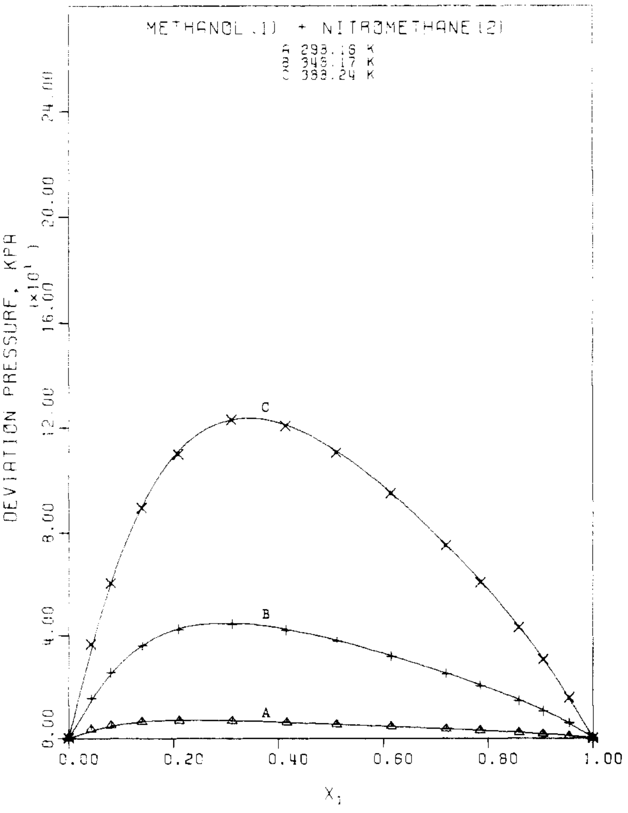

**Figure 1.** Deviation from Raoult's law for the methanol (1) + nitromethane (2) system. The ×10$^1$ multiplier means that the decimal point in the ordinate scale values must be moved one place to the right.

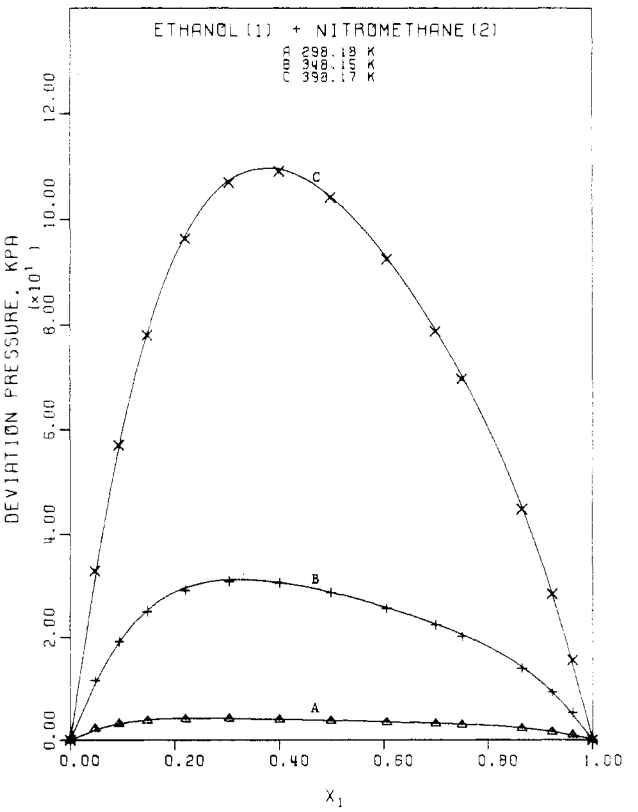

**Figure 2.** Deviation from Raoult's law for the ethanol (1) + nitromethane (2) system. The ×10$^1$ multiplier means that the decimal point in the ordinate scale values must be moved one place to the right.

