J. Chem. Eng. Data 1983, 28, 93-99

Table XII. 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 |
| Ethyl Acetate (1) + 1-Chlorobutane (2) |  |  |  |  |
| 298.15 | 0.055 | 0.055 | 0.033 | 0.033 |
| 348.16 | 0.018 | 0.018 | 0.010 | 0.011 |
| 398.18 | 0.022 | 0.019 | 0.008 | 0.009 |
| 1-Chlorobutane (1) + Acetonitrile (2) |  |  |  |  |
| 298.69 | 0.332 | 0.139 | 0.158 | 0.085 |
| 348.18 | 0.386 | 0.169 | 0.133 | 0.074 |
| 398.89 | 0.276 | 0.156 | 0.109 | 0.083 |
| 1-Chlorobutane (1) + Nitromethane (2) |  |  |  |  |
| 298.18 | 0.160 | 0.059 | 0.071 | 0.025 |
| 348.16 | 0.036 | 0.047 | 0.019 | 0.023 |
| 398.16 | 0.037 | 0.049 | 0.020 | 0.020 |
| Acetone (1) + 1-Chlorobutane (2) |  |  |  |  |
| 298.16 | 0.049 | 0.053 | 0.029 | 0.030 |
| 348.16 | 0.068 | 0.060 | 0.033 | 0.029 |
| 398.17 | 0.048 | 0.038 | 0.018 | 0.020 |

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

Table XIII. Compound Constants Used for the Peng-Robinson Equation of State[a]

| compd | $T_c$, K | $P_c$, MPa | $\omega$ |
|---|---|---|---|
| 1-chlorobutane | 542.0 | 3.688 | 0.2180 |
| ethyl acetate | 523.2 | 3.830 | 0.3630 |
| acetonitrile | 548.0 | 4.833 | 0.3210 |
| nitromethane | 588.0 | 6.313 | 0.3460 |

[a] The binary interaction constant was set to 0.0 for all three binaries.

XII, the results obtained with the Mixon et al. procedure plus the Peng-Robinson equation of state were chosen for presentation in Tables VI-IX and Figures 5-8. Table XIII lists the compound constants used for the Peng-Robinson equation.

**Registry No.** 1-Chlorobutane, 109-69-3; ethyl acetate, 141-78-6; acetonitrile, 75-05-8; acetone, 67-64-1; nitromethane, 75-52-5.

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# Total-Pressure Vapor–Liquid Equilibrium Data for Binary Systems of 1-Chlorobutane with Pentane, Benzene, and Toluene

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**Total-pressure vapor–liquid equilibrium (VLE) data are reported at approximately 298, 348, and 398 K for each of three chlorobutane binaries with pentane, benzene, and toluene as the other component. 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. Various equations of state were used to estimate the vapor-phase fugacity coefficients; the Peng–Robinson results were used for the values reported.**

## Introduction

This paper reports total-pressure (*PTx*) vapor–liquid equilibrium data for three systems containing 1-chlorobutane plus a hydrocarbon (pentane, benzene, and toluene). The apparatus and techniques for the experimental measurements have been described in detail in a previous paper (*1*), along with the defining equation for the activity coefficient and the standard states used.

Table I. Chemicals Used

| component | vendor | stated purity % |
|---|---|---|
| 1-chlorobutane | Burdick and Jackson | 99.9+ |
| pentane | Burdick and Jackson | 99.9 |
| benzene | Burdick and Jackson | 99.9 |
| toluene | Burdick and Jackson | 99.9 |

## Chemicals Used

The sources and 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, the chemicals were poured into distillation flasks and then distilled through a Vigreux column (25-mm o.d. and 470 mm long). The first and last portions of the distillate were discarded. The retained samples were back-flushed with dry nitrogen and put into amber glass bottles for transfer to the loading operation. The stated purities

0021-9568/83/1728-0093$01.50/0

Table II. Experimental $P$ vs. $x_1$ Values for the Pentane (1) + 1-Chlorobutane (2) System

| 298.15 K | | | 348.25 K | | | 397.30 K | | |
|---|---|---|---|---|---|---|---|---|
| | PRESSURE, KPA | | | PRESSURE, KPA | | | PRESSURE, KPA | |
| X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH |
| .0000 | 13.615 | 13.615 | .0000 | 91.27 | 91.27 | .0000 | 346.5 | 346.5 |
| .0303 | 16.226 | 16.225 | .0301 | 101.41 | 101.39 | .0299 | 372.0 | 371.9 |
| .0700 | 19.464 | 19.469 | .0696 | 113.94 | 114.02 | .0692 | 403.1 | 403.2 |
| .1195 | 23.270 | 23.258 | .1189 | 129.02 | 128.91 | .1182 | 440.4 | 440.5 |
| .1712 | 26.938 | 26.950 | .1704 | 143.71 | 143.69 | .1694 | 478.6 | 478.4 |
| .2671 | 33.17 | 33.16 | .2661 | 169.18 | 169.30 | .2649 | 545.4 | 545.7 |
| .3800 | 39.64 | 39.65 | .3789 | 196.89 | 196.83 | .3774 | 619.6 | 619.6 |
| .4900 | 45.30 | 45.29 | .4890 | 221.55 | 221.48 | .4876 | 688.0 | 687.6 |
| .5839 | 49.75 | 49.75 | .5827 | 241.15 | 241.20 | .5810 | 742.8 | 743.1 |
| .6820 | 54.16 | 54.17 | .6810 | 260.92 | 261.03 | .6795 | 800.4 | 800.6 |
| .7749 | 58.23 | 58.23 | .7740 | 279.5 | 279.4 | .7728 | 854.4 | 854.2 |
| .8426 | 61.18 | 61.18 | .8420 | 292.6 | 292.7 | .8411 | 892.9 | 893.0 |
| .9215 | 64.68 | 64.66 | .9211 | 308.2 | 308.2 | .9207 | 938.5 | 938.3 |
| .9617 | 66.46 | 66.49 | .9616 | 316.1 | 316.1 | .9613 | 961.5 | 961.9 |
| 1.0000 | 68.28 | 68.27 | 1.0000 | 323.7 | 323.7 | 1.0000 | 984.8 | 984.7 |

