None of the three possible binaries exhibit azeotropic behavior, and as shown by Figure 1, neither does the ternary system. Table V contains also the group of parameters $A_{ij}$, $B_{ij}$, and $C_{ij}$ for the $T$–$x$ correlation (eq 5) which yield the smaller mean deviation between the calculated and observed values of $T$.

### Acknowledgment

Yehudit Reizner and Moshe Golden helped in the experimental work and numerical calculations.

### Glossary

| | |
|---|---|
| $A_{ij}$, $B_{ij}$, etc. | multicomponent adjustable parameters in eq 5 |
| $B_{ii}$, $B_{ij}$ | virial coefficients, eq 2 |
| $B_{ij}$, $C_{ij}$, $D_{ij}$ | Redlich–Kister constants, eq 4 |
| $V^L_i$ | molar volume, component $i$ |
| $n$ | number of components |
| $P$ | total pressure, mmHg |
| $P_i^\circ$ | vapor pressure of pure component $i$, mmHg |
| $T$ | boiling temperature of a mixture, K |
| $T_i^\circ$ | boiling temperature of pure component $i$, K |
| $t$ | temperature, °C |
| $x_i$, $y_i$ | mole fraction of component $i$ in the liquid and vapor phases |
| $\alpha_i$ | coefficient, Antoine equation |
| $\beta_i$ | coefficient, Antoine equation |
| $\gamma_i$ | activity coefficient of component $i$ |
| $\delta_i$ | coefficient, Antoine equation |
| $\delta_{ij}$ | virial coefficient parameter, eq 2 |

*Subscripts*

| | |
|---|---|
| calcd | calculated |
| obsd | observed |

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# The Systems Vinyl Acetate–Toluene and Vinyl Acetate–Propyl Bromide–Toluene

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**Vapor–liquid equilibrium at 760 mmHg has been determined for the title systems. The binary vinyl acetate–toluene deviates positively from ideal behavior and does not have an azeotrope. The binary and ternary data were correlated by various equations, and the appropriate parameters are reported.**

The present work was undertaken to measure VLE data for the title systems for which no isobaric data are available. Data for the two other binaries have already been measured (*1*, *2*).

## Experimental Section

***Purity of Materials.*** Vinyl acetate analytical grade (99%+) was purchased from Fluka, propyl bromide (99.4%) from Merck, and analytical grade toluene (99.6%+) from Frutarom. The reagents were used without further purification after gas chromatography failed to show any significant impurities. Properties of the pure components appear in Table I.

**Table I. Physical Constants of Pure Components**

| index | compd | refractive index (25 °C) | bp (760 mmHg), °C | purity, GLC (min) |
|---|---|---|---|---|
| 1 | vinyl acetate | 1.3932[a] | 72.56[a] | 99 |
| | | 1.3934[c] | 72.49[c] | |
| 2 | propyl bromide | 1.4320[a] | 70.55[a] | 99.4 |
| | | 1.4317[b] | 70.80[b] | |
| 3 | toluene | 1.4926[a] | 110.7[a] | 99.6 |
| | | 1.4940[b] | 110.63[b] | |

[a] Measured. [b] Reference *15*. [c] Reference *16*.

***Apparatus and Procedure.*** An all-glass modified Dvorak and Boublik recirculation still (*3*) was used in the equilibrium determination. A vacuum system connected the vapor condenser with a Swietoslawski ebulliometer and allowed total pressure regulation. The total pressure of the system was determined from the boiling temperature of the distilled water in the ebulliometer. The experimental features have been described in a previous publication (*4*). All analyses were carried out by gas chromatography on a Packard-Becker Model 417 apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter. Column packing, operating temperature, and injector and detector temperatures were as follows: 20% O.V. 17, 120 °C, 210 °C, 220 °C for the binary system; GP 20% SP-2100/0.1% Carbowax 1500 on 100/120 Supelcoport, 100 °C, 230 °C, 230 °C, for the ternary system. Very good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the weight composition of the sample. Concentration measurements were accurate to better than ±1%. The accuracy in determination of pressure and temperature was $\Delta P = \pm 1$ mmHg and $\Delta t = \pm 0.02$ °C.

