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# Isothermal Vapor−Liquid Equilibrium and Excess Enthalpy Data for the Binary Systems Diethyl Ether + Ethyl *tert*-Butyl Ether, 1-Pentene + Methyl Acetate, and Propene + 2-Propanol

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Isothermal vapor−liquid equilibrium (VLE) and excess enthalpy ($H^E$) data for the three binary systems diethyl ether + ethyl *tert*-butyl ether (ETBE), 1-pentene + methyl acetate, and propene + 2-propanol have been measured by means of the static technique and an isothermal flow calorimeter, respectively. The experimental VLE and $H^E$ data have been used simultaneously for a correlation of constant or linear temperature-dependent UNIQUAC parameters.

## Introduction

The reliable knowledge of the phase equilibrium behavior is a prerequisite for the synthesis and design of separation processes. For the description of the required separation factors of the system to be separated, excess Gibbs energy ($G^E$) models or equations of state can be used, which allow the prediction of the phase equilibrium behavior of multicomponent systems from binary data only. If there are no experimental data available, group contribution methods, such as ASOG, UNIFAC, mod. UNIFAC (Dortmund), or mod. UNIFAC (Lyngby), can be applied successfully. For the revision and extension of these methods the systematic extension of the existing database is desired.

In this paper vapor−liquid equilibrium (VLE) and excess enthalpy data are presented for the binary systems diethyl ether + ethyl *tert*-butyl ether, 1-pentene + methyl acetate, and propene + 2-propanol together with temperature-dependent UNIQUAC parameters to describe the phase equilibrium in a wide temperature range. These systems were studied as part of an ongoing investigation sponsored by Project 805c/96, of the Design Institute for Physical Property Data of the American Institute of Chemical Engineers.

## Chemicals

The suppliers of the chemicals are listed in Table 1. For the VLE measurements the chemicals were dried over molecular sieves, degassed, and distilled as described by Fischer and Gmehling (1994). In the case of ethyl *tert*-butyl ether further purification was required in order to remove small amounts of alcohol. Therefore ethyl *tert*-butyl ether was washed several times with water. For the $H^E$ measurements the compounds were used without degassing.

**Table 1. Suppliers of the Used Chemicals**

| component | supplier | component | supplier |
|---|---|---|---|
| diethyl ether, >99.5% | Riedel de Haën | methyl acetate, >99% | Riedel de Haën |
| ethyl *tert*-butyl ether, 92−93% | Veba-Oel AG | propene, 99.5% | Messer Griesheim |
| 1-pentene, >97% | ACROS | 2-propanol, >99.7% | Scharlau |

**Table 2. Experimental *P*−*x* Data for the System Diethyl Ether (1) + Ethyl *tert*-Butyl Ether (2) at 333.15 K**

| $x_1$ | $P$/kPa | $x_1$ | $P$/kPa |
|---|---|---|---|
| 0.00000 | 66.747 | 0.62083 | 166.626 |
| 0.00596 | 67.664 | 0.63065 | 168.359 |
| 0.01174 | 68.565 | 0.64613 | 170.866 |
| 0.01746 | 69.465 | 0.65471 | 172.399 |
| 0.02300 | 70.344 | 0.66889 | 174.706 |
| 0.02825 | 71.182 | 0.69335 | 178.852 |
| 0.03357 | 72.015 | 0.71970 | 183.305 |
| 0.03914 | 72.882 | 0.74817 | 188.158 |
| 0.04465 | 73.727 | 0.77905 | 193.424 |
| 0.05042 | 74.629 | 0.80575 | 197.997 |
| 0.05550 | 75.427 | 0.83438 | 202.943 |
| 0.06290 | 76.607 | 0.86518 | 208.250 |
| 0.07638 | 78.714 | 0.88996 | 212.543 |
| 0.09300 | 81.305 | 0.91091 | 216.182 |
| 0.11070 | 84.093 | 0.92927 | 219.369 |
| 0.13171 | 87.355 | 0.94845 | 222.702 |
| 0.16007 | 91.818 | 0.96443 | 225.501 |
| 0.19422 | 97.187 | 0.97496 | 227.341 |
| 0.22901 | 102.73 | 0.98264 | 228.675 |
| 0.26414 | 108.32 | 0.98734 | 229.514 |
| 0.30176 | 114.37 | 0.99103 | 230.154 |
| 0.33828 | 120.24 | 0.99348 | 230.514 |
| 0.37355 | 125.95 | 0.99465 | 230.728 |
| 0.40924 | 131.77 | 0.99549 | 230.901 |
| 0.44298 | 137.27 | 0.99630 | 231.048 |
| 0.47444 | 142.43 | 0.99701 | 231.168 |
| 0.50546 | 147.54 | 0.99780 | 231.328 |
| 0.53806 | 152.92 | 0.99848 | 231.474 |
| 0.57083 | 158.37 | 0.99886 | 231.528 |
| 0.57583 | 159.12 | 0.99927 | 231.594 |
| 0.59748 | 162.71 | 0.99963 | 231.634 |
| 0.60297 | 163.72 | 1.00000 | 231.674 |