Table III. Experimental $P$ vs. $x_1$ Values for the 1-Chlorobutane (1) + Benzene (2) System

| 298.15 K | | | 348.16 K | | | 398.20 K | | |
|---|---|---|---|---|---|---|---|---|
| | PRESSURE, KPA | | | PRESSURE, KPA | | | PRESSURE, KPA | |
| X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH |
| .0000 | 12.762 | 12.765 | .0000 | 86.61 | 86.65 | .0000 | 338.8 | 338.9 |
| .0326 | 12.837 | 12.831 | .0326 | 87.09 | 87.01 | .0326 | 340.0 | 339.9 |
| .0801 | 12.901 | 12.905 | .0801 | 87.37 | 87.41 | .0800 | 341.1 | 341.2 |
| .2050 | 13.025 | 13.026 | .2050 | 88.04 | 88.06 | .2050 | 343.6 | 343.6 |
| .2999 | 13.100 | 13.098 | .2999 | 88.46 | 88.45 | .2998 | 345.2 | 345.1 |
| .3921 | 13.166 | 13.166 | .3921 | 88.83 | 88.82 | .3920 | 346.5 | 346.5 |
| .4800 | 13.230 | 13.231 | .4799 | 89.17 | 89.18 | .4799 | 347.8 | 347.8 |
| .5896 | 13.310 | 13.311 | .5896 | 89.62 | 89.62 | .5895 | 349.4 | 349.4 |
| .6891 | 13.389 | 13.387 | .6891 | 90.02 | 90.02 | .6891 | 350.7 | 350.7 |
| .7776 | 13.456 | 13.456 | .7776 | 90.38 | 90.37 | .7775 | 351.8 | 351.8 |
| .8341 | 13.503 | 13.503 | .8341 | 90.58 | 90.60 | .8341 | 352.5 | 352.5 |
| .8914 | 13.551 | 13.552 | .8914 | 90.82 | 90.82 | .8914 | 353.2 | 353.3 |
| .9723 | 13.617 | 13.616 | .9723 | 91.12 | 91.12 | .9723 | 354.4 | 354.3 |
| 1.0000 | 13.634 | 13.635 | 1.0000 | 91.21 | 91.22 | 1.0000 | 354.5 | 354.6 |

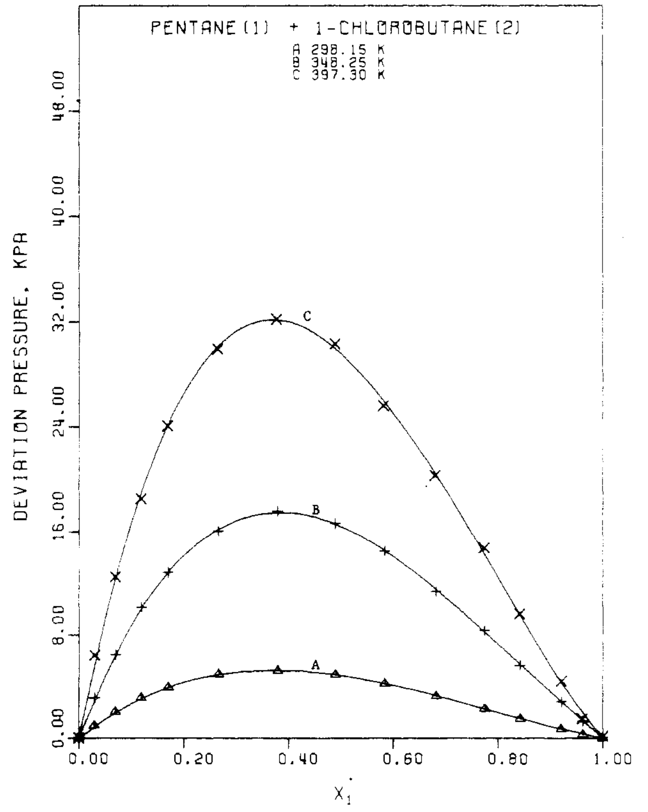

**Figure 1.** Deviation from Raoult's law for the pentane (1) + 1-chlorobutane (2) system.

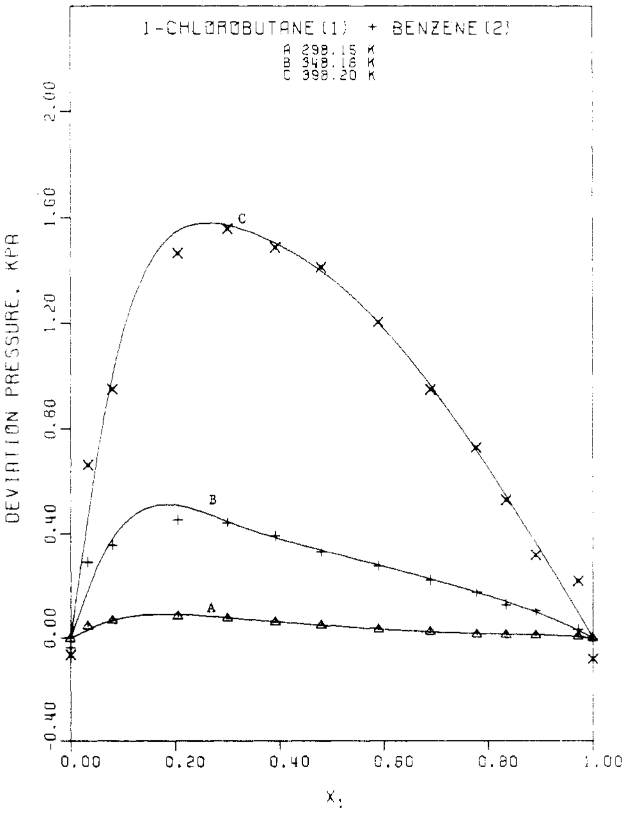

**Figure 2.** Deviation from Raoult's law for the 1-chlorobutane (1) + benzene (2) system.

Table IV. Experimental $P$ vs. $x_1$ Values for the 1-Chlorobutane (1) + Toluene (2) System

