*J. Chem. Eng. Data* **1996,** *41,* 1239−1251

# Phase Equilibrium Measurements on Nine Binary Mixtures

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Phase equilibrium measurements have been performed on nine binary mixtures. The *PTx* method was used to obtain vapor−liquid equilibrium data for the following systems at two temperatures each: (aminoethyl)piperazine + diethylenetriamine; 2-butoxyethyl acetate + 2-butoxyethanol; 2-methyl-2-propanol + 2-methylbutane; 2-methyl-2-propanol + 2-methyl-2-butene; methacrylonitrile + methanol; 1-chloro-1,1-difluoroethane + hydrogen chloride; 2-(hexyloxy)ethanol + ethylene glycol; butane + ammonia; propionaldehyde + butane. Equilibrium vapor and liquid phase compositions were derived from the *PTx* data using the Soave equation of state to represent the vapor phase and the Wilson or the NRTL activity coefficient model to represent the liquid phase. A large immiscibility region exists in the butane + ammonia system at 0 °C. Therefore, separate vapor−liquid−liquid equilibrium measurements were performed on this system to more precisely determine the miscibility limits and the composition of the vapor phase in equilibrium with the two liquid phases.

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## Introduction

This work is part of an ongoing investigation of the phase equilibrium for systems of industrial interest sponsored by Project 805 of the Design Institute for Physical Property Data, DIPPR, of the American Institute of Chemical Engineers. This paper reports experimental measurements that have been made under Project 805/93 to obtain phase equilibrium data on nine binary systems. These systems and their measurement conditions follow:

1. (aminoethyl)piperazine + diethylenetriamine at 125 and 210 °C
2. 2-butoxyethyl acetate + 2-butoxyethanol at 100 and 170 °C
3. 2-methyl-2-propanol + 2-methylbutane at 30 and 100 °C
4. 2-methyl-2-propanol + 2-methyl-2-butene at 30 and 100 °C
5. methacrylonitrile + methanol at 25 and 65 °C
6. 1-chloro-1,1-difluoroethane + hydrogen chloride at −40 and 0 °C
7. 2-(hexyloxy)ethanol + ethylene glycol at 100 and 180 °C
8. butane + ammonia at 0 and 50 °C
9. propionaldehyde + butane at 0 and 100 °C

Vapor−liquid equilibrium were determined from total pressure−temperature−composition (*PTx*) measurements. With accurate pressure measurements and equations to model the vapor and liquid phases, *PTx* data can yield reliable phase composition information. An equation of state was used to represent the nonidealities in the vapor phase and an activity coefficient equation was used to represent the nonidealities in the liquid phase. Vapor−liquid−liquid equilibrium data were obtained for the butane + ammonia system at 0 °C by directly analyzing each phase.

## Experimental Section

The measurements required to derive vapor and liquid compositions from *PTx* data are total pressure versus charge composition at constant temperature and known cell volume. In the *PTx* experiments, the entire composition range was traversed at a given temperature. Two or more runs were required for each isotherm. Where possible, the pure compounds were degassed prior to the start of a *PTx* run. To initiate a run, the cell was charged with a known amount of one component. The cell contents were degassed by removing vapor into a weighed, evacuated cell or sample train in order to remove any air that may have been introduced to the cell upon charging, as well as any light impurities that may still have been present in the chemicals. The cell contents were allowed to reach equilibrium at the desired temperature, and the pure component vapor pressure was measured. Further degassing was performed until a repeatable vapor pressure was obtained. Increments of the second component were then charged to the cell. After each increment, the cell contents were again degassed and allowed to equilibrate before the pressure was measured. The second and subsequent runs were similar to the first except that the second component was charged to the cell before adding increments of the first component. The ranges of compositions covered in the runs were designed to overlap to check for consistency between the runs.

Temperatures were measured with platinum resistance thermometers that were calibrated using ice and steam points and referenced to a NIST traceable standard resistance thermometer using the ITS-90 temperature scale. Temperatures were measured to an accuracy of ±0.05 deg or better.

Measurements were performed in the glass still apparatus shown in Figure 1 for systems 1, 2, and 7. The cell was connected to a large ballast tank and to a mercury or oil manometer. Lines through the top of the cell were used for charging and degassing. A thermowell extended through the top of the cell into the liquid in the cell. The cell was placed in a constant temperature bath that was controlled at a temperature 2 deg warmer than the saturation temperature of the material in the cell to promote refluxing in the cell. The liquid in the cell was vigorously stirred to ensure good contact between the vapor and liquid phases and to prevent superheating in the liquid. The ballast tank pressure was used to control the cell temperature. This pressure was adjusted to obtain the desired temperature. Once equilibrium was established, the pressure and temperature were recorded. The oil and mercury levels in the manometer were read with a cathetometer to ±0.05 mm. Pressures measured with this apparatus are estimated to be accurate to within ±0.025 kPa.

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S0021-9568(96)00162-8 CCC: $12.00

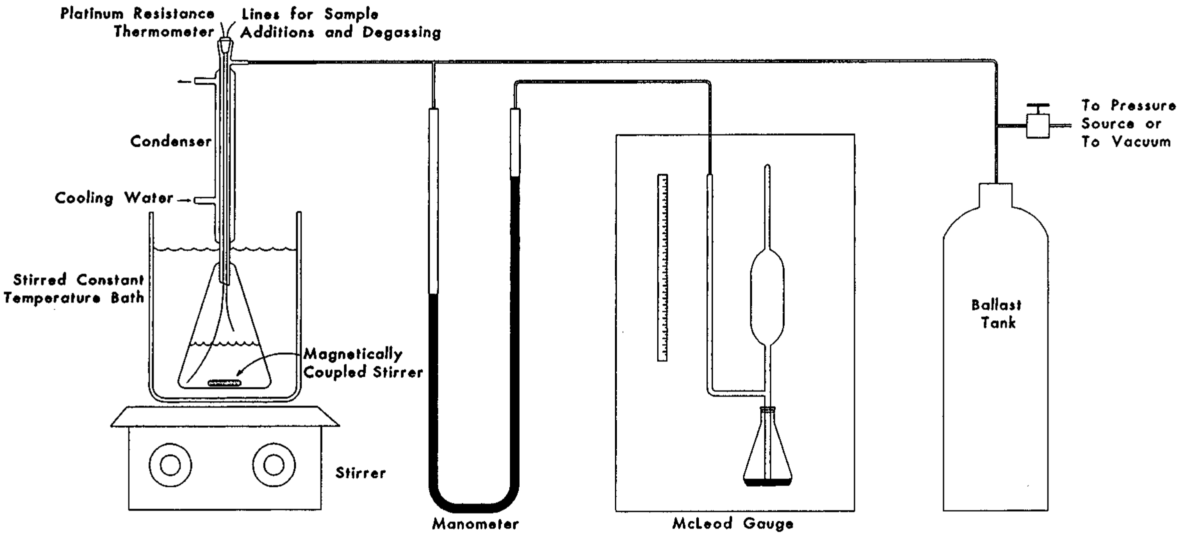

**Figure 1.** Glass still *PTx* apparatus.

**Table 1. *PTx* Measurement Results on (Aminoethyl)piperazine (A) + Diethylenetriamine (B)**

| run no. | $100z_A$ | $100x_A$ | $100y_A$ | $P$/kPa meas | $P$/kPa calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $t$ = 125 °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 4.819 | 4.819 | 1.000 | 1.100 | 0.997 | 0.998 | 1.0000 | 0.9999 | 1.596 |
| 1 | 97.37 | 97.37 | 95.89 | 4.874 | 4.894 | 1.000 | 1.094 | 0.997 | 0.998 | 1.0000 | 0.9999 | 1.588 |
| 1 | 94.83 | 94.84 | 92.08 | 4.945 | 4.965 | 1.000 | 1.089 | 0.997 | 0.998 | 1.0000 | 0.9999 | 1.580 |
| 1 | 89.57 | 89.57 | 84.60 | 5.089 | 5.108 | 1.001 | 1.079 | 0.997 | 0.997 | 1.0000 | 0.9999 | 1.564 |
| 1 | 79.45 | 79.46 | 71.60 | 5.363 | 5.371 | 1.004 | 1.062 | 0.997 | 0.997 | 1.0000 | 0.9999 | 1.535 |
| 1 | 68.77 | 68.78 | 59.44 | 5.644 | 5.631 | 1.009 | 1.046 | 0.997 | 0.997 | 1.0000 | 1.0000 | 1.504 |
| 2 | 60.26 | 60.27 | 50.63 | 5.781 | 5.827 | 1.015 | 1.035 | 0.997 | 0.997 | 1.0000 | 1.0000 | 1.480 |
| 1 | 58.31 | 58.32 | 48.70 | 5.900 | 5.871 | 1.017 | 1.033 | 0.997 | 0.997 | 1.0000 | 1.0000 | 1.474 |
| 1 | 48.86 | 48.87 | 39.76 | 6.101 | 6.076 | 1.025 | 1.023 | 0.997 | 0.997 | 1.0001 | 1.0000 | 1.448 |
| 2 | 48.54 | 48.55 | 39.47 | 6.064 | 6.083 | 1.026 | 1.023 | 0.997 | 0.997 | 1.0001 | 1.0000 | 1.447 |
| 1 | 40.07 | 40.07 | 31.96 | 6.293 | 6.258 | 1.035 | 1.015 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.424 |
| 2 | 39.72 | 39.73 | 31.66 | 6.251 | 6.265 | 1.035 | 1.015 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.423 |
| 2 | 29.78 | 29.79 | 23.31 | 6.462 | 6.461 | 1.048 | 1.008 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.396 |
| 2 | 19.42 | 19.43 | 14.98 | 6.661 | 6.656 | 1.064 | 1.004 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.369 |
| 2 | 9.57 | 9.58 | 7.31 | 6.832 | 6.834 | 1.081 | 1.001 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.343 |
| 2 | 5.03 | 5.03 | 3.82 | 6.911 | 6.914 | 1.090 | 1.000 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.332 |
| 2 | 2.42 | 2.42 | 1.84 | 6.979 | 6.959 | 1.095 | 1.000 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.325 |
| 2 | 0.00 | 0.00 | 0.00 | 7.000 | 7.000 | 1.100 | 1.000 | 0.996 | 0.997 | 1.0001 | 1.0000 | 1.319 |
| | | | | | $t$ = 210 °C[b] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 75.710 | 75.710 | 1.000 | 1.080 | 0.975 | 0.980 | 1.0000 | 0.9989 | 1.558 |
| 1 | 96.70 | 96.74 | 95.03 | 76.459 | 77.115 | 1.000 | 1.074 | 0.975 | 0.979 | 1.0001 | 0.9989 | 1.550 |
| 1 | 94.91 | 94.96 | 92.42 | 77.566 | 77.870 | 1.000 | 1.072 | 0.975 | 0.979 | 1.0001 | 0.9989 | 1.546 |
| 1 | 90.69 | 90.78 | 86.50 | 79.384 | 79.617 | 1.001 | 1.065 | 0.974 | 0.979 | 1.0002 | 0.9990 | 1.536 |
| 1 | 80.30 | 80.45 | 73.14 | 83.378 | 83.771 | 1.003 | 1.051 | 0.973 | 0.977 | 1.0003 | 0.9991 | 1.511 |
| 1 | 69.69 | 69.85 | 60.91 | 87.836 | 87.815 | 1.007 | 1.038 | 0.972 | 0.976 | 1.0005 | 0.9993 | 1.487 |
| 2 | 63.41 | 63.50 | 54.17 | 90.089 | 90.142 | 1.010 | 1.031 | 0.971 | 0.976 | 1.0006 | 0.9993 | 1.472 |
| 1 | 59.28 | 59.43 | 50.04 | 91.825 | 91.599 | 1.013 | 1.027 | 0.970 | 0.975 | 1.0006 | 0.9994 | 1.463 |
| 2 | 52.50 | 52.62 | 43.42 | 94.061 | 93.978 | 1.017 | 1.021 | 0.970 | 0.975 | 1.0007 | 0.9995 | 1.447 |
| 1 | 48.95 | 49.07 | 40.10 | 95.294 | 95.193 | 1.020 | 1.019 | 0.969 | 0.974 | 1.0008 | 0.9995 | 1.439 |
| 2 | 42.64 | 42.78 | 34.41 | 97.317 | 97.301 | 1.025 | 1.014 | 0.969 | 0.974 | 1.0008 | 0.9996 | 1.425 |
| 1 | 38.62 | 38.70 | 30.83 | 98.657 | 98.642 | 1.029 | 1.012 | 0.968 | 0.973 | 1.0009 | 0.9996 | 1.416 |
| 2 | 32.15 | 32.30 | 25.38 | 100.61 | 100.70 | 1.036 | 1.008 | 0.967 | 0.973 | 1.0010 | 0.9997 | 1.402 |
| 2 | 20.78 | 20.91 | 16.10 | 104.20 | 104.26 | 1.049 | 1.003 | 0.966 | 0.972 | 1.0011 | 0.9998 | 1.378 |
| 2 | 10.79 | 10.87 | 8.25 | 107.19 | 107.28 | 1.063 | 1.001 | 0.965 | 0.971 | 1.0012 | 0.9999 | 1.357 |
| 2 | 5.44 | 5.49 | 4.14 | 108.97 | 108.86 | 1.071 | 1.000 | 0.965 | 0.970 | 1.0013 | 0.9999 | 1.345 |
| 2 | 2.54 | 2.56 | 1.92 | 109.74 | 109.71 | 1.076 | 1.000 | 0.965 | 0.970 | 1.0013 | 1.0000 | 1.339 |
| 2 | 0.00 | 0.00 | 0.00 | 110.44 | 110.44 | 1.080 | 1.000 | 0.964 | 0.970 | 1.0014 | 1.0000 | 1.334 |

[a] Wilson equation parameters: $\Lambda_{AB} = 0.9530$, $\Lambda_{BA} = 0.9530$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.9620$, $\Lambda_{BA} = 0.9620$.

Measurements for system 5 and for the lower isotherms of systems 3, 4, and 9 were performed in the glass cell shown in Figure 2. The cell was made of thick-walled borosilicate glass with a TFE cap and had an internal volume of approximately 300 cm$^3$. The cap screwed into the cell and formed a seal with an O-ring. Small-bore lines through the cap were used for adding components and degassing. A thermowell into which a platinum resistance thermometer was inserted also extended into the cell.