Table IV. Calculated Data for the Methanol (1) + Nitromethane (2) System at 298.16, 348.17, and 388.24 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 40.800 VL(2) = 54.000

| X1 | TOTAL PRESSURE, KPA EXPTL. | TOTAL PRESSURE, KPA CALC. | MIXTURE FUGACITY COEFFICIENTS 1 | MIXTURE FUGACITY COEFFICIENTS 2 | Y1 | ACTIVITY COEFFICIENTS 1 | ACTIVITY COEFFICIENTS 2 | EXCESS GIBBS FUNCTION, J/MOLE |
|---|---|---|---|---|---|---|---|---|
| .0000 | 4.775 | 4.775 | .9989 | .9980 | .0000 | 6.8609 | 1.0000 | 0.00 |
| .1000 | 11.576 | 11.576 | .9971 | .9953 | .6182 | 4.2222 | 1.0256 | 413.46 |
| .2000 | 14.032 | 14.032 | .9965 | .9943 | .7009 | 2.8995 | 1.0945 | 706.90 |
| .3000 | 15.203 | 15.203 | .9962 | .9938 | .7350 | 2.1954 | 1.2003 | 901.63 |
| .4000 | 15.875 | 15.875 | .9960 | .9936 | .7555 | 1.7672 | 1.3484 | 1009.26 |
| .5000 | 16.347 | 16.347 | .9959 | .9934 | .7722 | 1.4878 | 1.5519 | 1037.24 |
| .6000 | 16.743 | 16.743 | .9958 | .9932 | .7900 | 1.2988 | 1.8320 | 989.25 |
| .7000 | 17.081 | 17.081 | .9957 | .9931 | .8113 | 1.1664 | 2.2382 | 866.23 |
| .8000 | 17.343 | 17.343 | .9956 | .9930 | .8416 | 1.0749 | 2.8614 | 664.33 |
| .9000 | 17.439 | 17.439 | .9956 | .9930 | .8941 | 1.0235 | 3.8485 | 379.40 |
| 1.0000 | 16.973 | 16.973 | .9957 | .9933 | 1.0000 | 1.0000 | 5.7062 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 43.650 VL(2) = 56.700

| X1 | TOTAL PRESSURE, KPA EXPTL. | TOTAL PRESSURE, KPA CALC. | MIXTURE FUGACITY COEFFICIENTS 1 | MIXTURE FUGACITY COEFFICIENTS 2 | Y1 | ACTIVITY COEFFICIENTS 1 | ACTIVITY COEFFICIENTS 2 | EXCESS GIBBS FUNCTION, J/MOLE |
|---|---|---|---|---|---|---|---|---|
| .0000 | 41.975 | 41.975 | .9938 | .9884 | .0000 | 3.8130 | 1.0000 | 0.00 |
| .1000 | 82.576 | 82.577 | .9869 | .9775 | .5306 | 2.9333 | 1.0140 | 347.78 |
| .2000 | 105.318 | 105.322 | .9831 | .9716 | .6564 | 2.3046 | 1.0581 | 614.07 |
| .3000 | 119.157 | 119.162 | .9808 | .9680 | .7150 | 1.8886 | 1.1304 | 800.53 |
| .4000 | 128.251 | 128.254 | .9793 | .9657 | .7511 | 1.5988 | 1.2364 | 911.90 |
| .5000 | 134.939 | 134.940 | .9782 | .9640 | .7791 | 1.3942 | 1.3828 | 950.13 |
| .6000 | 140.297 | 140.296 | .9773 | .9627 | .8048 | 1.2466 | 1.5857 | 916.61 |
| .7000 | 144.828 | 144.827 | .9765 | .9616 | .8322 | 1.1396 | 1.8739 | 810.15 |
| .8000 | 148.578 | 148.576 | .9759 | .9607 | .8653 | 1.0630 | 2.3116 | 626.52 |
| .9000 | 151.412 | 151.411 | .9754 | .9602 | .9168 | 1.0196 | 2.9094 | 359.64 |
| 1.0000 | 151.276 | 151.276 | .9754 | .9606 | 1.0000 | 1.0000 | 4.6191 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 47.000 VL(2) = 60.200