## Results

The temperature–concentration measurements at 760 mmHg for the binary and ternary systems are reported in Figures 1 and

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**Table II. Experimental Vapor-Liquid Equilibria Data for Vinyl Acetate (1)-Toluene (3) at 760 mmHg**

| $t$, °C | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|
| 74.20 | 0.923 | 0.967 | 0.991 | 1.324 |
| 74.61 | 0.854 | 0.939 | 1.027 | 1.272 |
| 77.20 | 0.752 | 0.894 | 1.029 | 1.194 |
| 78.72 | 0.698 | 0.865 | 1.023 | 1.181 |
| 79.52 | 0.667 | 0.847 | 1.023 | 1.182 |
| 80.20 | 0.638 | 0.835 | 1.034 | 1.146 |
| 80.34 | 0.636 | 0.830 | 1.026 | 1.168 |
| 81.98 | 0.574 | 0.797 | 1.041 | 1.129 |
| 84.95 | 0.470 | 0.730 | 1.069 | 1.094 |
| 87.55 | 0.398 | 0.675 | 1.085 | 1.067 |
| 90.10 | 0.325 | 0.619 | 1.135 | 1.029 |
| 91.30 | 0.289 | 0.583 | 1.164 | 1.030 |
| 92.11 | 0.276 | 0.570 | 1.165 | 1.017 |
| 95.27 | 0.212 | 0.482 | 1.179 | 1.022 |
| 97.54 | 0.170 | 0.417 | 1.199 | 1.020 |
| 97.62 | 0.161 | 0.408 | 1.234 | 1.021 |
| 99.19 | 0.140 | 0.371 | 1.241 | 1.011 |
| 100.34 | 0.127 | 0.337 | 1.256 | 1.013 |
| 106.04 | 0.048 | 0.157 | 1.291 | 1.006 |

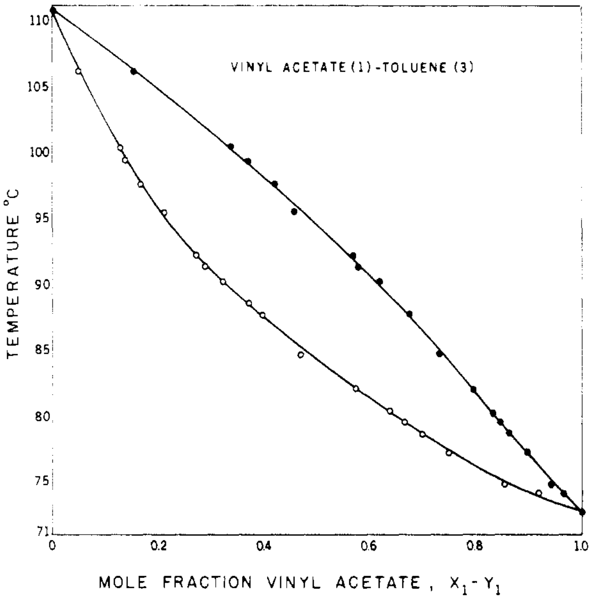

**Figure 1.** Boiling point diagram for the binary vinyl acetate-toluene.

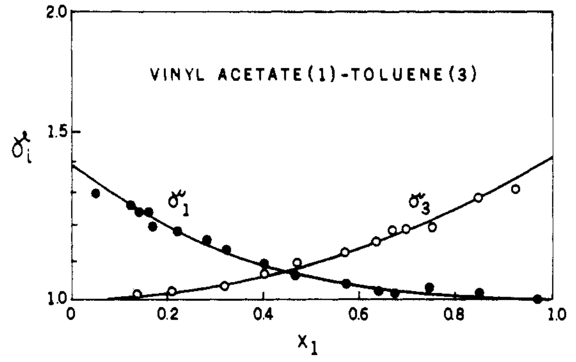

**Figure 2.** Activity coefficients for the binary vinyl acetate-toluene.

3 and Tables II and III, together with the activity coefficients which were calculated from the following equation (*5*):

$$\ln \gamma_i = \ln (Py_i/P_i^\circ x_i) + (B_{ii} - v_i^L)(P - P_i^\circ)/RT + (P/2RT)\sum\sum y_j y_k (2\delta_{ji} - \delta_{jk}) \quad (1)$$

where

$$\delta_{ji} = 2B_{ji} - B_{jj} - B_{ii} \quad (2)$$

**Table III. Experimental Vapor-Liquid Equilibria Data for Vinyl Acetate (1)-Propyl Bromide (2)-Toluene (3) at 760 mmHg**