| 298.16 K |  |  | 348.18 K |  |  | 398.22 K |  |  |
|---|---|---|---|---|---|---|---|---|
|  | PRESSURE, KPA |  |  | PRESSURE, KPA |  |  | PRESSURE, KPA |  |
| X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH | X1 | EXPTL | SMOOTH |
| .0000 | 3.833 | 3.835 | .0000 | 32.74 | 32.74 | .0000 | 150.69 | 150.72 |
| .0447 | 4.348 | 4.340 | .0447 | 35.63 | 35.61 | .0446 | 160.55 | 160.46 |
| .0871 | 4.758 | 4.766 | .0870 | 38.10 | 38.12 | .0869 | 169.09 | 169.15 |
| .1423 | 5.287 | 5.288 | .1422 | 41.28 | 41.28 | .1420 | 180.11 | 180.16 |
| .2089 | 5.923 | 5.917 | .2088 | 45.09 | 45.09 | .2085 | 193.49 | 193.43 |
| .3031 | 6.824 | 6.822 | .3029 | 50.56 | 50.56 | .3026 | 212.39 | 212.37 |
| .3938 | 7.702 | 7.708 | .3936 | 55.85 | 55.85 | .3932 | 230.66 | 230.69 |
| .4954 | 8.703 | 8.707 | .4951 | 61.80 | 61.76 | .4948 | 251.22 | 251.21 |
| .5869 | 9.619 | 9.608 | .5867 | 66.99 | 67.08 | .5863 | 269.71 | 269.75 |
| .6952 | 10.672 | 10.673 | .6950 | 73.46 | 73.41 | .6947 | 291.9 | 291.8 |
| .7867 | 11.570 | 11.574 | .7866 | 78.82 | 78.82 | .7863 | 310.7 | 310.7 |
| .8376 | 12.073 | 12.074 | .8375 | 81.83 | 81.85 | .8373 | 321.2 | 321.3 |
| .9151 | 12.837 | 12.834 | .9151 | 86.43 | 86.45 | .9149 | 337.4 | 337.5 |
| .9559 | 13.230 | 13.230 | .9559 | 88.86 | 88.83 | .9559 | 346.0 | 345.9 |
| 1.0000 | 13.654 | 13.654 | 1.0000 | 91.31 | 91.32 | 1.0000 | 354.8 | 354.9 |

Table V. Calculated Data for the Pentane (1) + 1-Chlorobutane (2) System at 298.15, 348.25, and 397.30 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 116.181 VL(2) = 105.125

|  | TOTAL PRESSURE, KPA |  | MIXTURE FUGACITY COEFFICIENTS |  |  | ACTIVITY COEFFICIENTS |  | EXCESS GIBBS FUNCTION, |
|---|---|---|---|---|---|---|---|---|
| X1 | EXPTL. | CALC. | 1 | 2 | Y1 | 1 | 2 | J/MOLE |
| .0000 | 13.615 | 13.615 | .9945 | .9928 | .0000 | 1.5218 | 1.0000 | 0.00 |
| .1000 | 21.800 | 21.801 | .9911 | .9884 | .4331 | 1.4131 | 1.0039 | 94.36 |
| .2000 | 28.894 | 28.894 | .9882 | .9847 | .6137 | 1.3227 | 1.0157 | 169.52 |
| .3000 | 35.133 | 35.133 | .9857 | .9815 | .7155 | 1.2463 | 1.0360 | 225.19 |
| .4000 | 40.715 | 40.714 | .9834 | .9786 | .7827 | 1.1820 | 1.0661 | 260.97 |
| .5000 | 45.785 | 45.784 | .9813 | .9759 | .8322 | 1.1279 | 1.1078 | 276.10 |
| .6000 | 50.487 | 50.486 | .9794 | .9735 | .8718 | 1.0834 | 1.1638 | 269.56 |
| .7000 | 54.958 | 54.957 | .9776 | .9712 | .9058 | 1.0481 | 1.2377 | 240.21 |
| .8000 | 59.322 | 59.321 | .9758 | .9689 | .9371 | 1.0220 | 1.3354 | 186.63 |
| .9000 | 63.700 | 63.700 | .9740 | .9667 | .9677 | 1.0054 | 1.4662 | 106.95 |
| 1.0000 | 68.270 | 68.270 | .9721 | .9643 | 1.0000 | 1.0000 | 1.6108 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 127.140 VL(2) = 112.255

|  | TOTAL PRESSURE, KPA |  | MIXTURE FUGACITY COEFFICIENTS |  |  | ACTIVITY COEFFICIENTS |  | EXCESS GIBBS FUNCTION, |
|---|---|---|---|---|---|---|---|---|
| X1 | EXPTL. | CALC. | 1 | 2 | Y1 | 1 | 2 | J/MOLE |
| .0000 | 91.274 | 91.274 | .9761 | .9676 | .0000 | 1.4076 | 1.0000 | 0.00 |
| .1000 | 123.297 | 123.293 | .9673 | .9563 | .3226 | 1.3123 | 1.0036 | 88.09 |
| .2000 | 151.855 | 151.849 | .9596 | .9464 | .5007 | 1.2426 | 1.0133 | 156.30 |
| .3000 | 177.844 | 177.837 | .9526 | .9374 | .6170 | 1.1856 | 1.0293 | 206.35 |
| .4000 | 201.700 | 201.693 | .9463 | .9292 | .7011 | 1.1370 | 1.0528 | 238.02 |
| .5000 | 223.857 | 223.851 | .9403 | .9216 | .7666 | 1.0958 | 1.0851 | 250.66 |
| .6000 | 244.746 | 244.742 | .9348 | .9145 | .8210 | 1.0620 | 1.1275 | 243.49 |
| .7000 | 264.800 | 264.797 | .9294 | .9077 | .8688 | 1.0354 | 1.1819 | 215.73 |
| .8000 | 284.449 | 284.448 | .9242 | .9011 | .9132 | 1.0163 | 1.2499 | 166.65 |
| .9000 | 304.027 | 304.027 | .9190 | .8945 | .9563 | 1.0045 | 1.3358 | 95.63 |
| 1.0000 | 323.682 | 323.682 | .9138 | .8879 | 1.0000 | 1.0000 | 1.4661 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 143.046 VL(2) = 121.088