| X1 | TOTAL PRESSURE, KPA EXPTL. | TOTAL PRESSURE, KPA CALC. | MIXTURE FUGACITY COEFFICIENTS 1 | MIXTURE FUGACITY COEFFICIENTS 2 | Y1 | ACTIVITY COEFFICIENTS 1 | ACTIVITY COEFFICIENTS 2 | EXCESS GIBBS FUNCTION, J/MOLE |
|---|---|---|---|---|---|---|---|---|
| .0000 | 151.578 | 151.578 | .9843 | .9688 | .0000 | 2.8756 | 1.0000 | 0.00 |
| .1000 | 263.516 | 263.522 | .9702 | .9466 | .4629 | 2.2788 | 1.0116 | 299.38 |
| .2000 | 340.973 | 340.979 | .9609 | .9318 | .6136 | 1.9332 | 1.0413 | 530.03 |
| .3000 | 395.803 | 395.807 | .9543 | .9215 | .6905 | 1.6705 | 1.0933 | 698.51 |
| .4000 | 435.450 | 435.452 | .9496 | .9142 | .7391 | 1.4674 | 1.1724 | 803.19 |
| .5000 | 466.736 | 466.737 | .9459 | .9084 | .7769 | 1.3167 | 1.2810 | 843.76 |
| .6000 | 492.627 | 492.627 | .9428 | .9038 | .8101 | 1.2032 | 1.4304 | 820.54 |
| .7000 | 514.602 | 514.602 | .9402 | .8999 | .8427 | 1.1173 | 1.6420 | 730.90 |
| .8000 | 533.841 | 533.840 | .9379 | .8967 | .8796 | 1.0557 | 1.9484 | 570.54 |
| .9000 | 549.336 | 549.335 | .9360 | .8944 | .9264 | 1.0147 | 2.4459 | 331.08 |
| 1.0000 | 557.924 | 557.924 | .9350 | .8939 | 1.0000 | 1.0000 | 3.2349 | 0.00 |

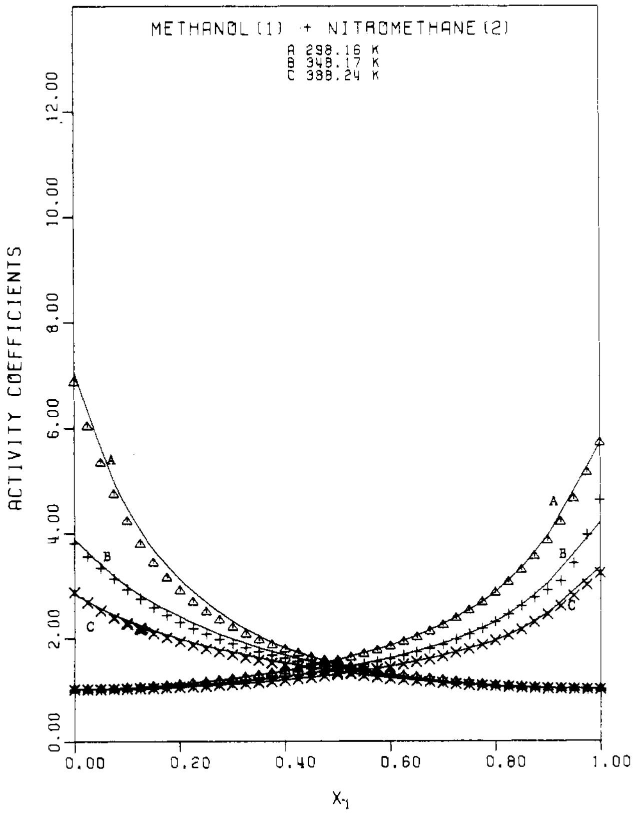

Figure 3. Activity coefficients for the methanol (1) + nitromethane (2) system. Curves are from Barker method; points are from Mixon et al. method.

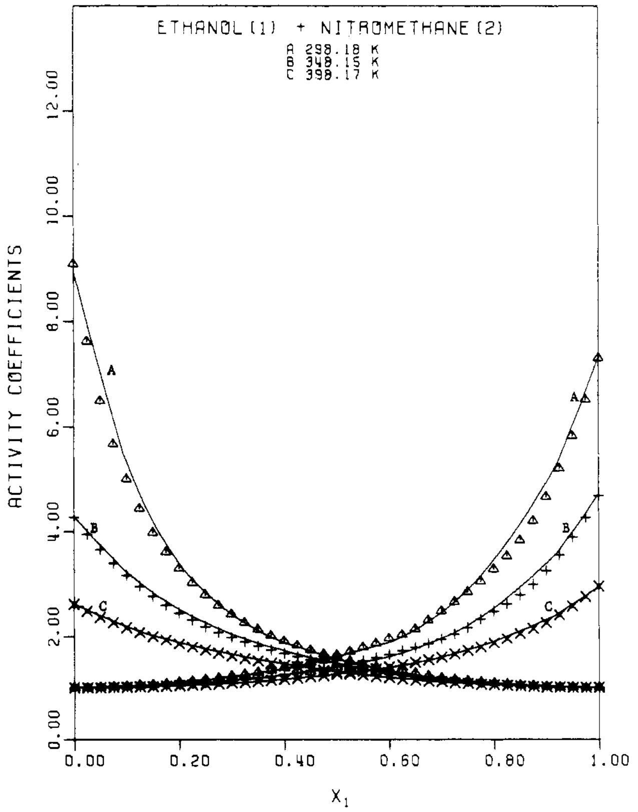

Figure 4. Activity coefficients for the ethanol (1) + nitromethane (2) system. Curves are from Barker method; points are from Mixon et al. method.