| $t$, °C | $x_1$ | $x_2$ | $y_1$ | $y_2$ | $\gamma_1$ | $\gamma_2$ | $\gamma_3$ |
|---|---|---|---|---|---|---|---|
| 70.5 | 0.381 | 0.562 | 0.390 | 0.593 | 1.087 | 1.071 | 1.048 |
| 71.3 | 0.290 | 0.631 | 0.324 | 0.650 | 1.157 | 1.021 | 1.123 |
| 71.4 | 0.077 | 0.871 | 0.099 | 0.885 | 1.325 | 1.003 | 1.044 |
| 71.5 | 0.213 | 0.701 | 0.250 | 0.721 | 1.206 | 1.012 | 1.141 |
| 71.7 | 0.100 | 0.835 | 0.122 | 0.857 | 1.247 | 1.005 | 1.086 |
| 71.7 | 0.471 | 0.403 | 0.497 | 0.470 | 1.078 | 1.141 | 0.8806 |
| 71.8 | 0.115 | 0.812 | 0.144 | 0.831 | 1.275 | 0.9987 | 1.146 |
| 72.6 | 0.205 | 0.670 | 0.248 | 0.711 | 1.204 | 1.013 | 1.071 |
| 72.6 | 0.423 | 0.444 | 0.461 | 0.495 | 1.084 | 1.063 | 1.080 |
| 72.7 | 0.224 | 0.644 | 0.272 | 0.686 | 1.204 | 1.013 | 1.033 |
| 72.7 | 0.846 | 0.096 | 0.850 | 0.130 | 0.9946 | 1.285 | 1.121 |
| 73.0 | 0.336 | 0.508 | 0.385 | 0.564 | 1.127 | 1.048 | 1.053 |
| 73.0 | 0.050 | 0.846 | 0.065 | 0.902 | 1.274 | 1.004 | 1.017 |
| 73.1 | 0.072 | 0.815 | 0.096 | 0.865 | 1.306 | 0.9984 | 1.106 |
| 73.1 | 0.750 | 0.150 | 0.770 | 0.193 | 1.004 | 1.207 | 1.186 |
| 73.2 | 0.630 | 0.232 | 0.665 | 0.287 | 1.029 | 1.157 | 1.110 |
| 73.4 | 0.653 | 0.214 | 0.690 | 0.260 | 1.024 | 1.130 | 1.192 |
| 73.7 | 0.880 | 0.041 | 0.910 | 0.056 | 0.9951 | 1.262 | 1.355 |
| 73.7 | 0.089 | 0.770 | 0.117 | 0.838 | 1.264 | 1.006 | 1.001 |
| 73.8 | 0.524 | 0.308 | 0.573 | 0.368 | 1.048 | 1.010 | 1.099 |
| 73.8 | 0.064 | 0.792 | 0.088 | 0.865 | 1.315 | 1.004 | 1.017 |
| 73.9 | 0.510 | 0.320 | 0.570 | 0.370 | 1.067 | 1.061 | 1.100 |
| 74.1 | 0.102 | 0.736 | 0.136 | 0.813 | 1.267 | 1.009 | 0.9743 |
| 74.2 | 0.503 | 0.307 | 0.563 | 0.367 | 1.058 | 1.086 | 1.135 |
| 74.3 | 0.830 | 0.057 | 0.873 | 0.077 | 0.9927 | 1.225 | 1.363 |
| 74.5 | 0.577 | 0.227 | 0.643 | 0.280 | 1.043 | 1.110 | 1.198 |
| 74.9 | 0.125 | 0.673 | 0.172 | 0.760 | 1.272 | 1.005 | 1.010 |
| 75.5 | 0.411 | 0.341 | 0.498 | 0.410 | 1.103 | 1.054 | 1.094 |
| 75.6 | 0.056 | 0.730 | 0.081 | 0.847 | 1.311 | 1.013 | 0.9865 |
| 75.8 | 0.147 | 0.614 | 0.205 | 0.709 | 1.256 | 1.002 | 1.048 |
| 76.0 | 0.690 | 0.093 | 0.790 | 0.122 | 1.024 | 1.130 | 1.174 |
| 76.3 | 0.289 | 0.430 | 0.373 | 0.522 | 1.145 | 1.038 | 1.070 |
| 76.4 | 0.170 | 0.559 | 0.239 | 0.670 | 1.243 | 1.023 | 0.9581 |