|  | TOTAL PRESSURE, KPA |  | MIXTURE FUGACITY COEFFICIENTS |  |  | ACTIVITY COEFFICIENTS |  | EXCESS GIBBS FUNCTION, |
|---|---|---|---|---|---|---|---|---|
| X1 | EXPTL. | CALC. | 1 | 2 | Y1 | 1 | 2 | J/MOLE |
| .0000 | 346.466 | 346.466 | .9384 | .9140 | .0000 | 1.3579 | 1.0000 | 0.00 |
| .1000 | 426.764 | 426.768 | .9233 | .8944 | .2481 | 1.2375 | 1.0041 | 82.45 |
| .2000 | 500.453 | 500.462 | .9095 | .8767 | .4125 | 1.1847 | 1.0117 | 142.84 |
| .3000 | 569.331 | 569.345 | .8970 | .8602 | .5324 | 1.1401 | 1.0248 | 186.63 |
| .4000 | 633.801 | 633.816 | .8852 | .8450 | .6255 | 1.1008 | 1.0444 | 212.96 |
| .5000 | 695.043 | 695.055 | .8741 | .8306 | .7027 | 1.0683 | 1.0703 | 221.31 |
| .6000 | 754.298 | 754.305 | .8633 | .8168 | .7700 | 1.0430 | 1.1020 | 211.83 |
| .7000 | 812.462 | 812.464 | .8528 | .8033 | .8312 | 1.0242 | 1.1398 | 185.09 |
| .8000 | 869.649 | 869.646 | .8425 | .7901 | .8884 | 1.0104 | 1.1875 | 140.92 |
| .9000 | 926.478 | 926.473 | .8323 | .7771 | .9441 | 1.0020 | 1.2448 | 78.24 |
| 1.0000 | 984.697 | 984.697 | .8219 | .7640 | 1.0000 | 1.0000 | 1.2812 | 0.00 |

of the chemicals were verified chromatographically 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 still perfectly clear when removed from the cells at the end of the last isotherm.

## Experimental Data

Tables II–IV present the experimental $PTx$ data. The "smooth" pressure values reported there are from the least-squares cubic splined fits used to interpolate the experimental $P$ vs. $x_1$ values to provide the evenly spaced values required by the finite-difference Mixon–Gumowski–Carpenter method (*2*) for reduction of $PTx$ data.

Figures 1–3 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. $x_1$

Table VI. Calculated Data for the 1-Chlorobutane (1) + Benzene (2) System at 298.15, 348.16, and 398.20 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.126 VL(2) = 89.409

| 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 | 12.765 | 12.765 | .9933 | .9944 | .0000 | 1.0987 | 1.0000 | 0.00 |
| .1000 | 12.930 | 12.930 | .9932 | .9943 | .1086 | 1.0299 | 1.0032 | 14.38 |
| .2000 | 13.022 | 13.022 | .9931 | .9943 | .2097 | 1.0018 | 1.0076 | 15.90 |
| .3000 | 13.098 | 13.098 | .9931 | .9943 | .3120 | 0.9993 | 1.0084 | 13.94 |
| .4000 | 13.172 | 13.172 | .9930 | .9942 | .4133 | 0.9985 | 1.0088 | 11.54 |
| .5000 | 13.245 | 13.245 | .9930 | .9942 | .5138 | 0.9984 | 1.0089 | 8.96 |
| .6000 | 13.319 | 13.319 | .9929 | .9942 | .6133 | 0.9988 | 1.0084 | 6.46 |
| .7000 | 13.395 | 13.395 | .9929 | .9942 | .7120 | 0.9994 | 1.0071 | 4.28 |
| .8000 | 13.475 | 13.475 | .9928 | .9941 | .8096 | 1.0003 | 1.0046 | 2.77 |
| .9000 | 13.559 | 13.559 | .9928 | .9941 | .9055 | 1.0006 | 1.0034 | 2.12 |
| 1.0000 | 13.635 | 13.635 | .9927 | .9941 | 1.0000 | 1.0000 | 1.0173 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 112.244 VL(2) = 95.342

| 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 | 86.649 | 86.649 | .9695 | .9745 | .0000 | 1.0815 | 1.0000 | 0.00 |
| .1000 | 87.545 | 87.541 | .9691 | .9743 | .1066 | 1.0244 | 1.0026 | 13.85 |
| .2000 | 88.035 | 88.032 | .9689 | .9742 | .2075 | 1.0026 | 1.0060 | 15.42 |
| .3000 | 88.446 | 88.444 | .9687 | .9741 | .3095 | 1.0015 | 1.0064 | 14.10 |
| .4000 | 88.854 | 88.853 | .9685 | .9740 | .4106 | 1.0011 | 1.0065 | 12.61 |
| .5000 | 89.258 | 89.258 | .9683 | .9739 | .5110 | 1.0009 | 1.0067 | 10.97 |
| .6000 | 89.661 | 89.661 | .9682 | .9738 | .6104 | 1.0007 | 1.0069 | 9.22 |
| .7000 | 90.063 | 90.063 | .9680 | .9737 | .7090 | 1.0006 | 1.0071 | 7.38 |
| .8000 | 90.461 | 90.462 | .9679 | .9736 | .8067 | 1.0004 | 1.0077 | 5.42 |
| .9000 | 90.849 | 90.849 | .9677 | .9736 | .9036 | 1.0001 | 1.0094 | 3.07 |
| 1.0000 | 91.215 | 91.215 | .9676 | .9735 | 1.0000 | 1.0000 | 1.0123 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 121.277 VL(2) = 102.570

| 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 | 338.875 | 338.875 | .9173 | .9306 | .0000 | 1.0491 | 1.0000 | 0.00 |
| .1000 | 341.618 | 341.610 | .9165 | .9300 | .1054 | 1.0201 | 1.0014 | 10.64 |
| .2000 | 343.498 | 343.491 | .9158 | .9297 | .2073 | 1.0078 | 1.0033 | 13.92 |
| .3000 | 345.129 | 345.125 | .9153 | .9294 | .3088 | 1.0052 | 1.0042 | 14.76 |
| .4000 | 346.663 | 346.660 | .9148 | .9291 | .4094 | 1.0033 | 1.0051 | 14.62 |
| .5000 | 348.112 | 348.112 | .9144 | .9289 | .5092 | 1.0020 | 1.0062 | 13.62 |
| .6000 | 349.494 | 349.495 | .9140 | .9288 | .6084 | 1.0011 | 1.0073 | 11.88 |
| .7000 | 350.822 | 350.823 | .9136 | .9286 | .7071 | 1.0005 | 1.0084 | 9.55 |
| .8000 | 352.110 | 352.112 | .9132 | .9285 | .8052 | 1.0002 | 1.0094 | 6.73 |
| .9000 | 353.369 | 353.370 | .9129 | .9284 | .9028 | 1.0000 | 1.0103 | 3.52 |
| 1.0000 | 354.609 | 354.609 | .9126 | .9283 | 1.0000 | 1.0000 | 1.0111 | 0.00 |