Table V. Calculated Data for the Ethanol (1) + Nitromethane (2) System at 298.18, 348.15, and 398.17 K

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =    58.824   VL(2) =    53.990

                                                                                      EXCESS
                                    MIXTURE FUGACITY                                  GIBBS
        TOTAL PRESSURE, KPA          COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1     EXPTL.       CALC.          1        2        Y1          1           2        J/MOLE
 .0000     4.790       4.790       .9984    .9980     .0000      9.0906      1.0000       0.00
 .1000     8.407       8.407       .9971    .9965     .4711      4.9990      1.0297     464.35
 .2000     9.475       9.475       .9968    .9961     .5515      3.2961      1.1068     792.63
 .3000     9.886       9.886       .9966    .9959     .5835      2.4256      1.2252    1011.52
 .4000    10.076      10.076       .9966    .9958     .6022      1.9132      1.3915    1134.87
 .5000    10.168      10.168       .9965    .9958     .6156      1.5788      1.6283    1170.49
 .6000    10.209      10.209       .9965    .9958     .6299      1.3519      1.9672    1119.46
 .7000    10.216      10.216       .9965    .9958     .6482      1.1931      2.4954     986.52
 .8000    10.058      10.058       .9965    .9958     .6862      1.0881      3.2874     757.56
 .9000     9.548       9.548       .9967    .9960     .7652      1.0241      4.6714     435.35
1.0000     7.922       7.922       .9973    .9967    1.0000      1.0000      7.3129       0.00
```

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =    63.686   VL(2) =    57.389

                                                                                      EXCESS
                                    MIXTURE FUGACITY                                  GIBBS
        TOTAL PRESSURE, KPA          COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1     EXPTL.       CALC.          1        2        Y1          1           2        J/MOLE
 .0000    42.127      42.127       .9910    .9883     .0000      4.2653      1.0000       0.00
 .1000    66.854      66.856       .9855    .9815     .4197      3.1696      1.0157     374.62
 .2000    79.777      79.780       .9828    .9780     .5461      2.4531      1.0624     659.75
 .3000    86.943      86.947       .9812    .9760     .6079      1.9804      1.1408     860.37
 .4000    91.376      91.379       .9802    .9748     .6482      1.6628      1.2532     980.79
 .5000    94.206      94.207       .9796    .9741     .6790      1.4356      1.4134    1024.15
 .6000    96.047      96.048       .9792    .9736     .7072      1.2698      1.6422     989.18
 .7000    97.318      97.318       .9789    .9732     .7424      1.1573      1.9510     876.47
 .8000    97.503      97.502       .9789    .9732     .7817      1.0681      2.4853     679.72
 .9000    95.759      95.758       .9792    .9737     .8542      1.0194      3.2613     392.37
1.0000    89.008      89.008       .9807    .9757    1.0000      1.0000      4.6878       0.00
```

```
LIQUID MOLAR VOLUMES, CC/MOL: VL(1) =    70.087   VL(2) =    61.450

                                                                                      EXCESS
                                    MIXTURE FUGACITY                                  GIBBS
        TOTAL PRESSURE, KPA          COEFFICIENTS                ACTIVITY COEFFICIENTS   FUNCTION,
  X1     EXPTL.       CALC.          1        2        Y1          1           2        J/MOLE
 .0000   200.829     200.829       .9720    .9615     .0000      2.6204      1.0000       0.00
 .1000   290.429     290.440       .9589    .9445     .3592      2.1704      1.0098     285.62
 .2000   352.603     352.614       .9499    .9329     .5111      1.8544      1.0382     508.23
 .3000   396.566     396.574       .9436    .9247     .5977      1.6139      1.0874     669.56
 .4000   429.105     429.110       .9389    .9187     .6579      1.4334      1.1591     770.07
 .5000   453.609     453.612       .9354    .9142     .7051      1.2936      1.2608     809.71
 .6000   472.497     472.499       .9327    .9108     .7470      1.1857      1.4026     786.29
 .7000   487.680     487.681       .9305    .9081     .7904      1.1070      1.5938     698.38
 .8000   498.641     498.642       .9289    .9062     .8389      1.0491      1.8743     542.90
 .9000   504.064     504.064       .9281    .9054     .9033      1.0140      2.2727     313.26
1.0000   498.442     498.442       .9289    .9068    1.0000      1.0000      2.9689       0.00
```

Table VI. Parameters for Peng-Robinson Equation[a]

| component | $T_c$, K | $P_c$, MPa | $\omega$ |
|---|---|---|---|
| nitromethane | 588.0 | 6.313 | 0.3460 |
| ethanol | 516.2 | 6.383 | 0.6350 |
| methanol | 512.6 | 8.096 | 0.5590 |

[a] Binary interaction constant was set at 0.0 for all systems.

actual comparison of the splined-fit values and the experimental $P$ values, see Tables II and III.