| 77.1 | 0.243 | 0.452 | 0.330 | 0.560 | 1.176 | 1.036 | 1.005 |
| 77.1 | 0.338 | 0.367 | 0.438 | 0.452 | 1.121 | 1.029 | 1.038 |
| 77.5 | 0.510 | 0.184 | 0.637 | 0.240 | 1.068 | 1.077 | 1.105 |
| 77.9 | 0.671 | 0.046 | 0.811 | 0.066 | 1.0235 | 1.174 | 1.183 |
| 78.3 | 0.550 | 0.131 | 0.684 | 0.181 | 1.038 | 1.115 | 1.132 |
| 79.4 | 0.463 | 0.156 | 0.614 | 0.224 | 1.072 | 1.124 | 1.096 |
| 79.5 | 0.191 | 0.427 | 0.288 | 0.568 | 1.215 | 1.039 | 0.9682 |
| 79.7 | 0.369 | 0.239 | 0.520 | 0.320 | 1.131 | 1.040 | 1.043 |
| 80.0 | 0.089 | 0.562 | 0.144 | 0.712 | 1.285 | 0.9761 | 1.042 |
| 80.7 | 0.272 | 0.312 | 0.416 | 0.412 | 1.190 | 0.9968 | 1.020 |
| 81.1 | 0.367 | 0.289 | 0.464 | 0.350 | 0.9722 | 0.9042 | 1.317 |
| 81.4 | 0.530 | 0.041 | 0.747 | 0.059 | 1.074 | 1.065 | 1.091 |
| 81.7 | 0.214 | 0.333 | 0.348 | 0.466 | 1.230 | 1.029 | 0.9814 |
| 81.8 | 0.321 | 0.233 | 0.478 | 0.325 | 1.122 | 1.021 | 1.051 |
| 83.3 | 0.174 | 0.332 | 0.298 | 0.480 | 1.235 | 1.016 | 1.017 |
| 83.7 | 0.228 | 0.266 | 0.380 | 0.394 | 1.190 | 1.030 | 0.9993 |
| 84.1 | 0.418 | 0.072 | 0.639 | 0.110 | 1.078 | 1.050 | 1.087 |
| 85.3 | 0.259 | 0.190 | 0.441 | 0.290 | 1.159 | 1.015 | 1.035 |
| 86.5 | 0.324 | 0.095 | 0.544 | 0.160 | 1.106 | 1.085 | 1.041 |
| 87.8 | 0.221 | 0.163 | 0.415 | 0.268 | 1.192 | 1.022 | 1.007 |
| 88.3 | 0.081 | 0.315 | 0.169 | 0.518 | 1.307 | 1.011 | 0.9988 |
| 89.4 | 0.260 | 0.078 | 0.499 | 0.137 | 1.166 | 1.048 | 1.024 |
| 89.9 | 0.190 | 0.104 | 0.387 | 0.243 | 1.222 | 1.377 | 0.9614 |
| 90.2 | 0.105 | 0.204 | 0.225 | 0.415 | 1.273 | 1.189 | 0.9454 |
| 92.4 | 0.131 | 0.154 | 0.296 | 0.286 | 1.264 | 1.024 | 0.9904 |
| 92.7 | 0.197 | 0.067 | 0.425 | 0.128 | 1.200 | 1.048 | 1.022 |
| 93.0 | 0.152 | 0.118 | 0.338 | 0.218 | 1.225 | 1.004 | 1.013 |
| 97.5 | 0.073 | 0.117 | 0.194 | 0.243 | 1.301 | 1.008 | 1.010 |
| 98.0 | 0.033 | 0.160 | 0.093 | 0.337 | 1.363 | 1.012 | 1.013 |
| 98.1 | 0.096 | 0.080 | 0.248 | 0.167 | 1.246 | 0.9995 | 1.015 |
| 99.7 | 0.066 | 0.089 | 0.185 | 0.195 | 1.295 | 1.007 | 0.9981 |
| 100.0 | 0.039 | 0.127 | 0.109 | 0.274 | 1.283 | 0.9860 | 0.9995 |
| 101.4 | 0.086 | 0.032 | 0.239 | 0.072 | 1.231 | 0.9929 | 1.013 |
| 102.9 | 0.060 | 0.049 | 0.171 | 0.114 | 1.214 | 0.9896 | 0.9949 |
| 104.1 | 0.043 | 0.038 | 0.131 | 0.090 | 1.261 | 0.9799 | 1.016 |