The pressure was measured with the mercury manometer which extended from the side of the cell. The density and vapor pressure of the mercury at the bath temperature were properly accounted for in the pressure determinations. The manometer was connected to a McLeod gauge for cell pressures below about 50 kPa or was left open to the atmosphere for higher pressures. Atmospheric pressure was measured with a barometer. The mercury levels in the cell manometer were read with a cathetometer to ±0.05

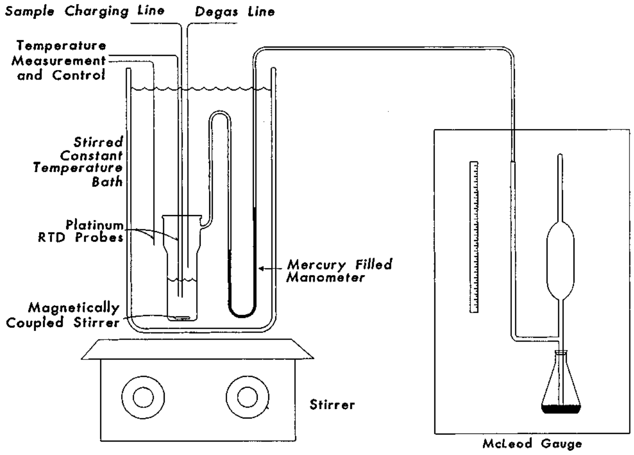

**Figure 2.** Glass *PTx* apparatus.

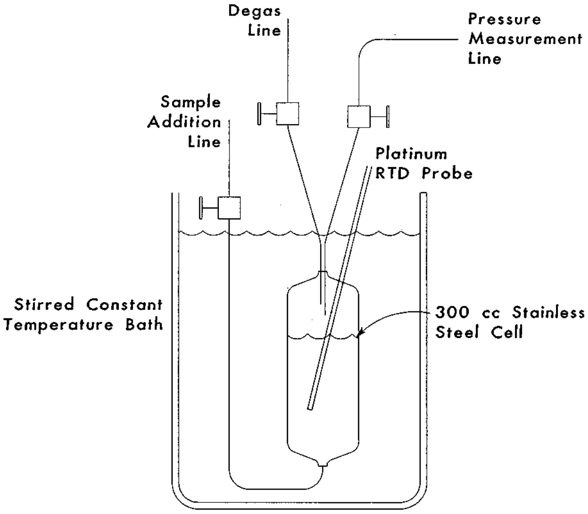

**Figure 3.** Stainless steel *PTx* apparatus.

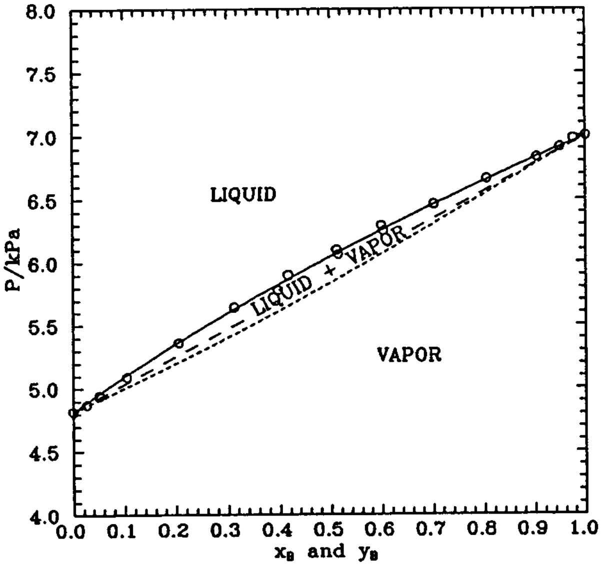

**Figure 4.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for (aminoethyl)piperazine (A) + diethylenetriamine (B) at 125 °C.

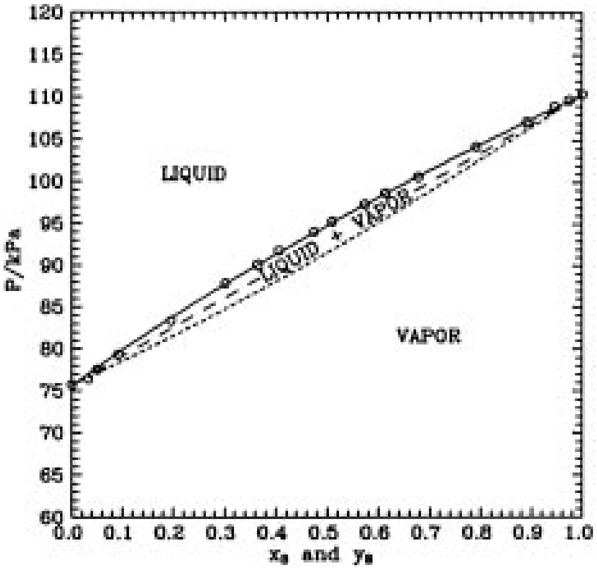

**Figure 5.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for (aminoethyl)piperazine (A) + diethylenetriamine (B) at 210 °C.

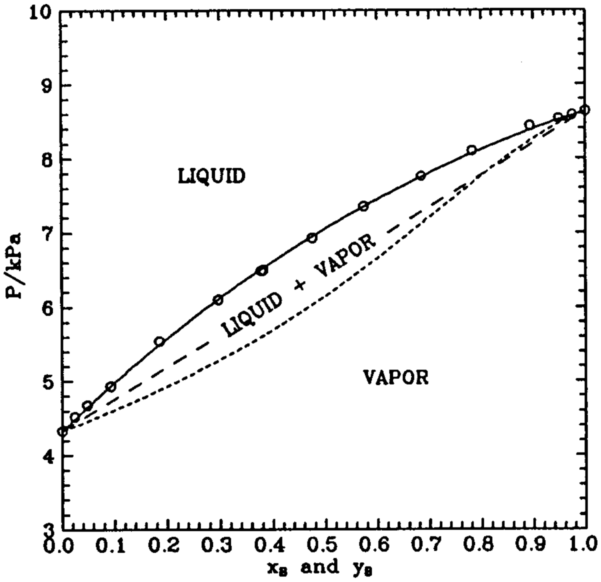

**Figure 6.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-butoxyethyl acetate (A) + 2-butoxyethanol (B) at 100 °C.

mm. Pressures were measured with this apparatus with an estimated accuracy of ±0.05 kPa.

Systems 6 and 8 as well as the higher isotherms of systems 3, 4, and 9 were studied in the stainless steel cell shown in Figure 3. The cell had a volume of 300 cm$^3$ and was connected to a pressure transducer or to a manometer depending on the pressure range. Lines were connected to the cell for charging, sampling, and degassing. A thermowell also extended into the cell into which a platinum resistance thermometer was inserted.

The cell and its connections were attached to a rigid support and immersed in a constant temperature bath. The cell was manually agitated to ensure the contents were at equilibrium at the desired temperature. Pressures less than about 200 kPa were measured with a mercury manometer and are estimated to be accurate to ±0.05 kPa. Higher pressures were measured using a calibrated Paroscientific pressure transducer. These pressures were measured to within ±0.3 kPa.

Vapor−liquid−liquid equilibrium (VLLE) data for the lower isotherm of system 8 were obtained by sampling and analyzing the equilibrium phases. Sample lines extended into the vapor and two liquid phases. The cell contents were agitated to ensure that they were well mixed and that equilibrium was attained. The phases were allowed to settle before withdrawing multiple samples of both liquid phases and the vapor phase into previously weighed sample

**Table 2. *PTx* Measurement Results on 2-Butoxyethyl Acetate (A) + 2-Butoxyethanol (B)**

| | | | | P/kPa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $100z_A$ | $100x_A$ | $100y_A$ | meas | calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
| $t = 100$ °C[a] | | | | | | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 4.329 | 4.329 | 1.000 | 1.293 | 0.996 | 0.998 | 1.0000 | 0.9998 | 2.572 |
| 1 | 97.59 | 97.59 | 94.08 | 4.521 | 4.492 | 1.000 | 1.282 | 0.996 | 0.998 | 1.0000 | 0.9998 | 2.551 |
| 1 | 95.19 | 95.21 | 88.70 | 4.673 | 4.650 | 1.000 | 1.272 | 0.995 | 0.998 | 1.0000 | 0.9998 | 2.530 |
| 1 | 90.74 | 90.76 | 79.77 | 4.931 | 4.936 | 1.002 | 1.254 | 0.995 | 0.997 | 1.0000 | 0.9998 | 2.490 |
| 1 | 81.40 | 81.43 | 64.61 | 5.541 | 5.498 | 1.007 | 1.216 | 0.995 | 0.997 | 1.0001 | 0.9999 | 2.402 |
| 1 | 70.24 | 70.28 | 50.81 | 6.098 | 6.108 | 1.018 | 1.172 | 0.994 | 0.997 | 1.0001 | 0.9999 | 2.289 |
| 2 | 62.17 | 62.19 | 42.77 | 6.487 | 6.510 | 1.032 | 1.142 | 0.994 | 0.996 | 1.0001 | 0.9999 | 2.201 |
| 1 | 61.82 | 61.86 | 42.47 | 6.494 | 6.526 | 1.033 | 1.141 | 0.994 | 0.996 | 1.0001 | 0.9999 | 2.197 |
| 2 | 52.42 | 52.44 | 34.56 | 6.926 | 6.951 | 1.055 | 1.108 | 0.993 | 0.996 | 1.0002 | 0.9999 | 2.088 |
| 2 | 42.58 | 42.61 | 27.42 | 7.350 | 7.351 | 1.090 | 1.077 | 0.993 | 0.996 | 1.0002 | 0.9999 | 1.965 |
| 2 | 31.50 | 31.52 | 20.22 | 7.762 | 7.752 | 1.145 | 1.046 | 0.993 | 0.996 | 1.0002 | 1.0000 | 1.816 |
| 2 | 21.78 | 21.80 | 14.26 | 8.100 | 8.066 | 1.215 | 1.024 | 0.992 | 0.995 | 1.0002 | 1.0000 | 1.676 |
| 2 | 10.66 | 10.67 | 7.36 | 8.438 | 8.382 | 1.330 | 1.006 | 0.992 | 0.995 | 1.0002 | 1.0000 | 1.504 |
| 2 | 5.14 | 5.14 | 3.69 | 8.538 | 8.521 | 1.408 | 1.002 | 0.992 | 0.995 | 1.0002 | 1.0000 | 1.414 |
| 2 | 2.55 | 2.56 | 1.88 | 8.585 | 8.582 | 1.450 | 1.000 | 0.992 | 0.995 | 1.0003 | 1.0000 | 1.371 |
| 2 | 0.00 | 0.00 | 0.00 | 8.638 | 8.638 | 1.497 | 1.000 | 0.992 | 0.995 | 1.0003 | 1.0000 | 1.328 |
| $t = 170$ °C[b] | | | | | | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 55.522 | 55.522 | 1.000 | 1.131 | 0.969 | 0.983 | 1.0000 | 0.9981 | 1.988 |
| 1 | 97.43 | 97.48 | 95.13 | 56.511 | 56.946 | 1.000 | 1.127 | 0.968 | 0.983 | 1.0001 | 0.9982 | 1.981 |
| 1 | 94.77 | 94.87 | 90.36 | 58.363 | 58.409 | 1.000 | 1.123 | 0.967 | 0.982 | 1.0002 | 0.9983 | 1.973 |
| 1 | 90.69 | 90.85 | 83.52 | 60.712 | 60.628 | 1.001 | 1.117 | 0.966 | 0.981 | 1.0003 | 0.9984 | 1.960 |
| 1 | 80.45 | 80.72 | 68.49 | 66.145 | 66.058 | 1.003 | 1.101 | 0.963 | 0.979 | 1.0006 | 0.9986 | 1.926 |
| 1 | 69.69 | 69.99 | 55.31 | 71.224 | 71.526 | 1.008 | 1.084 | 0.961 | 0.977 | 1.0009 | 0.9988 | 1.884 |
| 2 | 62.38 | 62.50 | 47.37 | 75.350 | 75.165 | 1.014 | 1.072 | 0.959 | 0.976 | 1.0011 | 0.9990 | 1.852 |
| 1 | 59.61 | 59.90 | 44.80 | 76.311 | 76.396 | 1.017 | 1.068 | 0.958 | 0.975 | 1.0012 | 0.9990 | 1.840 |
| 2 | 52.25 | 52.42 | 37.93 | 80.455 | 79.821 | 1.025 | 1.056 | 0.957 | 0.974 | 1.0013 | 0.9992 | 1.803 |
| 1 | 49.59 | 49.82 | 35.69 | 80.693 | 80.977 | 1.029 | 1.052 | 0.956 | 0.974 | 1.0014 | 0.9992 | 1.789 |
| 2 | 41.32 | 41.52 | 28.96 | 84.778 | 84.536 | 1.044 | 1.039 | 0.954 | 0.972 | 1.0016 | 0.9994 | 1.742 |
| 1 | 38.49 | 38.64 | 26.76 | 84.962 | 85.723 | 1.050 | 1.035 | 0.954 | 0.972 | 1.0017 | 0.9994 | 1.724 |
| 2 | 30.20 | 30.40 | 20.74 | 88.961 | 88.997 | 1.072 | 1.024 | 0.952 | 0.971 | 1.0019 | 0.9996 | 1.669 |
| 2 | 18.96 | 19.12 | 12.99 | 93.158 | 93.166 | 1.115 | 1.011 | 0.950 | 0.969 | 1.0021 | 0.9997 | 1.584 |
| 2 | 9.78 | 9.87 | 6.79 | 96.619 | 96.319 | 1.166 | 1.003 | 0.949 | 0.968 | 1.0023 | 0.9999 | 1.503 |
| 2 | 4.27 | 4.31 | 3.01 | 98.210 | 98.096 | 1.206 | 1.001 | 0.948 | 0.968 | 1.0024 | 0.9999 | 1.449 |
| 2 | 1.92 | 1.94 | 1.37 | 98.802 | 98.825 | 1.226 | 1.000 | 0.948 | 0.967 | 1.0024 | 1.0000 | 1.425 |
| 2 | 0.00 | 0.00 | 0.00 | 99.407 | 99.407 | 1.244 | 1.000 | 0.948 | 0.967 | 1.0024 | 1.0000 | 1.405 |

[a] Wilson equation parameters: $\Lambda_{AB} = 0.5208$, $\Lambda_{BA} = 1.2492$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.5348$, $\Lambda_{BA} = 1.4077$.