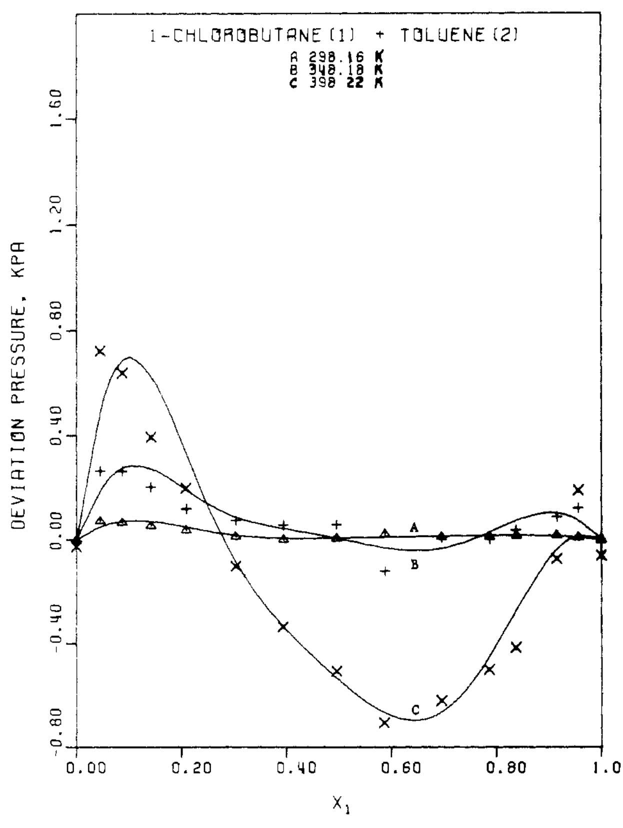

**Figure 3.** Deviation from Raoult's law for the 1-chlorobutane (1) + toluene (2) system.

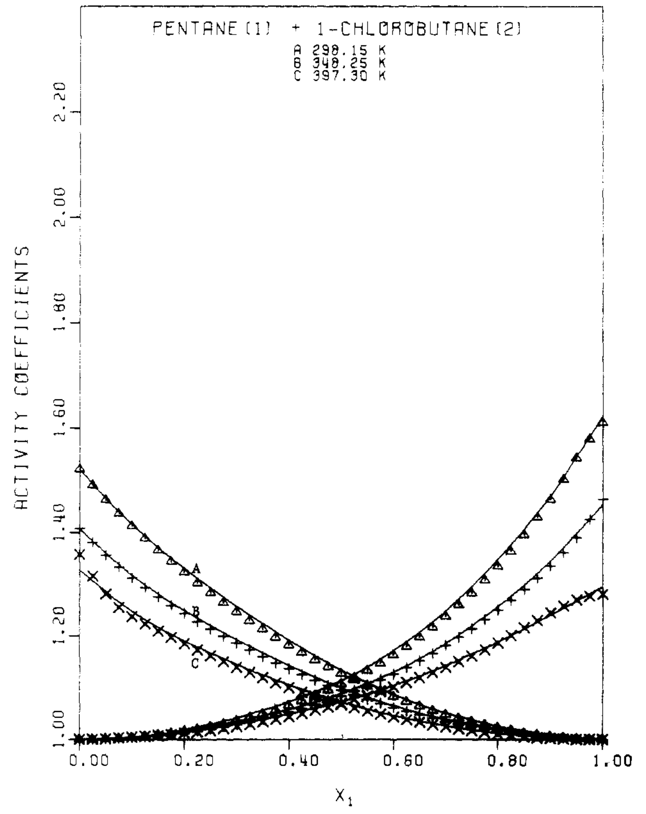

**Figure 4.** Activity coefficients for the pentane (1) + 1-chlorobutane (2) system. Curves are from Barker method and points are from Mixon et al. method.

Table VII. Calculated Data for the 1-Chlorobutane (1) + Toluene (2) System at 298.16, 348.18, and 398.22 K

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 105.126 VL(2) = 106.859

| 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 | 3.835 | 3.835 | .9980 | .9977 | .0000 | 1.1701 | 1.0000 | 0.00 |
| .1000 | 4.890 | 4.890 | .9974 | .9970 | .2897 | 1.0429 | 1.0056 | 22.77 |
| .2000 | 5.832 | 5.832 | .9969 | .9964 | .4669 | 1.0016 | 1.0119 | 24.27 |
| .3000 | 6.793 | 6.793 | .9964 | .9958 | .5987 | 0.9968 | 1.0133 | 20.58 |
| .4000 | 7.769 | 7.769 | .9959 | .9953 | .6993 | 0.9981 | 1.0125 | 16.68 |
| .5000 | 8.753 | 8.753 | .9953 | .9947 | .7778 | 0.9999 | 1.0111 | 13.55 |
| .6000 | 9.737 | 9.737 | .9948 | .9941 | .8403 | 1.0009 | 1.0099 | 11.09 |
| .7000 | 10.721 | 10.721 | .9943 | .9935 | .8912 | 1.0013 | 1.0092 | 9.02 |
| .8000 | 11.705 | 11.705 | .9938 | .9929 | .9335 | 1.0014 | 1.0087 | 7.15 |
| .9000 | 12.686 | 12.686 | .9933 | .9923 | .9693 | 1.0012 | 1.0107 | 5.23 |
| 1.0000 | 13.654 | 13.654 | .9927 | .9917 | 1.0000 | 1.0000 | 1.0533 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 112.244 VL(2) = 113.129

| 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 | 32.741 | 32.741 | .9884 | .9865 | .0000 | 1.1086 | 1.0000 | 0.00 |
| .1000 | 38.870 | 38.869 | .9862 | .9840 | .2371 | 1.0310 | 1.0034 | 17.79 |
| .2000 | 44.586 | 44.585 | .9842 | .9817 | .4053 | 1.0081 | 1.0069 | 20.59 |
| .3000 | 50.391 | 50.390 | .9821 | .9793 | .5381 | 1.0062 | 1.0074 | 20.42 |
| .4000 | 56.227 | 56.226 | .9800 | .9770 | .6441 | 1.0056 | 1.0078 | 19.97 |
| .5000 | 62.040 | 62.039 | .9779 | .9746 | .7301 | 1.0038 | 1.0093 | 18.90 |
| .6000 | 67.850 | 67.850 | .9759 | .9722 | .8017 | 1.0022 | 1.0113 | 16.77 |
| .7000 | 73.697 | 73.696 | .9738 | .9699 | .8625 | 1.0015 | 1.0125 | 13.79 |
| .8000 | 79.615 | 79.614 | .9717 | .9675 | .9151 | 1.0020 | 1.0109 | 10.77 |
| .9000 | 85.568 | 85.568 | .9696 | .9651 | .9604 | 1.0022 | 1.0100 | 8.73 |
| 1.0000 | 91.319 | 91.319 | .9675 | .9627 | 1.0000 | 1.0000 | 1.0950 | 0.00 |