Vapor pressures $P_i^\circ$ were calculated according to Antoine's equation:

$$\log P_i^\circ = \alpha_i - \beta_i/(\delta_i + t) \quad (3)$$

where the constants are reported in Table IV. The molar virial

Table IV. Vapor-Pressure Constants

| compound | $\alpha_i$ | $\beta_i$ | $\delta_i$ |
|---|---|---|---|
| vinyl acetate[a] | 6.992 27 | 1191.99 | 217.01 |
| propyl bromide[b] | 6.910 65 | 1194.889 | 225.51 |
| toluene[b] | 6.954 64 | 1344.800 | 219.482 |

[a] Reference *17*. [b] Reference *15*.

coefficients $B_{ii}$ and the molar mixed coefficient $B_{ij}$ were calculated by the method of Tsonopoulos (*6*) using the molecular parameters suggested by the same author. The last two terms contributed between 2 and 4% to the activity coefficient, and their influence was important only at very dilute concentrations.

The binary data in Figure 2 and Table II are thermodynamically consistent according to both the area and Herington's criteria (*7*) and show that the system vinyl acetate–toluene exhibits positive deviations from ideal behavior. The ternary data reported in Table III were found to be thermodynamically consistent as tested by the McDermot–Ellis method (*8*) modified by Wisniak and Tamir (*9*). According to this method two experimental points a and b are considered thermodynamically consistent if the following condition is fulfilled:

$$D < D_{\max} \tag{4}$$

The local deviation $D$ is given by

$$D = \sum_{i=1}^{n} (x_{ia} + x_{ib})(\ln \gamma_{ib} - \ln \gamma_{ia}) \tag{5}$$

where $n$ is the number of components and

$$D_{\max} = \sum_{i=1}^{n} (x_{ia} + x_{ib})(1/x_{ia} + 1/y_{ia} + 1/x_{ib} + 1/y_{ib})\Delta x + 2\sum_{i=1}^{n} |\ln \gamma_{ib} - \ln \gamma_{ia}|\Delta x + \sum_{i=1}^{n} (x_{ia} + x_{ib})\Delta P/P + \sum_{i=1}^{n} (x_{ia} + x_{ib})\beta_i\{(t_a + \delta_i)^{-2} + (t_b + \delta_i)^{-2}\}\Delta t \tag{6}$$

The errors in the measurements $\Delta x$, $\Delta P$, and $\Delta t$ were as previously indicated. The first term in eq 6 was the dominant one.

The binary data in Table II were also correlated using the Redlich–Kister (*10*) equation

$$\log (\gamma_1/\gamma_3) = A(x_3 - x_1) \tag{7}$$

with $A$ = 0.129 and a coefficient of determination 0.971.

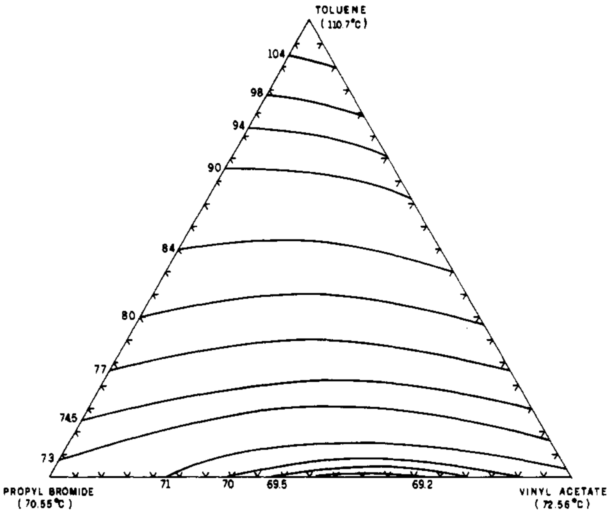

**Figure 3.** Isothermals for the ternary system (760 mmHg).

Equation 7 indicates that solutions of vinyl acetate and toluene behave like regular solutions so that

$$G^E/RT = 0.297x_1x_3 \tag{8}$$

The binary data were also correlated by using the Wilson model (*11*)

$$\ln \gamma_1 = -\ln (x_1 + A_{13}x_3) + x_3\left[\frac{A_{13}}{x_1 + A_{13}x_3} - \frac{A_{31}}{A_{31}x_1 + x_3}\right] \tag{9}$$

$$\ln \gamma_2 = -\ln (x_3 + A_{31}x_1) - x_1\left[\frac{A_{13}}{x_1 + A_{13}x_3} - \frac{A_{31}}{A_{31}x_1 + x_3}\right] \tag{10}$$

The constants $A_{13}$ and $A_{31}$ were determined by using the simplified method proposed by Apelblat and Wisniak (*12*)

$$A_{13} = 0.901\,61 \qquad A_{31} = 0.800\,05$$

With these values of the constants the Wilson model is capable of predicting the vapor composition of the binary with an av-