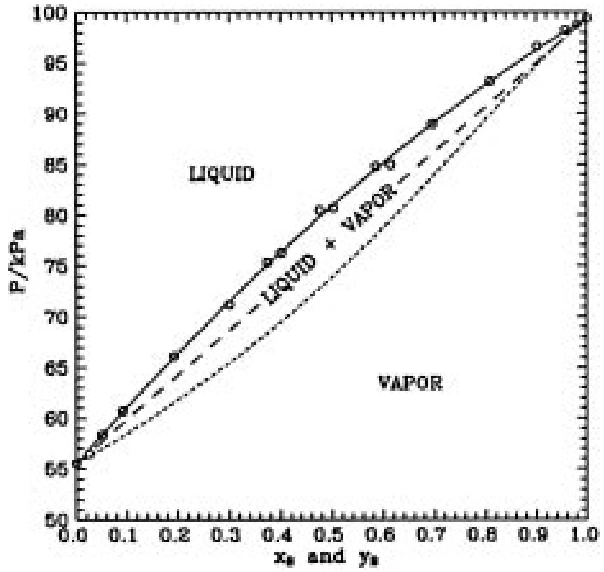

**Figure 7.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-butoxyethyl acetate (A) + 2-butoxyethanol (B) at 170 °C.

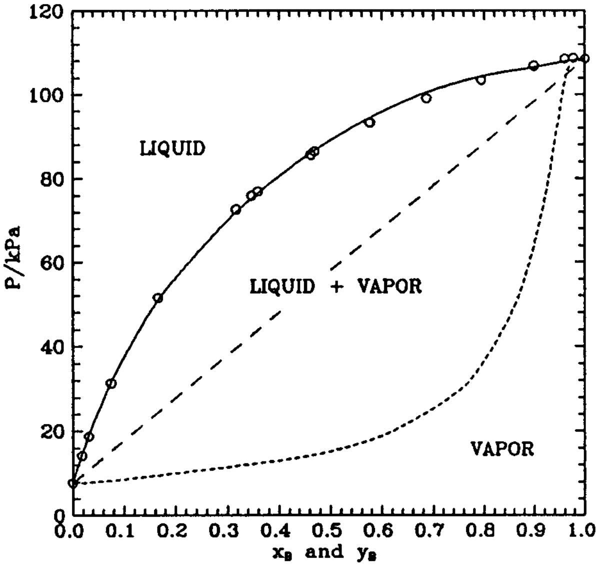

**Figure 8.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-methyl-2-propanol (A) + 2-methylbutane (B) at 30 °C.

cylinders. The amount of ammonia in a sample was determined by titration, and the amount of butane was determined by difference.

## *PTx* Data Reduction Procedure

The results of the *PTx* measurements, which are total pressure as a function of charge composition at constant temperature, were reduced to equilibrium phase compositions and activity and fugacity coefficients. Various activity coefficient models were used to represent the liquid-phase nonidealities. The Soave−Redlich−Kwong equation of state (Soave, 1972) was used to represent the vapor phase in the data reduction procedure. All Soave binary interaction parameters were assumed to be zero.

To derive equilibrium phase compositions from *PTx* data, an iterative procedure is used to solve the basic equation

**Table 3. *PTx* Measurement Results on 2-Methyl-2-propanol (A) + 2-Methylbutane (B)**

| | | | | $P$/kPa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $100z_A$ | $100x_A$ | $100y_A$ | meas | calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
| | | | | | $t$ = 30 °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 7.750 | 7.750 | 1.000 | 3.782 | 0.996 | 0.997 | 1.0000 | 0.9953 | 50.858 |
| 1 | 98.14 | 98.22 | 53.47 | 14.204 | 14.291 | 1.000 | 3.585 | 0.993 | 0.995 | 1.0002 | 0.9956 | 48.147 |
| 1 | 96.73 | 96.88 | 40.14 | 18.752 | 18.839 | 1.001 | 3.448 | 0.991 | 0.993 | 1.0004 | 0.9958 | 46.239 |
| 1 | 92.25 | 92.53 | 23.27 | 31.376 | 31.443 | 1.008 | 3.070 | 0.985 | 0.989 | 1.0009 | 0.9964 | 40.855 |
| 1 | 83.00 | 83.40 | 13.45 | 51.520 | 50.917 | 1.036 | 2.504 | 0.976 | 0.982 | 1.0016 | 0.9973 | 32.335 |
| 1 | 67.97 | 68.34 | 8.53 | 72.616 | 72.044 | 1.122 | 1.946 | 0.966 | 0.975 | 1.0024 | 0.9983 | 23.154 |
| 2 | 65.18 | 65.33 | 7.97 | 75.923 | 75.335 | 1.145 | 1.867 | 0.964 | 0.974 | 1.0026 | 0.9984 | 21.758 |
| 1 | 63.80 | 64.13 | 7.77 | 76.884 | 76.583 | 1.155 | 1.838 | 0.964 | 0.973 | 1.0026 | 0.9985 | 21.230 |
| 1 | 53.59 | 53.82 | 6.35 | 85.613 | 86.127 | 1.259 | 1.624 | 0.959 | 0.970 | 1.0030 | 0.9989 | 17.186 |
| 2 | 52.95 | 53.16 | 6.27 | 86.421 | 86.670 | 1.267 | 1.612 | 0.959 | 0.970 | 1.0030 | 0.9990 | 16.952 |
| 2 | 42.22 | 42.46 | 5.22 | 93.292 | 94.458 | 1.432 | 1.442 | 0.956 | 0.967 | 1.0033 | 0.9993 | 13.403 |
| 1 | 42.20 | 42.32 | 5.21 | 93.310 | 94.547 | 1.435 | 1.440 | 0.955 | 0.967 | 1.0033 | 0.9993 | 13.359 |
| 2 | 31.07 | 31.31 | 4.38 | 99.068 | 100.52 | 1.728 | 1.293 | 0.953 | 0.965 | 1.0035 | 0.9996 | 9.958 |
| 2 | 20.38 | 20.56 | 3.75 | 103.43 | 104.32 | 2.335 | 1.166 | 0.951 | 0.963 | 1.0037 | 0.9998 | 6.643 |
| 2 | 10.04 | 10.13 | 3.16 | 106.84 | 106.55 | 4.078 | 1.058 | 0.950 | 0.963 | 1.0037 | 0.9999 | 3.450 |
| 2 | 4.01 | 4.03 | 2.28 | 108.53 | 107.90 | 7.468 | 1.012 | 0.949 | 0.962 | 1.0038 | 1.0000 | 1.802 |
| 2 | 2.30 | 2.31 | 1.65 | 108.70 | 108.31 | 9.493 | 1.004 | 0.949 | 0.962 | 1.0038 | 1.0000 | 1.406 |
| 2 | 0.00 | 0.00 | 0.00 | 108.57 | 108.57 | 14.049 | 1.000 | 0.949 | 0.962 | 1.0038 | 1.0000 | 0.946 |
| | | | | | $t$ = 100 °C[b] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 192.43 | 192.43 | 1.000 | 2.782 | 0.951 | 0.964 | 1.0000 | 0.9769 | 9.100 |
| 1 | 95.59 | 96.07 | 74.54 | 253.73 | 252.99 | 1.002 | 2.566 | 0.936 | 0.952 | 1.0021 | 0.9795 | 8.352 |
| 1 | 90.34 | 91.21 | 57.91 | 316.74 | 317.22 | 1.008 | 2.339 | 0.920 | 0.939 | 1.0044 | 0.9823 | 7.540 |
| 1 | 80.62 | 81.80 | 41.85 | 415.55 | 416.03 | 1.033 | 1.997 | 0.896 | 0.920 | 1.0079 | 0.9866 | 6.245 |
| 1 | 70.49 | 71.60 | 32.92 | 496.83 | 496.24 | 1.080 | 1.725 | 0.876 | 0.905 | 1.0107 | 0.9901 | 5.137 |
| 1 | 58.49 | 59.26 | 26.34 | 569.51 | 568.75 | 1.169 | 1.485 | 0.858 | 0.891 | 1.0133 | 0.9933 | 4.068 |
| 2 | 57.78 | 58.21 | 25.89 | 573.30 | 573.97 | 1.178 | 1.468 | 0.856 | 0.890 | 1.0135 | 0.9935 | 3.987 |
| 2 | 46.18 | 46.78 | 21.62 | 621.15 | 623.60 | 1.309 | 1.308 | 0.844 | 0.880 | 1.0153 | 0.9957 | 3.187 |
| 1 | 45.43 | 45.76 | 21.27 | 630.80 | 627.47 | 1.323 | 1.295 | 0.843 | 0.879 | 1.0154 | 0.9959 | 3.121 |
| 2 | 35.16 | 35.77 | 18.09 | 660.72 | 661.19 | 1.500 | 1.189 | 0.835 | 0.873 | 1.0166 | 0.9974 | 2.522 |
| 2 | 22.13 | 22.55 | 13.77 | 696.51 | 696.40 | 1.886 | 1.083 | 0.826 | 0.866 | 1.0179 | 0.9989 | 1.823 |
| 2 | 11.31 | 11.46 | 9.01 | 717.54 | 717.65 | 2.485 | 1.024 | 0.821 | 0.862 | 1.0187 | 0.9999 | 1.307 |
| 2 | 4.75 | 4.76 | 4.64 | 722.71 | 723.64 | 3.104 | 1.005 | 0.820 | 0.861 | 1.0189 | 1.0001 | 1.026 |
| 2 | 0.00 | 0.00 | 0.00 | 720.64 | 720.64 | 3.762 | 1.000 | 0.821 | 0.861 | 1.0188 | 1.0000 | 0.843 |

[a] NRTL parameters: $\tau_{AB} = 0.8230$, $\tau_{BA} = 2.1684$, $\alpha = 0.6700$. [b] NRTL parameters: $\tau_{AB} = 0.5546$, $\tau_{BA} = 0.9584$, $\alpha = 0.7465$.

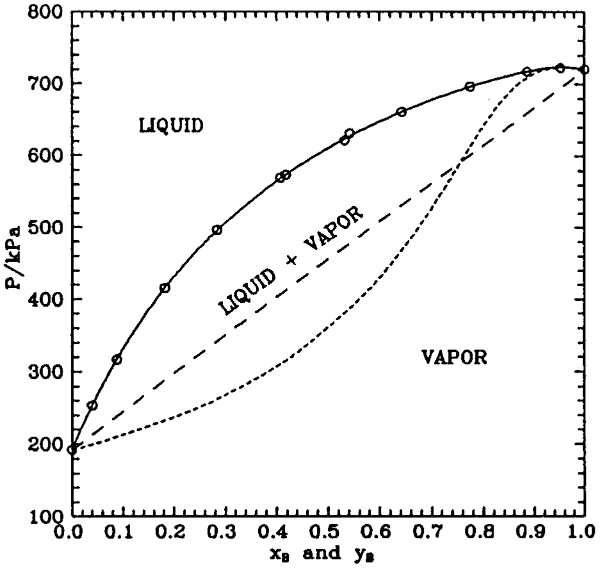

**Figure 9.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-methyl-2-propanol (A) + 2-methylbutane (B) at 100 °C.

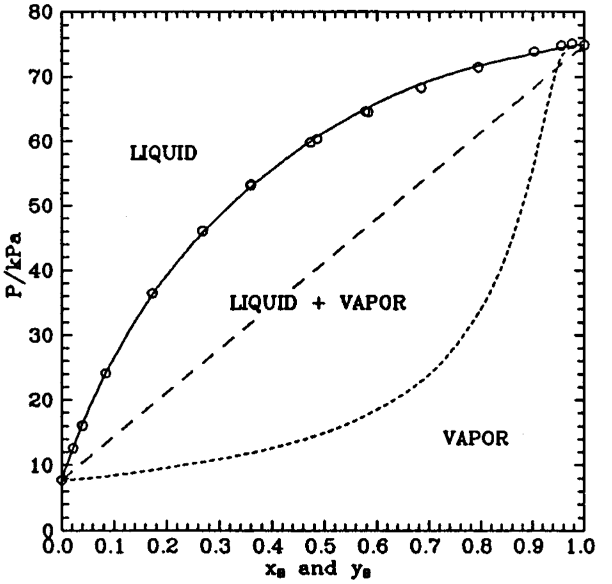

**Figure 10.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-methyl-2-propanol (A) + 2-methyl-2-butene (B) at 30 °C.

of vapor−liquid equilibrium, given as follows:

$$Py_i\phi_i = x_i\gamma_i P_i^\circ \phi_i^\circ \exp\left[\left(\frac{V_i}{RT}\right)(P - P_i^\circ)\right] \qquad (1)$$

where $P$ is the total pressure, $y_i$ is the vapor mole fraction of component $i$, $\phi_i$ is the fugacity coefficient of component $i$, $x_i$ is the liquid mole fraction of component $i$, $\gamma_i$ is the activity coefficient of component $i$, $P_i^\circ$ is the vapor pressure of component $i$ at the system temperature, $\phi_i^\circ$ is the fugacity coefficient of component $i$ at the system temperature and corresponding vapor pressure of component $i$, and the exponential term is the Poynting correction where $V_i$ is the molar volume of component $i$. In the above expression it is assumed that the molar volume of component $i$ is equal to the partial molar volume of component $i$ at these conditions. Pure component molar volumes were calculated from correlations of density data (Daubert et al., 1992).