Both systems showed only positive deviations from Raoult's law and those deviations increased with the temperature. The methanol system forms an azeotrope at 298.16 and 348.17 K but not at 388.24 K. The ethanol system has an azeotrope at all three temperatures.

## Reduced Data

The $y_i$, $\gamma_i$, and $G^E$ values selected for publication are given in Tables IV and V. Those values were obtained with the Mixon et al. data reduction method. The Peng–Robinson equation of state (*6*) was used to estimate the vapor-phase fugacity coefficients. The pure-compound parameters used for the Peng–Robinson equation are in Table VI.

The "experimental" pressure values tabulated in Tables IV and V are actually interpolated values from the cubic splined fits of the experimental $P$ vs. $x_1$ values. (The fidelity with which the splined fits represent the actual experimental $P$ values is shown in Tables II and III.) The "calculated" pressure values are from the Mixon et al. data reduction method. That method can usually be made to reproduce the input $P$ values to any desired precision.

The $PTx$ data were also reduced with the Barker method (*7*) using the seven $G^E$ correlations listed in Table VII. As shown there for the methanol + nitromethane system, the five-constant Redlich–Kister equation usually represents the experimental $P$ data best with the modified Margules equation (*9*) a close second. The maximum percent deviation and the root-mean-squared deviation (rmsd) are defined at the bottom of Table VIII, which gives a more complete comparison of the two data reduction methods insofar as the accuracy of the $P$ fits is concerned. The Barker results in Table VIII are from the five-constant Redlich–Kister $G^E$ correlation, and the Peng–Robinson equation of state was used for both data reduction methods. Usually the Mixon et al. method reproduces the experimental $P$ values better, but for the ethanol system the

Table VII. Effect of Calculation Method on $\gamma_i^\infty$ Values for the Methanol (1) + Nitromethane (2) System[a]

| calculation method | accuracy of $P$ fits, max % dev/rmsd | | | calcd $\gamma_i^\infty$ values | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | component 1 | | | component 2 | | |
| | 298.16 K | 348.17 K | 388.24 K | 298.16 K | 348.17 K | 388.24 K | 298.16 K | 348.17 K | 388.24 K |
| Mixon et al. | 0.1/0.0 | 0.1/0.0 | 0.1/0.1 | 6.876 | 3.821 | 2.869 | 5.600 | 4.459 | 3.107 |
| Barker: | | | | | | | | | |
| absolute Van Laar | 2.8/1.2 | 0.9/0.5 | 1.0/0.3 | 6.194 | 3.712 | 2.692 | 4.744 | 3.716 | 2.976 |
| Wilson | 0.3/0.1 | 0.3/0.1 | 0.5/0.2 | 7.173 | 3.930 | 2.764 | 5.543 | 3.961 | 3.063 |
| NRTL | 0.2/0.1 | 0.3/0.1 | 0.3/0.1 | 7.010 | 3.926 | 2.799 | 5.569 | 3.958 | 3.093 |
| modified Margules | 0.2/0.1 | 0.3/0.1 | 0.3/0.1 | 7.113 | 3.924 | 2.828 | 5.530 | 4.040 | 3.181 |
| UNIQUAC | 1.6/0.7 | 0.5/0.3 | 0.8/0.3 | 6.554 | 3.797 | 2.722 | 5.037 | 3.807 | 3.008 |
| Redlich-Kister, three constants | 0.5/0.2 | 0.3/0.1 | 0.3/0.2 | 6.826 | 3.918 | 2.803 | 5.668 | 3.945 | 3.080 |
| Redlich-Kister, five constants | 0.2/0.1 | 0.2/0.1 | 0.2/0.1 | 7.081 | 3.892 | 2.829 | 5.574 | 4.011 | 3.150 |
| Gautreaux-Coates: | | | | | | | | | |
| splined fits | | | | 6.874 | 3.819 | 2.875 | 5.592 | 4.433 | 3.106 |
| $P_D/x_1x_2$ plots | | | | 6.635 | 3.852 | 2.822 | 5.811 | 4.475 | 3.123 |

[a] Virial equation, Tsonopoulos correlation (*8*).