Table V. Redlich–Kister Correlation of Binary and Ternary Data

| system | $B_{ij}$ | $C_{ij}$ | $D_{ij}$ | rmsd $\gamma_1$ | rmsd $\gamma_2$ |
|---|---|---|---|---|---|
| vinyl acetate (1)–propyl bromide (2) | 0.270 51 | −0.010 220 | 0.139 50 | 0.025 | 0.39 |
| vinyl acetate (1)–toluene (3) | 0.313 30 | $0.270\,72 \times 10^{-3}$ | $0.247\,10 \times 10^{-4}$ | 0.026 | 0.017 |
| propyl bromide (2)–toluene (3) | −0.018 660 | $0.968\,7 \times 10^{-4}$ | $0.822\,98 \times 10^{-5}$ | 0.078 | 0.068 |

| system | | overall rmsd $\gamma_{ij}$ | overall rmsd $y_{ij}$ |
|---|---|---|---|
| vinyl acetate (1)–propyl bromide (2)–toluene (3) | $C_1 = 0$ | 0.056 | 0.015 |
| | $C_1 = 0.154\,26$ | 0.058 | 0.016 |

Table VI. Correlation of Boiling Points, Eq 12 and 13[a]

| system | $C_0$ | $C_1$ | $C_2$ | mean $D$% | rmsd |
|---|---|---|---|---|---|
| vinyl acetate (1)–propyl bromide (2) | -9.0730 | 0.50615 | 0.22946 | 0.061 | 0.066 |
| vinyl acetate (1)–toluene (3) | -29.941 | 17.106 | -15.781 | 0.21 | 0.19 |
| propyl bromide (2)–toluene (3) | -20.722 | 3.6560 | 12.854 | 0.22 | 0.26 |

| system | $A$ | $B$ | $D$% | rmsd |
|---|---|---|---|---|
| vinyl acetate (1)–propyl bromide (2)–toluene (3) | -2.8797 | 29.074 | 0.61 | 0.43 |

[a] $D = |(T_{\text{obsd}} - T_{\text{calcd}})|/T_{\text{obsd}}$; mean $D\% = (100/n)\sum D_i$.

**Table VII. Parameters of $T$–$x$ Correlation (Eq 14, $n = 3$) for Vinyl Acetate (1)–Propyl Bromide (2)–Toluene (3) at 760 mmHg**[a]

| $ij$ | $A_{ij}$ | $B_{ij}$ | $C_{ij}$ | $D_{ij}$ | $E_{ij}$ | $F_{ij}$ | $G_{ij}$ | mean $D\%$ | rmsd |
|---|---|---|---|---|---|---|---|---|---|
| 12 | −19.341 | 5.4133 | −1.583 | | | | | 0.148 | 0.0298 |
| 13 | −53.956 | 32.975 | −32.688 | 16.095 | 33.602 | 25.318 | −65.404 | 1.79 | 0.196 |
| 23 | −20.759 | 5.5655 | 12.836 | −6.485 | | | | 0.213 | 0.0507 |
| | | | | Ternary Parameters | | | | | |
| 12 | −17.833 | 9.0536 | 12.453 | | | | | | |
| 13 | −59.527 | 34.028 | −6.9215 | | | | | 0.440 | 0.0694 |
| 23 | −21.279 | 3.9775 | 5.7545 | | | | | | |

[a] $T_1° = 72.56$ °C; $T_2° = 70.55$ °C; $T_3° = 110.70$ °C. $D = |(T_{\text{obsd}} - T_{\text{calcd}})|/T_{\text{obsd}}$; mean $D\% = (100/n)\sum D_i$.

erage error of 2.2% for $y_1$ and 0.9% for $y_2$.

The activity coefficients for the ternary system were correlated by the following Redlich–Kister expansion (*10*):

$$\ln \gamma_1 = x_2x_3[(B_{12} + B_{13} - B_{23}) + C_{12}(2x_1 - x_2) + C_{13}(2x_1 - x_3) + 2C_{23}(x_3 - x_2) + D_{12}(x_1 - x_2) \times (3x_1 - x_2) + D_{13}(x_1 - x_3)(3x_1 - x_2) - 3D_{23}(x_3 - x_2)^2 + C_1(1 - 2x_1)] + x_2^2[B_{12} + C_{12}(3x_1 - x_2) + D_{12}(x_1 - x_2)(5x_1 - x_2)] + x_3^2[B_{13} + C_{13}(3x_1 - x_3) + D_{13}(x_1 - x_3)(5x_1 - x_3)] \quad (11)$$

where $B_{ij}$, $C_{ij}$, and $D_{ij}$ are the binary constants and $C_1$ is a ternary constant. The equations for two other activity coefficients were obtained by cyclic rotation of the indices. The binary data used for calculating the binary constants have been reported elsewhere (*1*, *2*).

The binary and ternary Redlich–Kister coefficients were obtained by a Simplex optimization technique and are reported in Table V. The relative values of the root mean square deviation and the ternary constant $C_1$ suggest that ternary data can be predicted directly from the binary systems.