**Table 4. *PTx* Measurement Results on 2-Methyl-2-propanol (A) + 2-Methyl-2-Butene (B)**

| run no. | $100z_A$ | $100x_A$ | $100y_A$ | $P$/kPa meas | $P$/kPa calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | PF$_A$ | PF$_B$ | $\alpha_{BA}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $t$ = 30 °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 7.723 | 7.723 | 1.000 | 3.341 | 0.996 | 0.997 | 1.0000 | 0.9971 | 31.468 |
| 1 | 97.75 | 97.81 | 60.06 | 12.619 | 12.619 | 1.001 | 3.162 | 0.994 | 0.995 | 1.0002 | 0.9973 | 29.757 |
| 1 | 95.95 | 96.06 | 46.10 | 16.037 | 16.195 | 1.002 | 3.032 | 0.992 | 0.994 | 1.0003 | 0.9975 | 28.486 |
| 1 | 91.41 | 91.60 | 29.85 | 24.115 | 24.101 | 1.008 | 2.746 | 0.988 | 0.991 | 1.0006 | 0.9978 | 25.616 |
| 1 | 82.44 | 82.70 | 18.50 | 36.447 | 36.234 | 1.034 | 2.318 | 0.983 | 0.986 | 1.0011 | 0.9984 | 21.063 |
| 1 | 72.96 | 73.22 | 13.59 | 46.048 | 45.770 | 1.078 | 1.997 | 0.978 | 0.983 | 1.0014 | 0.9988 | 17.389 |
| 1 | 63.81 | 64.04 | 10.89 | 53.129 | 52.964 | 1.140 | 1.769 | 0.975 | 0.980 | 1.0017 | 0.9991 | 14.563 |
| 2 | 63.92 | 64.01 | 10.89 | 53.265 | 52.981 | 1.140 | 1.768 | 0.975 | 0.980 | 1.0017 | 0.9991 | 14.556 |
| 2 | 52.59 | 52.72 | 8.71 | 59.809 | 59.965 | 1.249 | 1.556 | 0.971 | 0.977 | 1.0020 | 0.9994 | 11.682 |
| 1 | 51.36 | 51.50 | 8.52 | 60.328 | 60.619 | 1.264 | 1.536 | 0.971 | 0.977 | 1.0020 | 0.9994 | 11.398 |
| 2 | 42.10 | 42.25 | 7.26 | 64.600 | 65.017 | 1.404 | 1.400 | 0.969 | 0.975 | 1.0022 | 0.9996 | 9.343 |
| 1 | 41.66 | 41.75 | 7.20 | 64.528 | 65.227 | 1.414 | 1.393 | 0.969 | 0.975 | 1.0022 | 0.9996 | 9.235 |
| 2 | 31.47 | 31.61 | 6.11 | 68.309 | 68.883 | 1.670 | 1.266 | 0.967 | 0.974 | 1.0023 | 0.9997 | 7.100 |
| 2 | 20.52 | 20.63 | 5.13 | 71.448 | 71.644 | 2.231 | 1.145 | 0.966 | 0.973 | 1.0024 | 0.9999 | 4.807 |
| 2 | 9.70 | 9.75 | 4.01 | 73.866 | 73.568 | 3.786 | 1.045 | 0.965 | 0.972 | 1.0025 | 0.9999 | 2.586 |
| 2 | 4.46 | 4.48 | 2.82 | 74.787 | 74.466 | 5.857 | 1.012 | 0.965 | 0.972 | 1.0025 | 1.0000 | 1.617 |
| 2 | 2.38 | 2.38 | 1.88 | 75.085 | 74.774 | 7.369 | 1.004 | 0.964 | 0.971 | 1.0025 | 1.0000 | 1.275 |
| 2 | 0.00 | 0.00 | 0.00 | 74.888 | 74.888 | 10.100 | 1.000 | 0.964 | 0.971 | 1.0025 | 1.0000 | 0.927 |
| | | | | | $t$ = 100 °C[b] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 195.05 | 195.05 | 1.000 | 2.152 | 0.951 | 0.960 | 1.0000 | 0.9852 | 5.664 |
| 1 | 97.75 | 97.95 | 89.63 | 214.59 | 214.45 | 1.000 | 2.104 | 0.946 | 0.955 | 1.0007 | 0.9860 | 5.532 |
| 1 | 95.19 | 95.60 | 80.16 | 235.91 | 235.76 | 1.001 | 2.051 | 0.940 | 0.951 | 1.0014 | 0.9868 | 5.383 |
| 1 | 90.94 | 91.63 | 68.06 | 269.74 | 269.64 | 1.004 | 1.965 | 0.932 | 0.944 | 1.0026 | 0.9882 | 5.135 |
| 1 | 81.02 | 82.06 | 50.07 | 341.11 | 340.59 | 1.019 | 1.778 | 0.914 | 0.929 | 1.0050 | 0.9910 | 4.561 |
| 1 | 71.52 | 72.59 | 39.71 | 393.87 | 397.74 | 1.049 | 1.616 | 0.900 | 0.917 | 1.0070 | 0.9932 | 4.021 |
| 2 | 64.78 | 65.15 | 34.08 | 439.33 | 434.70 | 1.083 | 1.504 | 0.891 | 0.910 | 1.0083 | 0.9947 | 3.616 |
| 1 | 61.77 | 62.68 | 32.52 | 443.87 | 445.59 | 1.098 | 1.469 | 0.888 | 0.907 | 1.0087 | 0.9952 | 3.485 |
| 2 | 53.90 | 54.47 | 28.10 | 480.13 | 477.45 | 1.157 | 1.363 | 0.880 | 0.901 | 1.0098 | 0.9964 | 3.062 |
| 1 | 50.51 | 51.09 | 26.53 | 486.20 | 488.81 | 1.188 | 1.323 | 0.877 | 0.898 | 1.0102 | 0.9969 | 2.893 |
| 2 | 43.35 | 43.99 | 23.54 | 511.28 | 509.80 | 1.269 | 1.247 | 0.872 | 0.894 | 1.0109 | 0.9977 | 2.550 |
| 1 | 40.63 | 40.93 | 22.35 | 515.35 | 517.77 | 1.312 | 1.217 | 0.870 | 0.892 | 1.0112 | 0.9980 | 2.407 |
| 2 | 31.97 | 32.53 | 19.20 | 537.80 | 536.82 | 1.461 | 1.144 | 0.865 | 0.888 | 1.0119 | 0.9988 | 2.030 |
| 2 | 21.21 | 21.56 | 14.87 | 556.99 | 556.28 | 1.759 | 1.068 | 0.860 | 0.884 | 1.0126 | 0.9996 | 1.573 |
| 2 | 10.26 | 10.34 | 9.08 | 568.58 | 569.02 | 2.282 | 1.017 | 0.857 | 0.882 | 1.0130 | 1.0001 | 1.154 |
| 2 | 4.95 | 4.94 | 5.07 | 569.84 | 570.59 | 2.672 | 1.004 | 0.857 | 0.881 | 1.0131 | 1.0001 | 0.973 |
| 2 | 2.94 | 2.92 | 3.20 | 569.39 | 569.83 | 2.853 | 1.001 | 0.857 | 0.881 | 1.0130 | 1.0001 | 0.909 |
| 2 | 0.00 | 0.00 | 0.00 | 566.85 | 566.85 | 3.159 | 1.000 | 0.858 | 0.882 | 1.0129 | 1.0000 | 0.820 |

[a] NRTL parameters: $\tau_{AB} = 0.7046$, $\tau_{BA} = 1.8830$, $\alpha = 0.7025$. [b] NRTL parameters: $\tau_{AB} = 0.1941$, $\tau_{BA} = 0.9757$, $\alpha = 0.5465$.

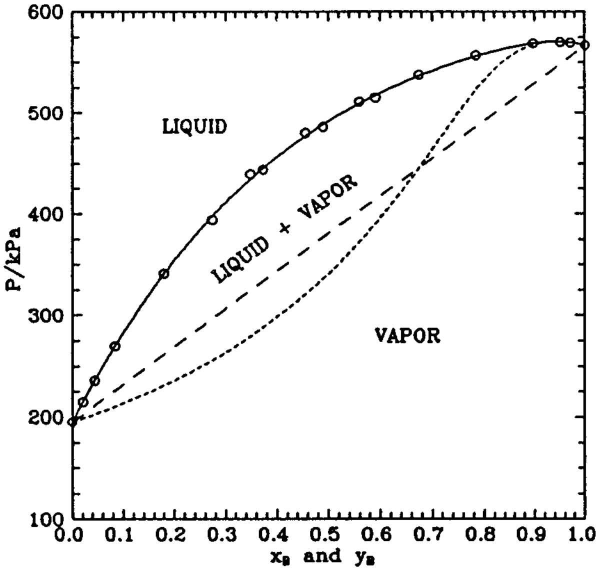

**Figure 11.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-methyl-2-propanol (A) + 2-methyl-2-butene (B) at 100 °C.

The data reduction procedure, similar to the method proposed by Barker (1953), consisted of fitting the pressure data to eq 1 across the entire composition range by adjusting the parameters of the activity coefficient model. The activity coefficient model that gave the best overall fit of the measured total pressure data for a given system was generally used to reduce the data for that system. The Wilson equation (Wilson, 1964) and the NRTL equation (Renon and Prausnitz, 1968) were used in the data reduction procedure and are given below:

Wilson equation:

$$\ln \gamma_A = -\ln(x_A + \Lambda_{AB}x_B) + x_B\left(\frac{\Lambda_{AB}}{x_A + \Lambda_{AB}x_B} - \frac{\Lambda_{BA}}{\Lambda_{BA}x_A + x_B}\right)$$

$$\ln \gamma_B = -\ln(x_B + \Lambda_{BA}x_A) - x_A\left(\frac{\Lambda_{AB}}{x_A + \Lambda_{AB}x_B} - \frac{\Lambda_{BA}}{\Lambda_{BA}x_A + x_B}\right) \qquad (2)$$

NRTL equation:

$$\ln \gamma_A = x_B^2\left[\tau_{BA}\left(\frac{G_{BA}}{x_A + x_BG_{BA}}\right)^2 + \left(\frac{\tau_{AB}G_{AB}}{(x_B + x_AG_{AB})^2}\right)\right]$$

$$\ln \gamma_B = x_A^2\left[\tau_{AB}\left(\frac{G_{AB}}{x_B + x_AG_{AB}}\right)^2 + \left(\frac{\tau_{BA}G_{BA}}{(x_A + x_BG_{BA})^2}\right)\right] \qquad (3)$$

$$G_{AB} = \exp(-\alpha\tau_{AB})$$

$$G_{BA} = \exp(-\alpha\tau_{BA})$$

**Table 5. *PTx* Measurement Results on Methacrylonitrile (A) + Methanol (B)**

| run no. | $100z_A$ | $100x_A$ | $100y_A$ | $P$/kPa meas | $P$/kPa calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | $t = 25\ °C^a$ | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 8.370 | 8.370 | 1.000 | 3.766 | 0.995 | 0.998 | 1.0000 | 0.9999 | 7.601 |
| 1 | 94.74 | 94.76 | 73.38 | 10.798 | 10.865 | 1.004 | 3.262 | 0.994 | 0.998 | 1.0001 | 0.9999 | 6.555 |
| 1 | 90.49 | 90.51 | 62.10 | 12.442 | 12.381 | 1.013 | 2.924 | 0.993 | 0.997 | 1.0001 | 0.9999 | 5.823 |
| 1 | 81.59 | 81.62 | 49.34 | 14.610 | 14.555 | 1.048 | 2.370 | 0.992 | 0.997 | 1.0002 | 1.0000 | 4.561 |
| 1 | 70.58 | 70.60 | 41.47 | 16.008 | 16.090 | 1.124 | 1.892 | 0.991 | 0.996 | 1.0003 | 1.0000 | 3.390 |
| 1 | 60.43 | 60.45 | 37.08 | 16.859 | 16.902 | 1.233 | 1.588 | 0.991 | 0.996 | 1.0003 | 1.0000 | 2.594 |
| 2 | 51.35 | 51.35 | 34.00 | 17.372 | 17.376 | 1.368 | 1.392 | 0.991 | 0.996 | 1.0003 | 1.0000 | 2.049 |
| 1 | 49.66 | 49.67 | 33.46 | 17.441 | 17.447 | 1.397 | 1.361 | 0.991 | 0.996 | 1.0003 | 1.0000 | 1.963 |
| 2 | 41.29 | 41.30 | 30.73 | 17.757 | 17.743 | 1.570 | 1.236 | 0.991 | 0.996 | 1.0003 | 1.0000 | 1.586 |
| 1 | 39.62 | 39.63 | 30.16 | 17.813 | 17.791 | 1.610 | 1.215 | 0.991 | 0.996 | 1.0003 | 1.0000 | 1.520 |
| 2 | 31.04 | 31.05 | 26.86 | 18.042 | 17.985 | 1.850 | 1.126 | 0.991 | 0.996 | 1.0003 | 1.0000 | 1.226 |
| 1 | 29.16 | 29.16 | 26.03 | 18.071 | 18.013 | 1.911 | 1.110 | 0.991 | 0.996 | 1.0003 | 1.0000 | 1.170 |
| 2 | 20.51 | 20.51 | 21.45 | 18.068 | 18.051 | 2.245 | 1.053 | 0.991 | 0.996 | 1.0003 | 1.0000 | 0.945 |
| 2 | 9.93 | 9.93 | 13.12 | 17.723 | 17.778 | 2.794 | 1.012 | 0.991 | 0.996 | 1.0003 | 1.0000 | 0.730 |
| 2 | 4.51 | 4.50 | 6.86 | 17.391 | 17.415 | 3.156 | 1.002 | 0.991 | 0.996 | 1.0003 | 1.0000 | 0.640 |
| 2 | 2.13 | 2.13 | 3.48 | 17.114 | 17.188 | 3.335 | 1.001 | 0.992 | 0.996 | 1.0003 | 1.0000 | 0.605 |
| 2 | 0.00 | 0.00 | 0.00 | 16.942 | 16.942 | 3.508 | 1.000 | 0.992 | 0.996 | 1.0003 | 1.0000 | 0.575 |
| | | | | | $t = 65\ °C^b$ | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 44.565 | 44.565 | 1.000 | 2.696 | 0.983 | 0.995 | 1.0000 | 0.9991 | 6.154 |
| 1 | 97.66 | 97.70 | 87.78 | 49.151 | 49.730 | 1.000 | 2.588 | 0.981 | 0.993 | 1.0002 | 0.9992 | 5.900 |
| 1 | 95.21 | 95.28 | 78.13 | 54.486 | 54.682 | 1.002 | 2.482 | 0.979 | 0.992 | 1.0003 | 0.9993 | 5.643 |
| 1 | 90.70 | 90.80 | 65.53 | 63.007 | 62.699 | 1.008 | 2.301 | 0.976 | 0.991 | 1.0006 | 0.9994 | 5.195 |
| 1 | 81.01 | 81.15 | 49.84 | 76.391 | 75.941 | 1.033 | 1.972 | 0.971 | 0.988 | 1.0010 | 0.9996 | 4.333 |
| 1 | 70.05 | 70.17 | 40.15 | 86.088 | 86.111 | 1.088 | 1.682 | 0.968 | 0.986 | 1.0013 | 0.9997 | 3.506 |
| 1 | 60.08 | 60.18 | 34.46 | 92.152 | 92.407 | 1.165 | 1.479 | 0.966 | 0.985 | 1.0015 | 0.9998 | 2.874 |
| 2 | 53.29 | 53.32 | 31.37 | 95.494 | 95.640 | 1.238 | 1.367 | 0.965 | 0.984 | 1.0016 | 0.9999 | 2.499 |
| 1 | 50.93 | 50.99 | 30.41 | 96.370 | 96.588 | 1.267 | 1.333 | 0.964 | 0.984 | 1.0017 | 0.9999 | 2.381 |
| 2 | 42.25 | 42.28 | 26.99 | 99.673 | 99.609 | 1.397 | 1.223 | 0.964 | 0.983 | 1.0017 | 0.9999 | 1.982 |
| 1 | 39.98 | 40.01 | 26.11 | 100.155 | 100.284 | 1.438 | 1.199 | 0.963 | 0.983 | 1.0018 | 1.0000 | 1.887 |
| 2 | 31.64 | 31.67 | 22.77 | 102.485 | 102.414 | 1.616 | 1.123 | 0.963 | 0.983 | 1.0018 | 1.0000 | 1.572 |
| 1 | 29.63 | 29.64 | 21.90 | 102.954 | 102.852 | 1.668 | 1.108 | 0.963 | 0.983 | 1.0019 | 1.0000 | 1.502 |
| 2 | 20.88 | 20.89 | 17.66 | 104.497 | 104.347 | 1.936 | 1.053 | 0.963 | 0.982 | 1.0019 | 1.0000 | 1.231 |
| 2 | 10.70 | 10.70 | 11.01 | 105.075 | 104.951 | 2.372 | 1.014 | 0.963 | 0.982 | 1.0019 | 1.0000 | 0.968 |
| 2 | 5.28 | 5.27 | 6.16 | 104.558 | 104.451 | 2.679 | 1.003 | 0.964 | 0.982 | 1.0019 | 1.0000 | 0.848 |
| 2 | 2.27 | 2.27 | 2.86 | 103.857 | 103.805 | 2.879 | 1.001 | 0.964 | 0.982 | 1.0019 | 1.0000 | 0.788 |
| 2 | 0.00 | 0.00 | 0.00 | 103.095 | 103.095 | 3.045 | 1.000 | 0.965 | 0.982 | 1.0019 | 1.0000 | 0.745 |