Table VIII. Comparison of the Barker and Mixon et al. Pressure Fits

| temp, K | max % dev in $P$[a] | | rms for % dev[b] | |
|---|---|---|---|---|
| | Barker | Mixon | Barker | Mixon |
| Methanol (1) + Nitromethane (2), Peng-Robinson | | | | |
| 298.16 | 0.184 | 0.066 | 0.071 | 0.035 |
| 348.17 | 0.226 | 0.090 | 0.082 | 0.046 |
| 388.24 | 0.235 | 0.136 | 0.095 | 0.065 |
| Ethanol (1) + Nitromethane (2), Peng-Robinson | | | | |
| 298.18 | 0.055 | 0.177 | 0.028 | 0.066 |
| 348.15 | 0.087 | 0.063 | 0.038 | 0.031 |
| 398.17 | 0.033 | 0.047 | 0.017 | 0.023 |

[a] % dev = $100[|P_{calcd} - P_{exptl}|/P_{exptl}]$. [b] rms for % dev = $[\Sigma^n(\%\ \mathrm{dev})^2/n]^{1/2}$.

Barker method with the five-constant Redlich-Kister equation did better for two of the three isotherms.

Figures 3 and 4 show that the activity coefficient values provided by the two data reduction methods agree very well for these two systems. The points represent the Mixon et al. results while the curves approximate the Barker results. The Barker results were obtained with the five-constant Redlich-Kister equation. The Peng-Robinson equation of state was used by both methods.

Table VII illustrates how the calculated $\gamma_i^\infty$ values will vary with the $G^E$ correlation used by the Barker method. (Note that the numbers in Table VII are based on the virial equation and the Tsonopoulos (*8*) correlation.) The use of the Gautreaux-Coates (*10*) equations to calculate $\gamma_i^\infty$ values has been discussed in a previous paper (*11*). The $(dP/dx_1)_i^\infty$ values needed by those equations can be obtained from the cubic splined fits or from a $P_D/x_1x_2$ or $x_1x_2/P_D$ plot (*11*). There is always some uncertainty in the extrapolations to $x_1 = 0.0$ and 1.0 on the plots, and the use of the splined-fit values is usually more reliable. The $\gamma_i^\infty$ values calculated by using the splined-fit slopes agree very well with the Mixon et al. values. Even though the Mixon et al. method is based on the splined fits, the agreement of its $\gamma_i^\infty$ values with the Gautreaux-Coates values is not automatic. The finite-difference Mixon et al. method uses a quadratic fit of $G^E$ at $x_1 = 0.0$ or 1.0 plus the two adjacent $G^E$ values to "reach" the $\gamma_i^\infty$ values, and that quadratic extrapolation in general will provide different values than the Gautreaux-Coates method using the splined-fit slopes. The difference is usually small but can be sizable.

Table IX. Effect of Equation of State Choice on $\gamma_i^\infty$ Values Obtained with the Mixon et al. Method for Methanol (1) + Nitromethane (2) at 388.24 K

| eq of state used | $\gamma_i^\infty$ | |
|---|---|---|
| | 1 | 2 |
| ideal gas | 2.8139 | 3.5010 |
| virial through $B_{ij}$: | | |
| Tsonopoulos (*8*) | 2.8694 | 3.1074 |
| Hayden-O'Connell (*12*) | 3.0333 | 3.6949 |
| Redlich-Kwong: Lu modification (*13*) | 2.8778 | 3.3397 |
| Peng-Robinson (*6*) | 2.8756 | 3.2349 |

The $\gamma_i^\infty$ values (as well as all the $y_i$, $\gamma_i$, and $G^E$ values calculated) are also functions of the equation of state used to estimate the vapor-phase fugacity coefficients. Table IX compares the Mixon results obtained with several equations of state. The pressure ranged from 151 to 558 kPa for the methanol system at 388.24 K and at those pressure levels the variation of the calculated results with the equation of state used can be significant.

**Registry No.** Methanol, 67-56-1; ethanol, 64-17-5; nitromethane, 75-52-5.

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Received for review July 29, 1982. Accepted September 24, 1982. We gratefully acknowledge the financial support received from the National Science Foundation Grant CPE-80000534 and from the Industrial Participants in the Thermodynamics Research Laboratory.