LIQUID MOLAR VOLUMES, CC/MOL: VL(1) = 121.279 VL(2) = 120.590

| 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 | 150.717 | 150.717 | .9629 | .9568 | .0000 | 1.0953 | 1.0000 | 0.00 |
| .1000 | 171.795 | 171.788 | .9576 | .9508 | .2027 | 1.0368 | 1.0026 | 19.71 |
| .2000 | 191.723 | 191.716 | .9527 | .9451 | .3589 | 1.0182 | 1.0054 | 26.30 |
| .3000 | 211.847 | 211.840 | .9477 | .9394 | .4882 | 1.0142 | 1.0067 | 29.50 |
| .4000 | 232.061 | 232.054 | .9427 | .9337 | .5962 | 1.0114 | 1.0082 | 31.31 |
| .5000 | 252.266 | 252.260 | .9377 | .9280 | .6875 | 1.0082 | 1.0109 | 31.42 |
| .6000 | 272.523 | 272.519 | .9327 | .9223 | .7662 | 1.0054 | 1.0143 | 29.50 |
| .7000 | 292.926 | 292.923 | .9277 | .9165 | .8351 | 1.0035 | 1.0179 | 25.63 |
| .8000 | 313.567 | 313.566 | .9226 | .9108 | .8963 | 1.0025 | 1.0208 | 20.18 |
| .9000 | 334.380 | 334.380 | .9175 | .9049 | .9508 | 1.0016 | 1.0263 | 13.48 |
| 1.0000 | 354.866 | 354.866 | .9125 | .8992 | 1.0000 | 1.0000 | 1.0772 | 0.00 |

Table VIII. Comparison of the Barker and Mixon et al. Pressure Fits. Peng-Robinson Equation of State

| temp, K | max % dev in $P^a$ Barker | max % dev in $P^a$ Mixon | rms for % dev$^b$ Barker | rms for % dev$^b$ Mixon |
|---|---|---|---|---|
| | Pentane (1) + 1-Chlorobutane (2) | | | |
| 298.15 | 0.064 | 0.050 | 0.027 | 0.025 |
| 348.25 | 0.078 | 0.084 | 0.037 | 0.042 |
| 397.30 | 0.099 | 0.061 | 0.043 | 0.030 |
| | 1-Chlorobutane (1) + Benzene (2) | | | |
| 298.15 | 0.045 | 0.049 | 0.017 | 0.018 |
| 348.16 | 0.087 | 0.090 | 0.030 | 0.031 |
| 398.20 | 0.038 | 0.042 | 0.016 | 0.018 |
| | 1-Chlorobutane (1) + Toluene (2) | | | |
| 298.16 | 0.214 | 0.175 | 0.085 | 0.080 |
| 348.18 | 0.094 | 0.133 | 0.049 | 0.050 |
| 398.22 | 0.066 | 0.057 | 0.030 | 0.027 |

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

Table IX. Effect of Equation of State Choice on $\gamma_i^\infty$ Values Obtained with Mixon et al. Method for 1-Chlorobutane (1) + Toluene (2) at 398.22 K

| eq of state used | $\gamma_i^\infty$ 1 | $\gamma_i^\infty$ 2 |
|---|---|---|
| ideal gas | 1.0668 | 1.0189 |
| virial through $B_{ij}$, Tsonopoulos | 1.0966 | 1.0801 |
| Redlich-Kwong, Lu modification | 1.0963 | 1.0809 |
| Peng-Robinson | 1.0953 | 1.0772 |

plot but has the disadvantage of not indicating whether an azeotrope exists.

The symbols in Figures 1-3 denote the experimental data points. The curves approximate—sometimes not very closely—the cubic splined fits of those data points. Interpolated values (at 0.025 increments in $x_1$) from the splined fits are fed to the plotting software which then makes its own fit of the input values. Those fits are often not very good if the curve is irregularly shaped. Nevertheless, the curves do help illustrate the scatter and the general behavior of the experimental points. For an accurate determination of how closely the splined fits represent the experimental points, Tables II-IV must be used.

The pentane and benzene systems showed positive deviations from Raoult's law at all temperatures at all compositions, and the deviations increased with temperature for both systems. Neither system formed an azeotrope at any of the three temperatures. The benzene system was close-boiling with low deviations from Raoult's law.

The toluene system was a mixed deviation system. As shown in Figure 3, the system had very low deviation values at room temperature but even at that temperature the $P_D$ curve sags in the middle. At 348.18 K, the positive deviations have increased at both ends but the sag in the middle persists. At 398.22 K, the trend toward higher positive deviations continues at low $x_1$ values but the tendency toward negative deviations in the middle has become much stronger and appears to be extending toward the high $x_1$ values. These trends are clearly

Table X. Effect of Calculation Method on $\gamma_i^\infty$ Values for 1-Chlorobutane (1) + Toluene (2) at 398.22 K[a]

| calculation method | $\gamma_i^\infty$ 1 | $\gamma_i^\infty$ 2 |
|---|---|---|
| Mixon-Gumowski-Carpenter (0.057/0.027)[b] | 1.0966 | 1.0801 |
| Barker: | | |
| "absolute" Van Laar (0.34/0.26) | 1.0472 | 1.0395 |
| Wilson (0.34/0.12) | 1.0472 | 1.0395 |
| NRTL (0.10/0.04) | 1.1359 | 1.0538 |
| modified Margules (0.16/0.05) | 1.1009 | 1.0782 |
| UNIQUAC (0.26/0.10) | 1.0593 | 1.0412 |
| Redlich-Kister, three constants (0.19/0.07) | 1.0708 | 1.0560 |
| Redlich-Kister, five constants (0.07/0.03) | 1.1074 | 1.0706 |
| Gautreaux-Coates: | | |
| splined fits | 1.0977 | 1.0877 |
| $P_D/x_1x_2$ plots | | |

[a] Virial equation through $B_{ij}$, Tsonopoulos correlation. [b] First number in parentheses is the maximum percent deviation in $P$. The second number is the root mean square of the percent deviation in $P$. See bottom of Table VIII.

visible despite the fact that the toluene system measurements showed more scatter than usual. No azeotrope was formed at any temperature.