[a] NRTL parameters: $\tau_{AB} = 0.8689$, $\tau_{BA} = 0.4917$, $\alpha = 0.1492$. [b] NRTL parameters: $\tau_{AB} = 0.2677$, $\tau_{BA} = 0.8599$, $\alpha = 0.2000$.

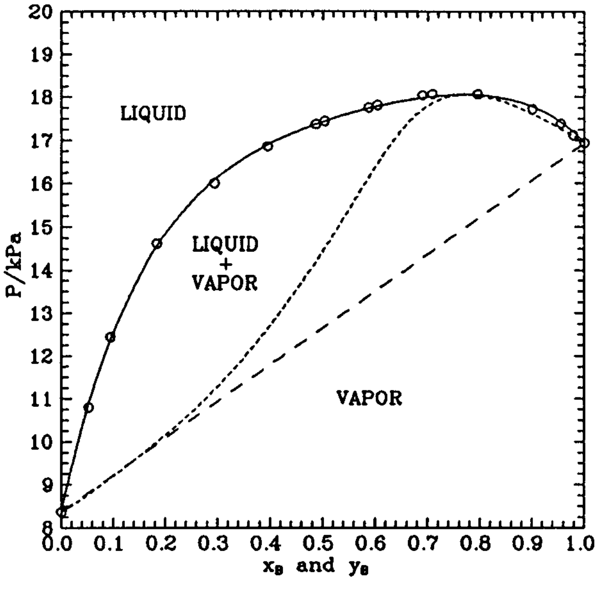

**Figure 12.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for methacrylonitrile (A) + methanol (B) at 25 °C.

As a beginning point, the ideal-solution parameters of the activity coefficient model were selected. Then assuming the liquid composition was the same as the charge composition and the fugacity coefficients were unity, eq 1 was solved for the product $Py_i$ for each component. The calculated pressure was then the sum of these terms:

$$P_{\mathrm{calc}} = \sum (Py_i) \qquad (4)$$

The vapor mole fraction for each component was then determined:

$$y_i = (Py_i)/P_{\mathrm{calc}} \qquad (5)$$

With values for the vapor-phase composition, the fugacity coefficients were calculated from the equation of state.

The next step was to correct the liquid composition for the amounts of each component in the vapor and to return to the step in which the activity coefficients were calculated and continue iterating until the calculated pressure converged. As part of each iteration step, the amount of material taken out of the cell as degas was subtracted from the total charge at the calculated vapor composition.

This procedure was performed for each of the measurement points across the composition range. The calculated pressures were compared to the measured pressures. The activity coefficient parameters were adjusted to improve the fit of the total pressure data, and the entire procedure was repeated until the best fit of the measured total pressure curve was obtained.

## Results and Discussion

The results of the phase equilibrium measurements are described below. The *PTx* data are presented in tables which give the run number, the charge compositions ($z_A$),

**Table 6. *PTx* Measurement Results on 1-Chloro-1,1-difluoroethane (A) + Hydrogen Chloride (B)**

| run no. | $100z_A$ | $100x_A$ | $100y_A$ | $P$/kPa meas | $P$/kPa calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | $t = -40$ °C[a] | | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 23.752 | 23.752 | 1.000 | 1.204 | 0.990 | 1.000 | 1.0000 | 0.9869 | 35.121 |
| 1 | 97.82 | 98.00 | 58.40 | 40.111 | 40.142 | 1.000 | 1.198 | 0.984 | 0.997 | 1.0007 | 0.9872 | 34.826 |
| 1 | 95.48 | 95.83 | 39.98 | 57.867 | 57.734 | 1.000 | 1.192 | 0.978 | 0.995 | 1.0014 | 0.9875 | 34.507 |
| 1 | 90.01 | 90.71 | 22.44 | 99.015 | 98.978 | 1.001 | 1.178 | 0.964 | 0.990 | 1.0031 | 0.9882 | 33.747 |
| 1 | 79.55 | 80.66 | 11.46 | 177.94 | 178.10 | 1.005 | 1.151 | 0.940 | 0.981 | 1.0063 | 0.9896 | 32.235 |
| 1 | 71.40 | 72.64 | 7.89 | 239.86 | 239.63 | 1.011 | 1.130 | 0.921 | 0.975 | 1.0088 | 0.9907 | 31.003 |
| 1 | 63.56 | 64.80 | 5.82 | 298.47 | 298.44 | 1.019 | 1.110 | 0.903 | 0.968 | 1.0113 | 0.9918 | 29.772 |
| 2 | 61.41 | 61.75 | 5.22 | 320.05 | 320.91 | 1.023 | 1.102 | 0.897 | 0.966 | 1.0122 | 0.9922 | 29.287 |
| 1 | 51.48 | 52.50 | 3.83 | 387.83 | 388.06 | 1.039 | 1.080 | 0.877 | 0.959 | 1.0149 | 0.9933 | 27.783 |
| 2 | 50.64 | 51.31 | 3.68 | 396.05 | 396.52 | 1.042 | 1.077 | 0.875 | 0.958 | 1.0153 | 0.9935 | 27.588 |
| 1 | 41.69 | 42.44 | 2.75 | 459.40 | 459.40 | 1.064 | 1.057 | 0.856 | 0.951 | 1.0179 | 0.9946 | 26.091 |
| 2 | 40.23 | 41.17 | 2.63 | 468.81 | 468.29 | 1.068 | 1.054 | 0.854 | 0.950 | 1.0183 | 0.9948 | 25.873 |
| 1 | 32.36 | 32.81 | 1.96 | 526.56 | 526.60 | 1.098 | 1.037 | 0.837 | 0.944 | 1.0207 | 0.9958 | 24.404 |
| 2 | 30.30 | 31.38 | 1.86 | 537.64 | 536.56 | 1.104 | 1.034 | 0.834 | 0.943 | 1.0211 | 0.9960 | 24.147 |
| 2 | 19.97 | 20.97 | 1.18 | 610.56 | 609.23 | 1.159 | 1.017 | 0.814 | 0.935 | 1.0241 | 0.9972 | 22.223 |
| 2 | 9.26 | 9.90 | 0.54 | 690.39 | 688.75 | 1.242 | 1.004 | 0.792 | 0.926 | 1.0275 | 0.9987 | 20.058 |
| 2 | 4.76 | 5.14 | 0.28 | 725.76 | 724.49 | 1.290 | 1.001 | 0.782 | 0.923 | 1.0290 | 0.9993 | 19.085 |
| 2 | 2.56 | 2.78 | 0.15 | 743.67 | 742.70 | 1.317 | 1.000 | 0.777 | 0.921 | 1.0297 | 0.9996 | 18.593 |
| 2 | 0.00 | 0.00 | 0.00 | 764.73 | 764.73 | 1.351 | 1.000 | 0.771 | 0.918 | 1.0306 | 1.0000 | 18.005 |
| | | | | $t = 0$ °C[b] | | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 144.42 | 144.42 | 1.000 | 1.098 | 0.960 | 1.002 | 1.0000 | 0.9576 | 15.606 |
| 1 | 97.70 | 98.09 | 76.84 | 185.94 | 186.80 | 1.000 | 1.095 | 0.949 | 0.996 | 1.0016 | 0.9583 | 15.469 |
| 1 | 93.59 | 94.61 | 53.54 | 264.25 | 264.34 | 1.000 | 1.091 | 0.931 | 0.988 | 1.0045 | 0.9596 | 15.218 |
| 1 | 90.69 | 92.10 | 43.67 | 320.19 | 320.36 | 1.000 | 1.088 | 0.919 | 0.983 | 1.0066 | 0.9606 | 15.037 |
| 1 | 82.10 | 84.42 | 27.23 | 492.89 | 493.22 | 1.002 | 1.079 | 0.884 | 0.969 | 1.0132 | 0.9635 | 14.480 |
| 1 | 72.48 | 75.36 | 18.13 | 699.94 | 699.42 | 1.004 | 1.068 | 0.845 | 0.954 | 1.0211 | 0.9670 | 13.816 |
| 1 | 61.01 | 63.99 | 12.05 | 962.91 | 962.36 | 1.010 | 1.054 | 0.797 | 0.935 | 1.0313 | 0.9715 | 12.971 |
| 2 | 59.37 | 60.13 | 10.63 | 1055.3 | 1052.8 | 1.013 | 1.049 | 0.780 | 0.929 | 1.0348 | 0.9730 | 12.681 |
| 1 | 53.22 | 55.95 | 9.31 | 1152.6 | 1151.4 | 1.016 | 1.044 | 0.763 | 0.922 | 1.0387 | 0.9747 | 12.365 |
| 2 | 48.84 | 50.50 | 7.87 | 1282.2 | 1281.0 | 1.022 | 1.038 | 0.741 | 0.913 | 1.0437 | 0.9769 | 11.950 |
| 1 | 42.92 | 45.01 | 6.63 | 1414.9 | 1413.2 | 1.028 | 1.032 | 0.718 | 0.904 | 1.0490 | 0.9792 | 11.527 |
| 2 | 39.58 | 42.06 | 6.04 | 1482.4 | 1484.9 | 1.033 | 1.028 | 0.706 | 0.899 | 1.0518 | 0.9804 | 11.299 |
| 1 | 32.25 | 33.48 | 4.52 | 1697.0 | 1696.9 | 1.047 | 1.020 | 0.671 | 0.885 | 1.0602 | 0.9841 | 10.625 |
| 2 | 30.24 | 33.20 | 4.48 | 1699.9 | 1703.8 | 1.048 | 1.019 | 0.670 | 0.884 | 1.0605 | 0.9842 | 10.604 |
| 2 | 19.40 | 22.48 | 2.89 | 1972.1 | 1978.3 | 1.074 | 1.010 | 0.627 | 0.866 | 1.0715 | 0.9889 | 9.741 |
| 2 | 9.65 | 11.98 | 1.51 | 2254.9 | 2261.4 | 1.109 | 1.003 | 0.584 | 0.846 | 1.0830 | 0.9939 | 8.868 |
| 2 | 5.37 | 6.91 | 0.87 | 2400.1 | 2405.1 | 1.131 | 1.001 | 0.562 | 0.837 | 1.0889 | 0.9964 | 8.436 |
| 2 | 3.18 | 4.22 | 0.53 | 2480.7 | 2484.0 | 1.144 | 1.000 | 0.551 | 0.831 | 1.0921 | 0.9978 | 8.202 |
| 2 | 0.00 | 0.00 | 0.00 | 2611.6 | 2611.6 | 1.168 | 1.000 | 0.532 | 0.822 | 1.0974 | 1.0000 | 7.830 |

[a] Wilson equation parameters: $\Lambda_{AB} = 0.5383$, $\Lambda_{BA} = 1.3182$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.5897$, $\Lambda_{BA} = 1.3731$.