Boiling points of the binary and ternary systems were correlated by the equation suggested by Wisniak and Tamir (*13*), based solely on the liquid composition:

binary system

$$T = \sum_{i=1}^{2} x_iT_i° + x_1x_2\sum_{k=0}^{i} C_k(x_1 - x_2)^k + ...] \quad (12)$$

ternary system

$$T = \sum_{i=1}^{i} x_iT_i° + \sum_{i,j=1}^{i} \{x_ix_j\sum_{k=0}^{1} C_k(x_i - x_j)^k\} + x_1x_2x_3\{A + B(x_1 - x_2) + C(x_1 - x_3) + D(x_2 - x_3) + ...\} \quad (13)$$

In these equations $T_i°$ is the boiling point of the pure component in K and $i$ is the number of terms in the series expansion of $(x_i - x_j)$. $C_k$ are the binary constants where $A$, $B$, $C$, and $D$ are ternary constants. The various constants of eq 13 are reported in Table VI, which also contains information indicating the degree of goodness of the correlation.

Tamir (*14*) had developed an alternative equation, based on the concept of "excess property" in which the boiling temperature of the mixture is also correlated solely with the liquid composition:

$$T = \sum_{i=1}^{n} x_iT_i° + \sum_{i=1}^{n=1} \sum_{j=i+1}^{n} x_ix_j[A_{ij} + B_{ij}(x_i - x_j) + C_{ij}(x_i - x_j)^2 + ...] \quad (14)$$

This equation is useful for obtaining isothermals and for exploring the azeotropic behavior and distillation paths of ternary mixtures (*14*). The coefficients $A_{ij}$, $B_{ij}$, and $C_{ij}$ are multicomponent parameters that are determined directly from the multicomponent data. Figure 3 reports the isothermals obtained on the basis of the parameters $A_{ij}$ and $B_{ij}$ reported in Table VII by applying eq 14 for $n = 3$. These isothermals might be used for considering possible distillation paths in ternary systems as well as to conclude whether a ternary system exhibits azeotropic behavior.

As observed from Figure 3, whereas one binary system has an azeotrope the ternary system does not. Table VII contains also the group of parameters $A_{ij}$, $B_{ij}$, and $C_{ij}$ for the $T$–$x$ correlation (eq 14) which yield the smaller mean deviation between the calculated and observed values of $T$.

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## Glossary

| | |
|---|---|
| $A_{ij}$, $B_{ij}$, etc. | multicomponent adjustable parameters in eq 14 |
| $A_{13}$, $A_{31}$ | Wilson constants, eq 9 and 10 |
| $B_{ij}$, $C_{ij}$ | virial coefficients, eq 2 |
| $B_{ii}$, $C_{ij}$, $D_{ii}$ | Redlich–Kister constants, eq 7 and 11 |
| $G^E$ | Gibbs excess function, cal·mol$^{-1}$ |
| $n$ | number of components |
| $P$ | total pressure, mmHg |
| $P_i°$ | vapor pressure of pure component $i$, mmHg |
| $R$ | gas constant, 62 363.3 cm$^3$·mmHg·mol$^{-1}$·K$^{-1}$ |
| $T$ | boiling temperature of a mixture, K |
| $T_i°$ | boiling temperature of pure component $i$, K |
| $t$ | temperature, °C |
| $v_i^L$ | molar volume of liquid component $i$, mL·mol$^{-1}$ |
| $x_i$, $y_i$ | mole fraction of component $i$ in the liquid and vapor phases, respectively |
| $\alpha_i$ | coefficient, Antoine equation |
| $\beta_i$ | coefficient, Antoine equation |
| $\gamma_i$ | activity coefficient of component $i$ |
| $\delta_i$ | coefficient, Antoine equation |

*Subscripts*

| | |
|---|---|
| $\delta_{ij}$ | virial coefficient parameter, eq 2 |
| calcd | calculated |
| obsd | observed |

**Registry No.** Vinyl acetate, 108-05-4; propyl bromide, 106-94-5; toluene, 108-88-3.

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# Vapor–Liquid Equilibria in the Carbon Dioxide–1-Hexene and Carbon Dioxide–1-Hexyne Systems

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**Vapor–liquid equilibrium data for $CO_2$–1-hexene mixtures at 309.3, 324.2, and 332.3 K and for $CO_2$–1-hexyne mixtures at 308.1, 323.0, and 332.6 K have been measured in a high-pressure recirculation apparatus. The pressure in the experiments ranged from 1.6 to 9.4 MPa. The experimental data were correlated by use of two simple equations of state: one containing three constants and the other containing four constants. The correlative capabilities of the two equations were found to be similar.**