## Reduced Data

The $y_i$, $\gamma_i$, and $G^E$ values selected for publication are in Tables V–VII. Those values were obtained with the Mixon et al. data reduction method, using the Peng–Robinson equation of state (*3*) to estimate the vapor-phase fugacity coefficients. The "experimental" pressure values tabulated in Tables V–VII 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–IV.) The "calculated" pressure values are from the Mixon et al. data reduction and show how well that method reproduces the original pressure data.

The calculated activity coefficient curves are shown in Figures 4–6 for both the Mixon et al. and the Barker (*4*) data reduction methods. The Barker results shown used the five-constant Redlich–Kister equation for $G^E$ and also used the Peng–Robinson equation of state for the estimation of the vapor-phase fugacity coefficients. The points in Figures 4–6 are the evenly spaced Mixon et al. values while the curves are from the Barker method. (The $\times 10^{-1}$ notation on the ordinate of some of the plots means that the decimal must be moved one place to the left in the ordinate scale numbers.)

Figures 5 and 6 illustrate the difficulties involved in getting good activity coefficient curves for almost ideal systems such as the 1-chlorobutane + benzene system, and for mixed deviation systems such as 1-chlorobutane + toluene. Note in Figure 6 that the temperature dependence of the $\gamma_i^\infty$ values at $x_1 = 0.0$ is the reverse of that at $x_1 = 1.0$. As shown in Table VIII and in Figures 7 and 8, both the Mixon et al. and Barker methods reproduce the experimental data very well. The two figures are resolution error band plots. The 0.0 line represents the experimental data point values. The boundaries formed by the large X's represent the maximum plus or minus experimental errors which could result due to the resolution limitations of the devices used to measure the pressure, temperature, and mole fraction values. The formula used to calculate the maximum possible resolution errors has been given in a previous paper (*5*). The resolution error does not include such errors as operator error, inadequate degassing, chemical reactions, etc. (Note that the $\times 10^{-1}$ notation means that the decimal must be moved one place to the left in the ordinate scale numbers.)

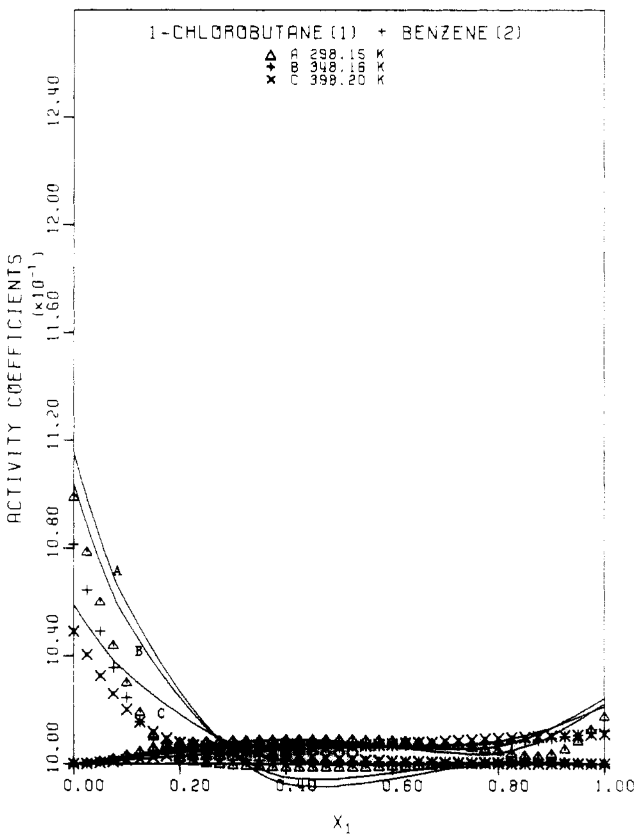

**Figure 5.** Activity coefficients for the 1-chlorobutane (1) + benzene (2) system. Curves are from Barker method and points are from Mixon et al. method. Move decimal point one place to left in ordinate scale values.

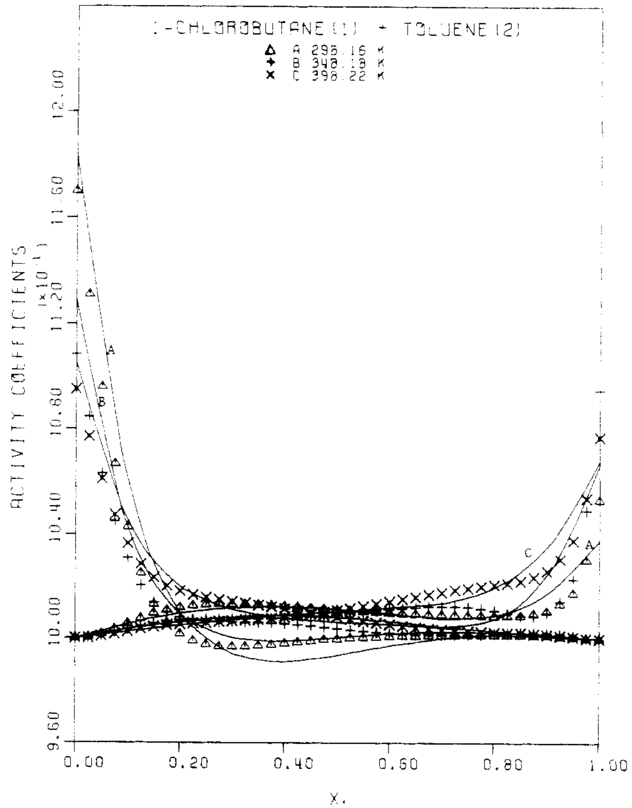

**Figure 6.** Activity coefficients for the 1-chlorobutane (1) + benzene (2) system. Curves are from Barker method and points are from Mixon et al. method. Move decimal point one place to left in ordinate scale values.