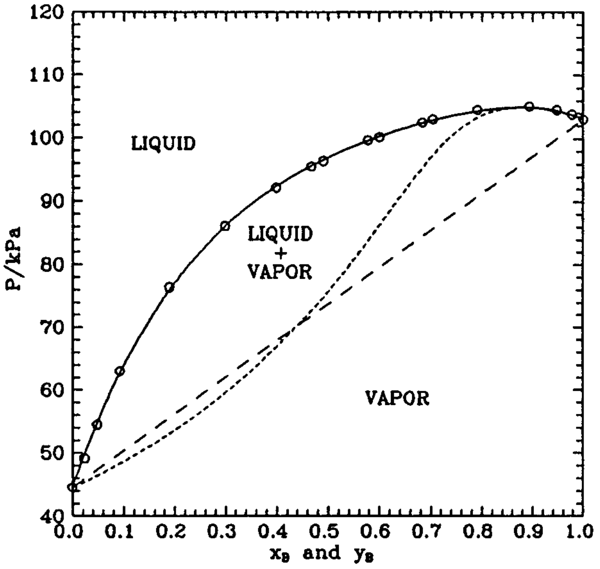

**Figure 13.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for methacrylonitrile (A) + methanol (B) at 65 °C

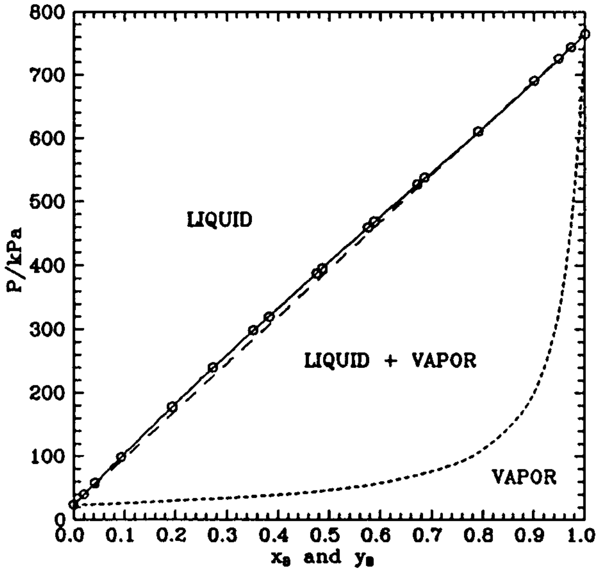

**Figure 14.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 1-chloro-1,1-difluoroethane (A) + hydrogen chloride (B) at −40 °C.

the calculated liquid ($x_A$) and vapor ($y_A$) compositions, the measured and correlated pressures, the activity ($\gamma_A$ and $\gamma_B$) and fugacity coefficients ($\phi_A$ and $\phi_B$), the Poynting corrections ($PF_A$ and $PF_B$), and the relative volatilities ($\alpha_{BA}$). The relative volatility was determined from

$$\alpha_{BA} = \frac{y_B/x_B}{y_A/x_A} \tag{6}$$

**Table 7. *PTx* Measurement Results on 2-(Hexyloxy)ethanol (A) + Ethylene Glycol (B)**

| | | | | $P$/kPa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $100z_A$ | $100x_A$ | $100y_A$ | meas | calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
| | | | | | $t$ = 100 °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 2.063 | 2.063 | 1.000 | 2.896 | 0.998 | 1.000 | 1.0000 | 1.0000 | 2.968 |
| 1 | 97.30 | 97.30 | 92.58 | 2.160 | 2.169 | 1.000 | 2.821 | 0.998 | 0.999 | 1.0000 | 1.0000 | 2.890 |
| 1 | 94.58 | 94.59 | 86.16 | 2.284 | 2.269 | 1.002 | 2.745 | 0.998 | 0.999 | 1.0000 | 1.0000 | 2.810 |
| 1 | 89.66 | 89.68 | 76.56 | 2.463 | 2.431 | 1.006 | 2.611 | 0.998 | 0.999 | 1.0000 | 1.0000 | 2.660 |
| 1 | 79.76 | 79.77 | 62.73 | 2.715 | 2.692 | 1.026 | 2.346 | 0.998 | 0.999 | 1.0000 | 1.0000 | 2.344 |
| 1 | 69.32 | 69.34 | 53.15 | 2.894 | 2.879 | 1.069 | 2.080 | 0.998 | 0.999 | 1.0000 | 1.0000 | 1.994 |
| 1 | 59.30 | 59.31 | 46.93 | 2.984 | 2.986 | 1.144 | 1.841 | 0.998 | 0.999 | 1.0001 | 1.0000 | 1.648 |
| 1 | 49.20 | 49.20 | 42.67 | 3.033 | 3.037 | 1.276 | 1.620 | 0.998 | 0.999 | 1.0001 | 1.0000 | 1.301 |
| 2 | 37.61 | 37.61 | 39.50 | 3.041 | 3.048 | 1.551 | 1.397 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.923 |
| 1 | 33.58 | 33.58 | 38.71 | 3.029 | 3.044 | 1.700 | 1.328 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.801 |
| 2 | 30.12 | 30.12 | 38.09 | 3.034 | 3.039 | 1.862 | 1.273 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.700 |
| 1 | 29.35 | 29.34 | 37.96 | 3.018 | 3.038 | 1.904 | 1.261 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.679 |
| 2 | 20.13 | 20.12 | 36.23 | 2.984 | 3.009 | 2.625 | 1.136 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.443 |
| 1 | 19.16 | 19.15 | 35.99 | 2.959 | 3.004 | 2.734 | 1.124 | 0.998 | 0.999 | 1.0001 | 1.0000 | 0.421 |
| 2 | 9.91 | 9.90 | 31.32 | 2.868 | 2.880 | 4.414 | 1.038 | 0.998 | 0.999 | 1.0000 | 1.0000 | 0.241 |
| 2 | 5.13 | 5.12 | 24.13 | 2.711 | 2.674 | 6.110 | 1.011 | 0.998 | 0.999 | 1.0000 | 1.0000 | 0.170 |
| 2 | 2.28 | 2.28 | 14.79 | 2.465 | 2.431 | 7.649 | 1.002 | 0.998 | 0.999 | 1.0000 | 1.0000 | 0.134 |
| 2 | 0.00 | 0.00 | 0.00 | 2.115 | 2.115 | 9.342 | 1.000 | 0.998 | 0.999 | 1.0000 | 1.0000 | 0.110 |
| | | | | | $t$ = 180 °C[b] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 46.604 | 46.604 | 1.000 | 2.359 | 0.979 | 0.994 | 1.0000 | 0.9998 | 2.957 |
| 1 | 96.03 | 96.15 | 89.68 | 49.940 | 50.085 | 1.001 | 2.299 | 0.977 | 0.993 | 1.0002 | 0.9999 | 2.878 |
| 1 | 94.27 | 94.44 | 85.66 | 50.519 | 51.563 | 1.001 | 2.272 | 0.976 | 0.993 | 1.0002 | 0.9999 | 2.842 |
| 1 | 90.55 | 90.81 | 78.15 | 53.959 | 54.536 | 1.003 | 2.213 | 0.975 | 0.992 | 1.0004 | 0.9999 | 2.761 |
| 1 | 81.30 | 81.66 | 63.70 | 61.375 | 61.058 | 1.015 | 2.060 | 0.973 | 0.990 | 1.0007 | 1.0000 | 2.538 |
| 1 | 68.83 | 69.18 | 50.61 | 68.552 | 67.706 | 1.052 | 1.846 | 0.970 | 0.989 | 1.0010 | 1.0001 | 2.191 |
| 1 | 58.99 | 59.26 | 43.57 | 71.570 | 71.213 | 1.111 | 1.676 | 0.969 | 0.988 | 1.0012 | 1.0002 | 1.884 |
| 1 | 48.78 | 48.93 | 38.29 | 73.631 | 73.386 | 1.218 | 1.506 | 0.968 | 0.987 | 1.0013 | 1.0002 | 1.544 |
| 2 | 41.06 | 41.11 | 35.27 | 74.193 | 74.207 | 1.350 | 1.385 | 0.968 | 0.987 | 1.0013 | 1.0003 | 1.281 |
| 1 | 38.33 | 38.38 | 34.36 | 74.367 | 74.357 | 1.411 | 1.345 | 0.968 | 0.987 | 1.0014 | 1.0003 | 1.190 |
| 2 | 30.36 | 30.34 | 31.97 | 74.366 | 74.461 | 1.663 | 1.235 | 0.968 | 0.987 | 1.0014 | 1.0003 | 0.927 |
| 1 | 28.94 | 28.92 | 31.56 | 74.367 | 74.431 | 1.723 | 1.216 | 0.968 | 0.987 | 1.0014 | 1.0003 | 0.882 |
| 2 | 19.86 | 19.76 | 28.74 | 73.676 | 73.819 | 2.278 | 1.113 | 0.969 | 0.987 | 1.0013 | 1.0003 | 0.611 |
| 1 | 18.64 | 18.59 | 28.30 | 73.392 | 73.667 | 2.379 | 1.102 | 0.969 | 0.987 | 1.0013 | 1.0002 | 0.579 |
| 2 | 9.37 | 9.20 | 22.39 | 70.751 | 70.853 | 3.664 | 1.029 | 0.970 | 0.987 | 1.0012 | 1.0002 | 0.351 |
| 2 | 4.60 | 4.46 | 15.30 | 66.892 | 66.853 | 4.884 | 1.007 | 0.973 | 0.988 | 1.0010 | 1.0001 | 0.259 |
| 2 | 2.25 | 2.17 | 9.16 | 63.191 | 63.447 | 5.731 | 1.002 | 0.975 | 0.988 | 1.0008 | 1.0001 | 0.219 |
| 2 | 0.00 | 0.00 | 0.00 | 58.748 | 58.748 | 6.760 | 1.000 | 0.977 | 0.989 | 1.0006 | 1.0000 | 0.186 |

[a] NRTL parameters: $\tau_{AB} = -0.0953$, $\tau_{BA} = 2.3325$, $\alpha = 0.3000$. NRTL parameters: $\tau_{AB} = -0.2818$, $\tau_{BA} = 2.2177$, $\alpha = 0.3000$.

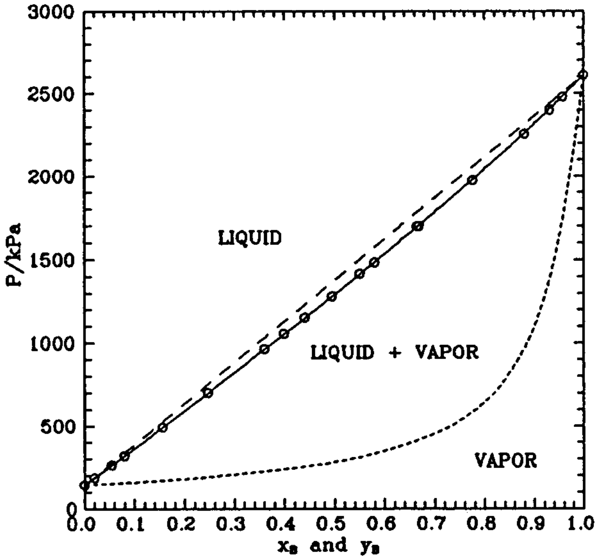

Figure 15. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 1-chloro-1,1-difluoroethane (A) + hydrogen chloride (B) at 0 °C.

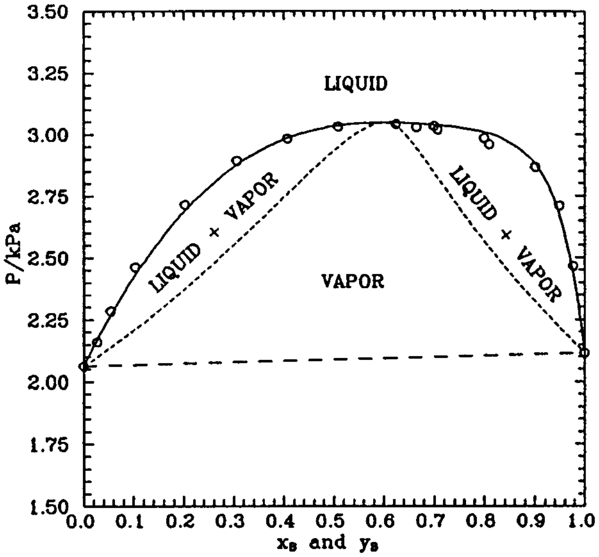

Figure 16. Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-(hexyloxy)ethanol (A) + ethylene glycol (B) at 100 °C.

The activity coefficient parameters used to obtain the correlation are given at the bottom of each table. Figures showing total pressure as a function of liquid and vapor composition are included to illustrate the data. The results of vapor−liquid−liquid equilibrium measurements on butane + ammonia at 0 °C are included with the *PTx* results for that binary.

***1. (Aminoethyl)piperazine + Diethylenetriamine.*** Results of the *PTx* measurements on (aminoethyl)piperazine + diethylenetriamine at 125 and 210 °C are given in