## 1. Introduction

The behavior of carbon dioxide–hydrocarbon mixtures has been of interest for many years because of their importance in natural gas and petroleum processing. More recently, these mixtures have received increased attention as solvent/cosolvent pairs in the supercritical extraction of coal as well as natural products. Phase equilibrium studies of carbon dioxide–alkane mixtures, with the *n*-alkane ranging from methane to decane, have been conducted by a large number of investigators (*1–3*). However, only a few investigators have studied carbon dioxide–alkene mixtures and there are no reported studies of carbon dioxide–alkyne mixtures. This work presents high-pressure vapor–liquid equilibrium data for the carbon dioxide–1-hexene and carbon dioxide–1-hexyne systems. There is some disagreement in the literature data presented by Wagner and Wichterle (*4*) and Orbey and Vera (*5*) for the $CO_2$–1-hexene system. The present work was carried out to verify the behavior of this system and to measure new data for the $CO_2$–1-hexyne system. Although the primary focus of the study was on experimental measurements, the ability of two simple equations of state to correlate the data was also examined and is discussed below.

## 2. Experimental Section

*2.1.* ***Apparatus.*** A schematic diagram of the apparatus used in this work is shown in Figure 1. The apparatus consisted of a stainless-steel view cell (similar to a Jerguson liquid level gauge of 40 $cm^3$ capacity) in which both the liquid and vapor phases were countercurrently recirculated in order to provide mixing of the phases and to ensure that equilibrium was established. An Emco magnetic pump (Model 101) was used for the recirculation of the vapor phase, while a Ruska magnetic pump (Model 2330-802) was used for the liquid phase. Each recirculation loop included ultra-low-volume high-pressure sampling valves manufactured by Valco Instruments Inc. The vapor sampling valve had a volume of 1.0 $\mu$L and the liquid valve 0.2 $\mu$L. The sampling valves were connected on-line to a Hewlett-Packard gas chromatograph (Model 5890A) equipped with a thermal conductivity detector. The carrier flow lines leading from the valves to the gas chromatograph were wrapped with heating tape to prevent condensation in the lines.

An additional feature of the apparatus was the use of an HIP pressure generator as a variable volume controller, similar to that used by Radosz (*6*). The variable volume allows the control and/or regulation of the system pressure and can be invaluable for correction of disturbances caused by sampling. It should be added that these disturbances were minimal in our apparatus because of the ultra-low-volume sampling valves used.

The entire assembly was placed in a constant-temperature air bath in which an Omega temperature controller (Model CN5001T1-A) connected to a heating element was used to control the air-bath temperature.

The pressure was measured by a digital Heise pressure gauge (Model 710A), and the temperature was determined by a thermistor inserted into the side of the view cell. The pressure gauge was calibrated against a Budenberg dead-weight tester and was estimated to be accurate to within ±0.014 MPa. The thermistor was calibrated by use of a Leeds and Northrup platinum resistance thermometer, and the temperature measurements were estimated to be accurate within ±0.1 K. The gas chromatograph was calibrated by preparing synthetic mixtures to determine response factors for the $CO_2$–1-hexene and $CO_2$–1-hexyne systems. The response factors were estimated to be accurate within 3%. The main source of error could be attributed to difficulties in the preparation of mixtures.

*2.2.* ***Experimental Procedure.*** The system was evacuated at the beginning of the experiment, and the liquid component was introduced into the equilibrium cell from the feed reservoir. Carbon dioxide was then charged into the apparatus. If pressures greater than cylinder supply pressure were desired, the carbon dioxide was liquified by passing through an ice bath and pumped into the apparatus by a Milton Roy simplex mini pump (Model 396-89). The recirculation pumps were then turned on and more $CO_2$ was introduced into the apparatus to achieve the desired pressures. Some trial and error in charging the apparatus to achieve acceptable liquid levels in the view cell was sometimes also necessary.

Recirculation of the phases was continued until equilibrium had been established. Both phases were then sampled, with the liquid phase being sampled first. Multiple samples (typically 4–6) were taken. After sampling the liquid phase, the vapor sample valve was heated by use of heating tape. The valve temperature was maintained slightly above the bath temperature to prevent any condensation of heavier components in the vapor valve sample slot. The heating was kept minimal to prevent disturbance of equilibrium. Several samples of the vapor phase were then taken until vapor-phase analyses became reproducible. The first few were often found to give

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