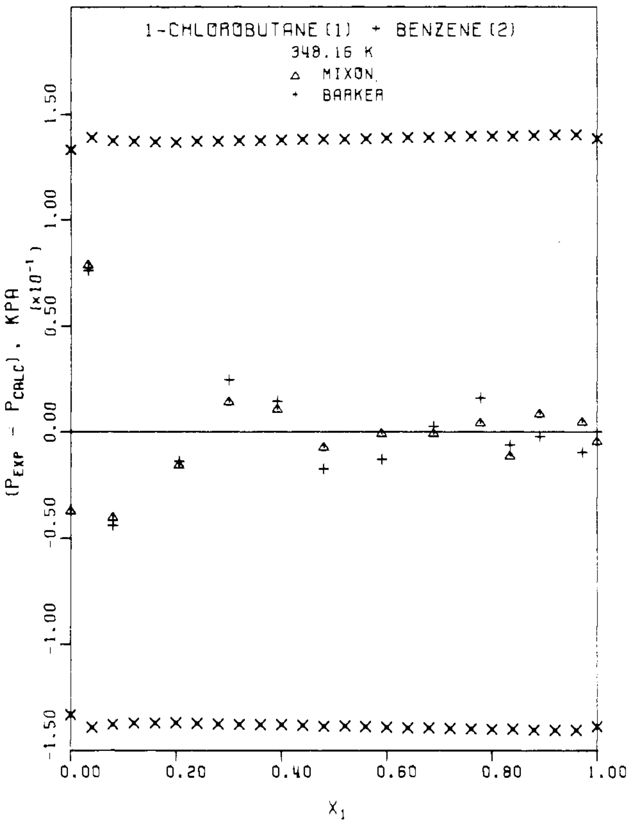

**Figure 7.** Comparison of Mixon et al. and Barker results on resolution error band plot for 1-chlorobutane (1) + benzene (2) system at 348.16 K. Peng–Robinson equation of state. Five-constant Redlich–Kister equation for Barker method.

Figures 7 and 8 are the worst of the three such plots for each of the two systems but, as can be seen, all the points fall within the resolution error band which indicates two things. First, there were no experimental errors greater than the possible resolution errors and, second, the Mixon et al. and Barker methods both did a good job of representing the experimental $P$ values. Nevertheless, the activity coefficient curves in Figures 5 and 6 do not inspire confidence.

There is no certain way to know whether or not the activity coefficient curves are correct—that is the basic disadvantage of the total-pressure approach to VLE measurements. The activity coefficient is a "slope" property; i.e., it is related to the slope of the $P$ vs. $x_1$ curve. When the slopes are unusual—as they certainly are in Figure 3, and to some extent in Figure 2 also—the activity coefficient curves must take on odd shapes. However, odd shapes may also result from any one of three areas of possible trouble in the data reduction process. The first area concerns the basic data reduction method used. The method must, of course, reproduce the original experimental $P$ values very closely, but, in addition, it must represent the shape (slopes) of the $P$ vs. $x_1$ curve. The best fit of the $P$ values is not always synonymous with the best representation of the slopes. For example, it is easy to overfit the $P$ vs. $x_1$ points with the cubic splined fits by using too many knot points to reduce the root-mean-squared deviation (rmsd). One has to watch the $dP/dx$ and $d^2P/dx^2$ values associated with the splined fits. Even when the derivatives appear well-behaved, the activity coefficient curve may still exhibit an unlikely bend or two due to some slight irregularity in the slope of the fit of the $P$ values.

The second trouble area is the equation of state used. However, as illustrated in Table IX for the 1-chlorobutane + toluene system, the calculated activity coefficient values were not a strong function of the equation of state for the systems covered in this paper.

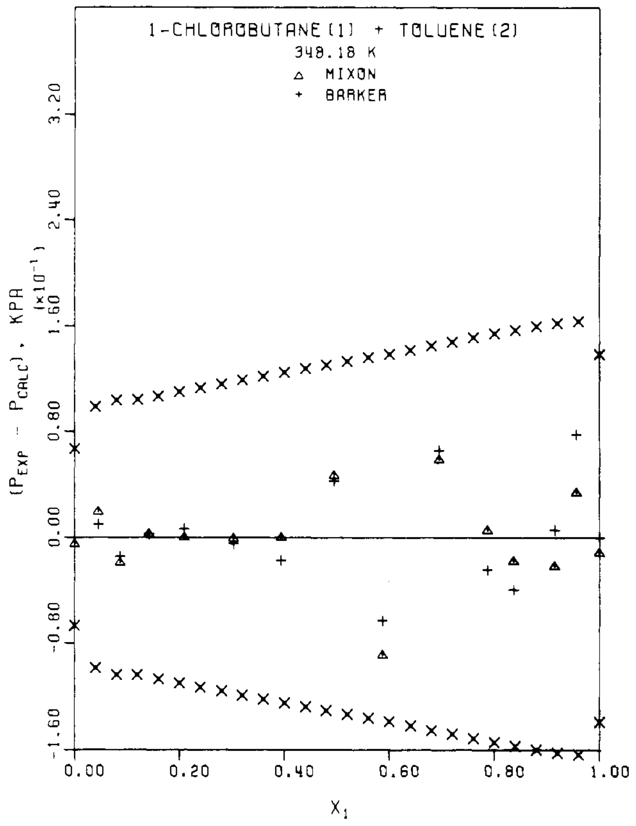

**Figure 8.** Same as for Figure 7 but for the 1-chlorobutane (1) + toluene (2) system at 348.18 K.

The third trouble area concerns only the Barker method. Table X shows how the infinite-dilution activity coefficients obtained with the Barker method vary with the correlation equation used to represent $G^E$. The $\gamma_1^\infty$ values vary from 1.0472 to 1.1359 while the $\gamma_2^\infty$ values range from 1.0395 to 1.0782. The 1.1359 − 1.0472 = 0.0887 variation is 92% of the departure from Raoult's law (deviation from 1.0) calculated by the Mixon et al. value. The Barker curves plotted in Figures 4–6 are based on the five-constant Redlich–Kister equation. The 398.22 K curve in Figure 6 has the lowest intercept of the three temperature curves at $x_1 = 0.0$. Note where the intercepts ($\gamma_1^\infty$ values) for the other $G^E$ correlations would fall in Figure 6. The five-constant Redlich–Kister equation usually fits the $P$ values best and hence usually agrees best with the Mixon et al. results.

Table X also shows the $\gamma_i^\infty$ values obtained with the Gautreaux–Coates equation (*6*, *7*) using $(dP/dx_1)^\infty$ values from the splined fits. Often those values agree well with the Mixon et al. method; both use the same splined fits. The $P_D/x_1x_2$ plots (*7*) did not provide reliable $(dP/dx_1)^\infty$ values for this system.

**Registry No.** 1-Chlorobutane, 109-69-3; benzene, 71-43-2; toluene, 108-88-3; pentane, 109-66-0.

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