**Table 8. *PTx* Measurement Results on Butane (A) + Ammonia (B)**

| | | | | $P$/kPa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $100z_A$ | $100x_A$ | $100y_A$ | meas | calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
| | | | | | $t$ = 0 °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 103.69 | 103.69 | 1.000 | 10.958 | 0.966 | 0.998 | 1.0000 | 0.9962 | 43.348 |
| 1 | 96.85 | 97.71 | 53.41 | 198.50 | 196.22 | 1.002 | 9.579 | 0.939 | 0.985 | 1.0039 | 0.9973 | 37.150 |
| 1 | 95.10 | 96.35 | 43.62 | 235.48 | 240.98 | 1.004 | 8.884 | 0.927 | 0.979 | 1.0059 | 0.9978 | 34.072 |
| 1 | 91.76 | 93.56 | 33.50 | 317.99 | 314.49 | 1.012 | 7.687 | 0.908 | 0.971 | 1.0090 | 0.9987 | 28.830 |
| 3[b] | | 85.26 | 19.18 | 529.15 | | | | | | | | 24.373 |
| 1 | 81.43 | | | 488.72 | | | | | | | | |
| 1 | 72.74 | | | 518.68 | | | | | | | | |
| 1 | 62.91 | | | 524.94 | | | | | | | | |
| 1 | 50.55 | | | 527.47 | | | | | | | | |
| 2 | 42.29 | | | 529.94 | | | | | | | | |
| 1 | 41.12 | | | 527.72 | | | | | | | | |
| 1 | 31.00 | | | 529.15 | | | | | | | | |
| 2 | 30.60 | | | 529.94 | | | | | | | | |
| 1 | 20.02 | | | 529.83 | | | | | | | | |
| 2 | 19.48 | | | 529.85 | | | | | | | | |
| 2 | 8.83 | | | 529.98 | | | | | | | | |
| 2 | 5.14 | | | 530.10 | | | | | | | | |
| 2 | 2.24 | | | 530.04 | | | | | | | | |
| 3[b] | | 1.06 | 19.18 | 529.15 | | | | | | | | 0.045 |
| 2 | 0.00 | 0.00 | 0.00 | 429.19 | 429.19 | 77.351 | 1.000 | 0.893 | 0.957 | 1.0139 | 1.0000 | 0.049 |
| | | | | | $t$ = 50 °C[c] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 494.84 | 494.84 | 1.000 | 5.401 | 0.899 | 0.998 | 1.0000 | 0.9828 | 19.138 |
| 1 | 97.14 | 98.36 | 77.33 | 654.16 | 656.51 | 1.000 | 5.094 | 0.868 | 0.983 | 1.0065 | 0.9846 | 17.611 |
| 1 | 93.80 | 96.29 | 61.99 | 838.20 | 840.52 | 1.002 | 4.745 | 0.835 | 0.968 | 1.0139 | 0.9866 | 15.926 |
| 1 | 87.78 | 92.13 | 47.05 | 1148.4 | 1152.4 | 1.011 | 4.155 | 0.784 | 0.945 | 1.0266 | 0.9901 | 13.174 |
| 1 | 80.78 | 86.50 | 38.06 | 1481.0 | 1477.4 | 1.030 | 3.535 | 0.733 | 0.923 | 1.0400 | 0.9937 | 10.423 |
| 1 | 70.64 | 76.81 | 31.23 | 1879.7 | 1858.4 | 1.087 | 2.786 | 0.675 | 0.899 | 1.0560 | 0.9980 | 7.291 |
| 1 | 60.69 | 65.92 | 27.51 | 2149.7 | 2120.4 | 1.188 | 2.232 | 0.637 | 0.882 | 1.0671 | 1.0010 | 5.099 |
| 1 | 52.80 | 56.79 | 25.50 | 2278.8 | 2257.6 | 1.313 | 1.903 | 0.618 | 0.873 | 1.0729 | 1.0025 | 3.839 |
| 2 | 48.50 | 48.77 | 24.16 | 2352.1 | 2335.8 | 1.470 | 1.678 | 0.608 | 0.868 | 1.0763 | 1.0034 | 2.989 |
| 1 | 39.19 | 40.84 | 23.07 | 2384.7 | 2384.1 | 1.692 | 1.498 | 0.602 | 0.864 | 1.0784 | 1.0039 | 2.302 |
| 2 | 30.44 | 30.92 | 21.95 | 2406.8 | 2414.8 | 2.142 | 1.313 | 0.600 | 0.861 | 1.0797 | 1.0043 | 1.591 |
| 1 | 30.06 | 30.62 | 21.92 | 2406.3 | 2415.4 | 2.161 | 1.308 | 0.600 | 0.861 | 1.0797 | 1.0043 | 1.572 |
| 2 | 19.94 | 19.87 | 20.76 | 2413.5 | 2423.8 | 3.169 | 1.152 | 0.601 | 0.860 | 1.0801 | 1.0044 | 0.947 |
| 1 | 17.69 | 17.62 | 20.41 | 2414.8 | 2422.6 | 3.520 | 1.124 | 0.602 | 0.859 | 1.0800 | 1.0044 | 0.834 |
| 2 | 11.01 | 10.26 | 18.21 | 2406.6 | 2396.8 | 5.424 | 1.049 | 0.612 | 0.859 | 1.0789 | 1.0041 | 0.513 |
| 2 | 5.31 | 4.50 | 12.76 | 2352.1 | 2293.7 | 8.705 | 1.011 | 0.639 | 0.862 | 1.0745 | 1.0029 | 0.322 |
| 2 | 2.76 | 2.21 | 7.95 | 2240.2 | 2194.4 | 11.004 | 1.003 | 0.664 | 0.867 | 1.0702 | 1.0018 | 0.262 |
| 2 | 0.00 | 0.00 | 0.00 | 2035.2 | 2035.2 | 14.260 | 1.000 | 0.702 | 0.875 | 1.0634 | 1.0000 | 0.212 |

[a] NRTL parameters: $\tau_{AB} = 1.5328$, $\tau_{BA} = 3.5181$, $\alpha = 0.4000$. [b] Run 3 is the vapor−liquid−liquid equilibrium measurement determined separately from the *PTx* measurements. [c] NRTL parameters: $\tau_{AB} = 0.9622$, $\tau_{BA} = 2.0669$, $\alpha = 0.5073$.

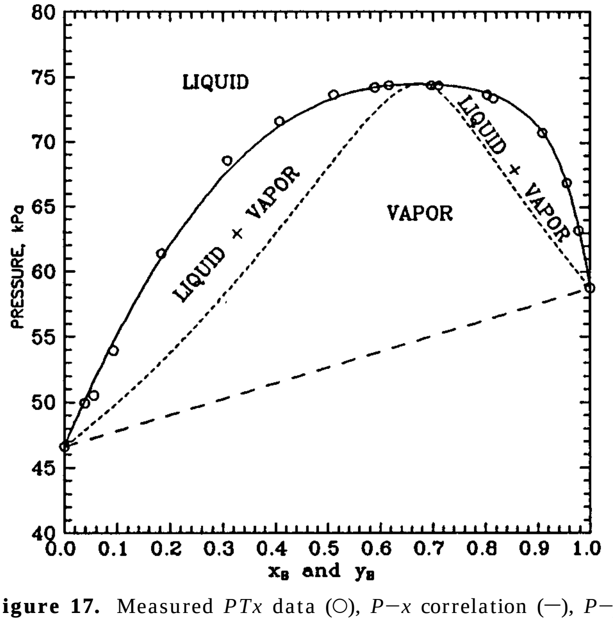

**Figure 17.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for 2-(hexyloxy)ethanol (A) + ethylene glycol (B) at 180 °C.

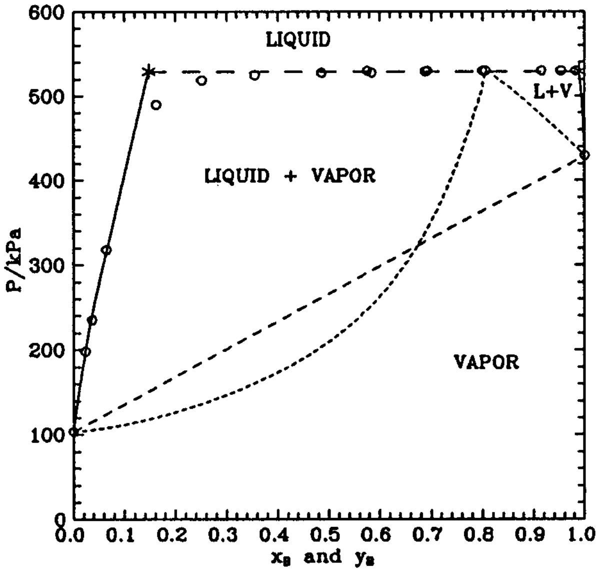

**Figure 18.** Measured *PTx* data (○), measured LLE point (∗), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for butane (A) + ammonia (B) at 0 °C.

Table 1. The Wilson activity coefficient equation was used to reduce the data. These data are plotted in Figure 4 for the 125 °C measurements and in Figure 5 for the 210 °C measurements. This system exhibits nearly ideal behavior with very slight positive deviation from Raoult's law. The

**Table 9. *PTx* Measurement Results on Propionaldehyde (A) + Butane (B)**

| | | | | $P$/kPa | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| run no. | $100z_A$ | $100x_A$ | $100y_A$ | meas | calc | $\gamma_A$ | $\gamma_B$ | $\phi_A$ | $\phi_B$ | $PF_A$ | $PF_B$ | $\alpha_{BA}$ |
| | | | | | $t = 0$ °C[a] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 13.088 | 13.088 | 1.000 | 4.905 | 0.994 | 0.996 | 1.0000 | 0.9964 | 37.348 |
| 1 | 97.94 | 98.04 | 58.88 | 21.844 | 21.895 | 1.001 | 4.591 | 0.991 | 0.993 | 1.0003 | 0.9967 | 34.912 |
| 1 | 95.76 | 95.95 | 42.15 | 29.919 | 30.114 | 1.003 | 4.292 | 0.987 | 0.990 | 1.0005 | 0.9971 | 32.546 |
| 1 | 89.90 | 90.24 | 25.47 | 48.173 | 47.846 | 1.016 | 3.617 | 0.979 | 0.984 | 1.0011 | 0.9978 | 27.038 |
| 1 | 77.84 | 78.23 | 16.08 | 70.449 | 70.325 | 1.075 | 2.663 | 0.970 | 0.977 | 1.0018 | 0.9987 | 18.764 |
| 1 | 71.57 | 71.93 | 14.10 | 77.231 | 77.420 | 1.125 | 2.320 | 0.967 | 0.975 | 1.0020 | 0.9990 | 15.609 |
| 2 | 64.19 | 64.34 | 12.57 | 84.294 | 83.477 | 1.206 | 2.000 | 0.964 | 0.973 | 1.0022 | 0.9992 | 12.545 |
| 1 | 61.63 | 61.90 | 12.20 | 84.428 | 85.015 | 1.238 | 1.913 | 0.964 | 0.972 | 1.0022 | 0.9993 | 11.693 |
| 2 | 54.02 | 54.20 | 11.23 | 89.122 | 88.934 | 1.359 | 1.681 | 0.962 | 0.971 | 1.0023 | 0.9994 | 9.352 |
| 1 | 50.66 | 50.83 | 10.88 | 90.057 | 90.314 | 1.425 | 1.595 | 0.961 | 0.970 | 1.0024 | 0.9995 | 8.464 |
| 2 | 41.24 | 41.44 | 10.03 | 93.334 | 93.443 | 1.664 | 1.398 | 0.960 | 0.969 | 1.0025 | 0.9996 | 6.351 |
| 1 | 40.53 | 40.61 | 9.95 | 92.832 | 93.684 | 1.690 | 1.383 | 0.960 | 0.969 | 1.0025 | 0.9996 | 6.185 |
| 2 | 30.30 | 30.47 | 9.06 | 96.367 | 96.355 | 2.105 | 1.226 | 0.959 | 0.968 | 1.0026 | 0.9997 | 4.400 |
| 2 | 20.47 | 20.58 | 7.94 | 99.067 | 98.787 | 2.797 | 1.113 | 0.958 | 0.968 | 1.0026 | 0.9998 | 3.006 |
| 2 | 9.65 | 9.69 | 5.67 | 102.010 | 101.559 | 4.358 | 1.030 | 0.957 | 0.967 | 1.0027 | 0.9999 | 1.785 |
| 2 | 4.76 | 4.77 | 3.63 | 103.096 | 102.678 | 5.732 | 1.008 | 0.956 | 0.966 | 1.0027 | 1.0000 | 1.328 |
| 2 | 2.29 | 2.29 | 2.05 | 103.453 | 103.044 | 6.757 | 1.002 | 0.956 | 0.966 | 1.0028 | 1.0000 | 1.120 |
| 2 | 0.00 | 0.00 | 0.00 | 103.097 | 103.097 | 8.031 | 1.000 | 0.956 | 0.966 | 1.0028 | 1.0000 | 0.941 |
| | | | | | $t = 100$ °C[b] | | | | | | | |
| 1 | 100.00 | 100.00 | 100.00 | 474.72 | 474.72 | 1.000 | 2.503 | 0.915 | 0.938 | 1.0000 | 0.9585 | 6.553 |
| 1 | 94.91 | 95.96 | 79.57 | 589.73 | 588.01 | 1.001 | 2.340 | 0.895 | 0.923 | 1.0031 | 0.9629 | 6.092 |
| 1 | 92.88 | 94.29 | 73.63 | 629.68 | 631.38 | 1.003 | 2.278 | 0.887 | 0.917 | 1.0042 | 0.9646 | 5.913 |
| 1 | 90.49 | 92.31 | 67.78 | 677.42 | 680.62 | 1.005 | 2.208 | 0.878 | 0.910 | 1.0056 | 0.9665 | 5.706 |
| 1 | 79.91 | 82.76 | 49.96 | 887.51 | 886.03 | 1.026 | 1.915 | 0.842 | 0.883 | 1.0112 | 0.9745 | 4.807 |
| 1 | 71.64 | 74.67 | 41.50 | 1025.7 | 1025.0 | 1.057 | 1.716 | 0.817 | 0.864 | 1.0150 | 0.9800 | 4.155 |
| 1 | 61.21 | 63.79 | 34.09 | 1170.1 | 1172.8 | 1.121 | 1.504 | 0.791 | 0.844 | 1.0190 | 0.9859 | 3.405 |
| 2 | 54.67 | 56.24 | 30.29 | 1264.7 | 1255.0 | 1.184 | 1.385 | 0.777 | 0.833 | 1.0213 | 0.9891 | 2.958 |
| 1 | 47.70 | 49.14 | 27.24 | 1314.3 | 1320.7 | 1.260 | 1.292 | 0.765 | 0.825 | 1.0231 | 0.9917 | 2.582 |
| 2 | 43.90 | 45.66 | 25.84 | 1354.5 | 1349.5 | 1.305 | 1.252 | 0.760 | 0.821 | 1.0239 | 0.9929 | 2.411 |
| 1 | 37.85 | 38.52 | 23.08 | 1395.0 | 1402.6 | 1.416 | 1.180 | 0.750 | 0.814 | 1.0254 | 0.9950 | 2.089 |
| 2 | 31.86 | 33.37 | 21.07 | 1438.6 | 1436.5 | 1.514 | 1.136 | 0.744 | 0.809 | 1.0263 | 0.9964 | 1.876 |
| 2 | 18.79 | 19.53 | 14.97 | 1509.4 | 1509.5 | 1.895 | 1.049 | 0.732 | 0.799 | 1.0283 | 0.9993 | 1.379 |
| 2 | 10.63 | 10.81 | 9.81 | 1533.7 | 1536.4 | 2.269 | 1.016 | 0.727 | 0.795 | 1.0291 | 1.0004 | 1.114 |
| 2 | 6.59 | 6.59 | 6.60 | 1537.1 | 1540.4 | 2.511 | 1.006 | 0.727 | 0.795 | 1.0292 | 1.0005 | 0.998 |
| 2 | 2.97 | 2.91 | 3.21 | 1534.3 | 1536.4 | 2.764 | 1.001 | 0.729 | 0.795 | 1.0291 | 1.0004 | 0.903 |
| 2 | 0.00 | 0.00 | 0.00 | 1526.7 | 1526.7 | 3.000 | 1.000 | 0.731 | 0.797 | 1.0288 | 1.0000 | 0.832 |

[a] Wilson equation parameters: $\Lambda_{AB} = 0.2166$, $\Lambda_{BA} = 0.4463$. [b] Wilson equation parameters: $\Lambda_{AB} = 0.4548$, $\Lambda_{BA} = 0.6891$.

**Table 10. Constants Used in Data Reduction Procedure**

| compound | MW | $T_C$/K | $P_C$/kPa | $Z_C$ | $\omega$ | ref |
|---|---|---|---|---|---|---|
| (aminoethyl)piperazine | 129.205 | 708.0 | 3850 | 0.266 | 0.5546 | *a* |
| diethylenetriamine | 103.167 | 676.0 | 4220 | 0.257 | 0.7002 | *a* |
| 2-butoxyethyl acetate | 160.0 | 637.33 | 2505 | 0.249 | 0.4522 | *b* |
| 2-butoxyethanol | 118.176 | 600.0 | 3240 | 0.260 | 0.8174 | *a* |
| 2-methyl-2-propanol | 74.123 | 506.20 | 3971.9 | 0.260 | 0.6158 | *a* |
| 2-methylbutane | 72.150 | 460.43 | 3381.2 | 0.270 | 0.2275 | *a* |
| 2-methyl-2-butene | 70.134 | 471.00 | 3400 | 0.292 | 0.2767 | *a* |
| methacrylonitrile | 67.090 | 554.0 | 3880 | 0.223 | 0.3013 | *a* |
| methanol | 32.042 | 512.58 | 8095.9 | 0.224 | 0.5656 | *a* |
| 1-chloro-1,1-difluoroethane | 100.495 | 410.20 | 4123.9 | 0.279 | 0.2368 | *a* |
| hydrogen chloride | 36.461 | 324.65 | 8308.7 | 0.249 | 0.1322 | *a* |
| 2-(hexyloxy)ethanol | 146.2 | 636.0 | 2738.3 | 0.2695 | 0.9235 | *b* |
| ethylene glycol | 62.068 | 645.0 | 7530 | 0.268 | 1.1367 | *a* |
| butane | 58.123 | 425.18 | 3796.9 | 0.274 | 0.1993 | *a* |
| ammonia | 17.031 | 405.65 | 11278 | 0.242 | 0.252 | *a* |
| propionaldehyde | 58.080 | 496.0 | 4660 | 0.237 | 0.3015 | *a* |

[a] Measured and/or estimated values reported by Daubert et al. (1992). [b] Estimated using techniques shown in Chapter 2 of Reid et al. (1987).

expression $P = \sum(P_i^\circ x_i)$ defines Raoult's law, where $P$ is the total system pressure, $P_i^\circ$ is the vapor pressure of component $i$, and $x_i$ is the liquid mole fraction of component $i$.

***2. 2-Butoxyethyl Acetate + 2-Butoxyethanol.*** *PTx* measurements on 2-butoxyethyl acetate + 2-butoxyethanol were performed at 100 and 170 °C. The Wilson activity coefficient equation was used to reduce the data. Results of the measurements are given in Table 2 and plotted in Figures 6 and 7. This system shows slight positive deviation from ideality.

***3. 2-Methyl-2-propanol + 2-Methylbutane.*** Results of measurements on 2-methyl-2-propanol + 2-methylbutane at 30 and 100 °C are reported in Table 3. The data were reduced using the NRTL activity coefficient equation. This system exhibits positive deviation from ideality with minimum-boiling azeotropes at both temperatures in the dilute 2-methyl-2-propanol region. The results are plotted in Figures 8 and 9.

***4. 2-Methyl-2-propanol + 2-Methyl-2-butene.*** The 2-methyl-2-propanol + 2-methyl-2-butene system also ex-

**Table 11. Measured and Literature Vapor Pressures**

| compound | *t*/°C | *P*/ kPa measured | *P*/ kPa lit.[a] | % dev[b] |
|---|---|---|---|---|
| (aminoethyl)piperazine | 125 | 4.819 | 4.145 | 16.3 |
| | 210 | 75.710 | 77.618 | −2.46 |
| diethylenetriamine | 125 | 7.000 | 7.508 | −6.77 |
| | 250 | 110.44 | 108.89 | 1.42 |
| 2-butoxyethyl acetate | 100 | 4.329 | | |
| | 170 | 55.522 | | |
| 2-butoxyethanol | 100 | 8.638 | 8.755 | −1.34 |
| | 170 | 99.407 | 98.222 | 1.21 |
| 2-methyl-2-propanol | 30 | 7.750 | 7.649 | 1.32 |
| | | 7.723 | | 0.97 |
| | 100 | 192.43 | 192.26 | 0.09 |
| | | 195.05 | | 1.45 |
| 2-methylbutane | 30 | 108.57 | 109.15 | −0.53 |
| | 100 | 720.64 | 721.22 | −0.08 |
| 2-methyl-2-butene | 30 | 74.888 | 75.066 | −0.24 |
| | 100 | 566.85 | 559.66 | 1.28 |
| methacrylonitrile | 25 | 8.370 | 9.489 | −11.8 |
| | 65 | 44.565 | 45.391 | −1.82 |
| methanol | 25 | 16.942 | 16.801 | 0.84 |
| | 65 | 103.095 | 103.122 | −0.03 |
| 1-chloro-1,1-difluoroethane | −40 | 23.752 | 26.334 | −9.80 |
| | 0 | 144.42 | 147.09 | −1.82 |
| hydrogen chloride | −40 | 764.73 | 759.48 | 0.69 |
| | 0 | 2611.6 | 2559.3 | 2.04 |
| 2-(hexyloxy)ethanol | 100 | 2.063 | | |
| | 180 | 46.604 | | |
| ethylene glycol | 100 | 2.115 | 2.130 | −0.70 |
| | 180 | 58.748 | 58.089 | 1.13 |
| butane | 0 | 103.69 | 103.59 | 0.10 |
| | | 103.097 | | −0.48 |
| | 50 | 494.84 | 496.54 | −0.34 |
| | 100 | 1526.7 | 1527.8 | −0.07 |
| ammonia | 0 | 429.19 | 429.13 | 0.01 |
| | 50 | 2035.2 | 2029.6 | 0.28 |
| propionaldehyde | 0 | 13.088 | 13.480 | −2.91 |
| | 100 | 474.72 | 469.88 | 1.03 |

[a] Literature data calculated from correlations in Daubert et al. (1992). [b] Percent deviation: 100 × (measured − literature)/literature.

hibits positive deviation from ideality and has a minimum-boiling azeotrope at both temperatures studied, 30 and 100 °C. Results of the *PTx* measurements are listed in Table 4 and are plotted in Figures 10 and 11. The NRTL activity coefficient equation was used to reduce the data.

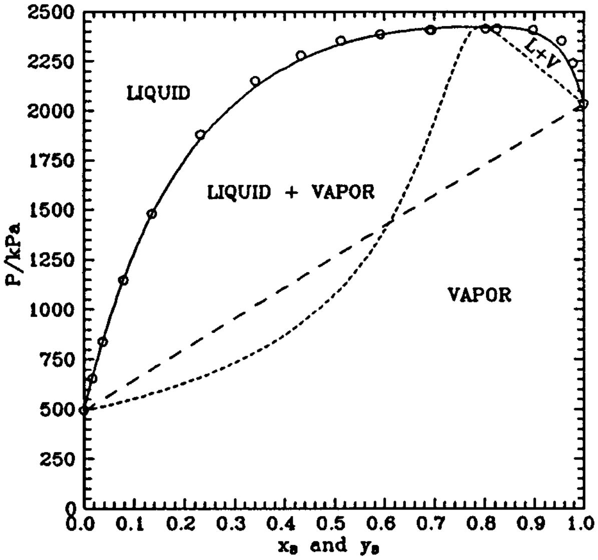

**Figure 19.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for butane (A) + ammonia (B) at 50 °C.

***5. Methacrylonitrile* + *Methanol.*** *PTx* data for methacrylonitrile + methanol were obtained at 25 and 65 °C. These data are reported in Table 5 and Figures 12 and 13. The data were reduced using the NRTL activity coefficient equation. This system shows positive deviation from ideality. Both sets of data have a minimum-boiling azeotrope.

***6. 1-Chloro-1,1-difluoroethane* + *Hydrogen Chloride.*** Results of the *PTx* measurements on 1-chloro-1,1-difluoroethane + hydrogen chloride at −40 and 0 °C are given in Table 6. The Wilson activity coefficient equation was used to reduce the data. This system exhibits nearly ideal behavior with activity coefficients that are only slightly greater than unity. Figures 14 and 15 show plots of these data.

***7. 2-(Hexyloxy)ethanol* + *Ethylene Glycol.*** Positive deviation from ideality is exhibited by 2-(hexyloxy)ethanol + ethylene glycol at 100 and 180 °C. The *PTx* measurement results are shown in Table 7. These data were reduced using the NRTL activity coefficient equation. The results are plotted in Figures 16 and 17. The vapor pressures of the two components are very similar; therefore, minimum-boiling azeotropes occur at both temperatures.

***8. Butane* + *Ammonia.*** *PTx* data were obtained for butane + ammonia at 0 and 50 °C. These data are reported in Table 8 and are plotted in Figures 18 and 19. At 0 °C there is a large immiscibility region extending from 1.06

**Table 12. Source and Purity of Chemicals**

| compound | CAS No.[a] | supplier | purity, mass % Wiltec analysis | purity, mass % supplier analysis |
|---|---|---|---|---|
| (aminoethyl)piperazine | 140-31-9 | Aldrich | | 99.2 |
| diethylenetriamine | 111-40-0 | Aldrich | | 99.6 |
| 2-butoxyethyl acetate | 112-07-2 | Aldrich | | 99.5 |
| 2-butoxyethanol | 111-76-2 | Aldrich | | 99.79 |
| 2-methyl-2-propanol | 75-65-0 | Aldrich | 99.9 | 99.6 |
| 2-methylbutane | 78-78-4 | Aldrich | 99.7 | 99.1 |
| 2-methyl-2-butene | 513-35-9 | Aldrich | | 99.2 |
| methacrylonitrile | 126-98-7 | Fluka | | 99.5+ |
| methanol | 67-56-1 | Aldrich | | 99+ |
| 1-chloro-1,1-difluoroethane | 75-68-3 | PCR | 99+ | |
| hydrogen chloride | 7647-01-0 | Matheson | | 99.9+ |
| 2-(hexyloxy)ethanol | 112-25-4 | Union Carbide | 97[b] | 99.2 |
| ethylene glycol | 107-21-1 | Aldrich | 99.6 | 99.9 |
| butane | 106-97-8 | Phillips | | 99.9+ |
| ammonia | 7664-41-7 | Matheson | | 99.9+ |
| propionaldehyde | 123-38-6 | Kodak | 99.9+ | 99+ |

[a] Supplied by the authors. [b] Mixture of several compounds that are isomers or at least close boilers.

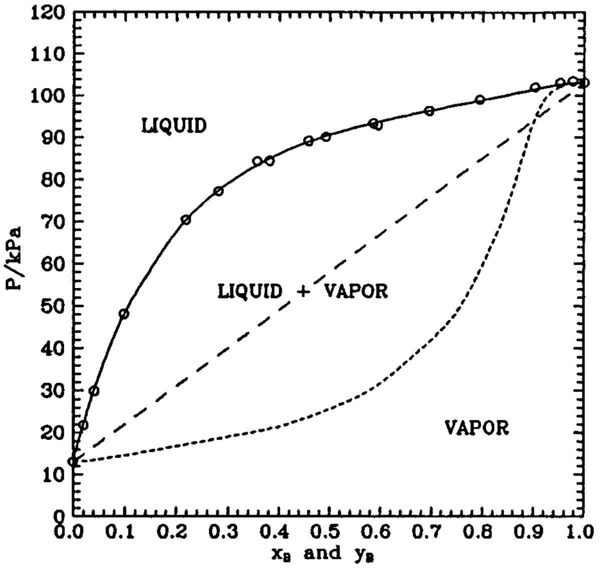

**Figure 20.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for propionaldehyde (A) + butane (B) at 0 °C.

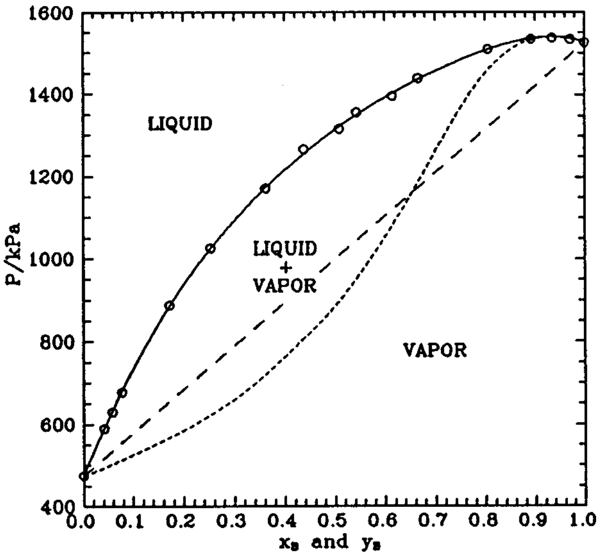

**Figure 21.** Measured *PTx* data (○), *P*−*x* correlation (—), *P*−*y* correlation (···), and Raoult's law (- - -) for propionaldehyde (A) + butane (B) at 100 °C.

mol % butane to 85.26 mol % in the liquid. A separate VLLE measurement was performed to determine more precisely the miscibility limits and the composition of the vapor phase in equilibrium with the two liquid phases. At 50 °C there is strong positive deviation resulting in a minimum-boiling azeotrope, but there is no immiscible region. The NRTL activity coefficient equation was used to reduce the data.

*9. **Propionaldehyde + Butane.*** The propionaldehyde + butane system shows positive deviation from ideality at 0 and 100 °C with minimum-boiling azeotropes in the dilute propionaldehyde region. Results of the *PTx* measurements are reported in Table 9 and plotted in Figures 20 and 21. The data were reduced using the Wilson activity coefficient equation.

***Ancillary Data.*** Table 10 gives the physical constants for each compound used in the data reduction procedure. Table 11 compares the measured pure component vapor pressures to correlations reported by Daubert et al. (1992). Table 12 lists the source and purity of the chemicals used in this study. The chemicals were all degassed before being used. Table 12 also lists the Chemical Abstracts Service Registry number for each chemical.

## Acknowledgment

We wish to thank Mark Swenson who helped measure the experimental data.

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Received for review May 9, 1996. Accepted September 3, 1996.[⊗] We are grateful to the DIPPR 805 steering committee and to the companies it represents for funding this research.

JE9601624

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[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1996.