## Experimental Part

The VLE measurements (isothermal *P*−*x* data) were carried out in two different static devices following the principle proposed by Gibbs and Van Ness (1972). For the measurement of the binary system diethyl ether + ethyl *tert*-butyl ether at 333.15 K and the system 1-pentene + methyl acetate at 323.15 K, a computer operated static apparatus was used. The apparatus, the measurement procedure, and the accuracy of the equipment have been

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**Table 3. Experimental $H^E$ Data for the System Diethyl Ether (1) + Ethyl *tert*-Butyl Ether (2) at 333.15 K and 1.96 MPa**

| $x_1$ | $H^E$/(J mol$^{-1}$) | $x_1$ | $H^E$/(J mol$^{-1}$) |
|---|---|---|---|
| 0.0792 | −4.2270 | 0.6826 | −13.160 |
| 0.1557 | −7.6820 | 0.7947 | −9.9420 |
| 0.3008 | −12.581 | 0.9003 | −5.5730 |
| 0.4364 | −14.760 | 0.9509 | −2.9970 |
| 0.5634 | −14.930 | | |

**Table 4. Experimental $P$−$x$ Data for the System 1-Pentene (1) + Methyl Acetate (2) at 323.15 K**

| $x_1$ | $P$/kPa | $x_1$ | $P$/kPa |
|---|---|---|---|
| 0.00000 | 79.431 | 0.48315 | 170.20 |
| 0.00352 | 80.897 | 0.48427 | 170.23 |
| 0.00697 | 82.341 | 0.50463 | 171.92 |
| 0.01042 | 83.714 | 0.51118 | 172.49 |
| 0.01401 | 85.102 | 0.54273 | 174.91 |
| 0.01758 | 86.478 | 0.57849 | 177.48 |
| 0.02125 | 87.922 | 0.61937 | 180.23 |
| 0.02458 | 89.222 | 0.65667 | 182.53 |
| 0.02813 | 90.531 | 0.69882 | 184.94 |
| 0.03153 | 91.779 | 0.74678 | 187.40 |
| 0.03616 | 93.418 | 0.78759 | 189.26 |
| 0.04108 | 95.098 | 0.82386 | 190.69 |
| 0.05228 | 98.915 | 0.85696 | 191.80 |
| 0.06510 | 102.98 | 0.89306 | 192.73 |
| 0.08027 | 107.55 | 0.92443 | 193.28 |
| 0.09736 | 112.35 | 0.94579 | 193.49 |
| 0.11585 | 117.17 | 0.96204 | 193.54 |
| 0.13840 | 122.58 | 0.97234 | 193.53 |
| 0.16273 | 127.94 | 0.98069 | 193.49 |
| 0.18848 | 133.11 | 0.98688 | 193.44 |
| 0.21533 | 138.00 | 0.98933 | 193.42 |
| 0.24415 | 142.75 | 0.99057 | 193.41 |
| 0.27311 | 147.12 | 0.99173 | 193.40 |
| 0.30304 | 151.24 | 0.99295 | 193.38 |
| 0.33063 | 154.72 | 0.99416 | 193.36 |
| 0.35780 | 157.91 | 0.99535 | 193.34 |
| 0.38546 | 160.91 | 0.99652 | 193.33 |
| 0.41287 | 163.72 | 0.99884 | 193.28 |
| 0.43790 | 166.12 | 1.00000 | 193.25 |
| 0.46213 | 168.31 | | |

**Table 5. Experimental $H^E$ Data for the System 1-Pentene (1) + Methyl Acetate (2) at 323.15 K and 0.86 MPa**

| $x_1$ | $H^E$/(J mol$^{-1}$) | $x_1$ | $H^E$/(J mol$^{-1}$) |
|---|---|---|---|
| 0.0183 | 43.553 | 0.4705 | 1089.5 |
| 0.0369 | 119.46 | 0.5216 | 1094.3 |
| 0.0747 | 273.86 | 0.5745 | 1077.4 |
| 0.1137 | 415.85 | 0.6291 | 1026.0 |
| 0.1538 | 545.81 | 0.6856 | 958.04 |
| 0.1951 | 661.63 | 0.7441 | 860.03 |
| 0.2375 | 767.43 | 0.8047 | 719.74 |
| 0.2813 | 854.03 | 0.8674 | 535.42 |
| 0.3264 | 947.83 | 0.9325 | 293.08 |
| 0.3730 | 1019.8 | 0.9659 | 151.44 |
| 0.4209 | 1065.8 | | |

**Table 6. Experimental $P$−$x$ Data for the System Propene (1) + 2-Propanol (2) at 298.06 K**

| $x_1$ | $P$/kPa | $x_1$ | $P$/kPa |
|---|---|---|---|
| 0.08242 | 233.53 | 0.42584 | 799.77 |
| 0.10398 | 281.96 | 0.47208 | 839.53 |
| 0.13604 | 346.37 | 0.52369 | 878.98 |
| 0.15491 | 391.41 | 0.71582 | 985.19 |
| 0.18679 | 454.07 | 0.89192 | 1064.0 |
| 0.22800 | 534.17 | 0.96115 | 1098.4 |
| 0.28412 | 626.64 | 0.98358 | 1111.6 |
| 0.34038 | 710.45 | 1.00000 | 1121.4 |
| 0.38203 | 756.87 | | |

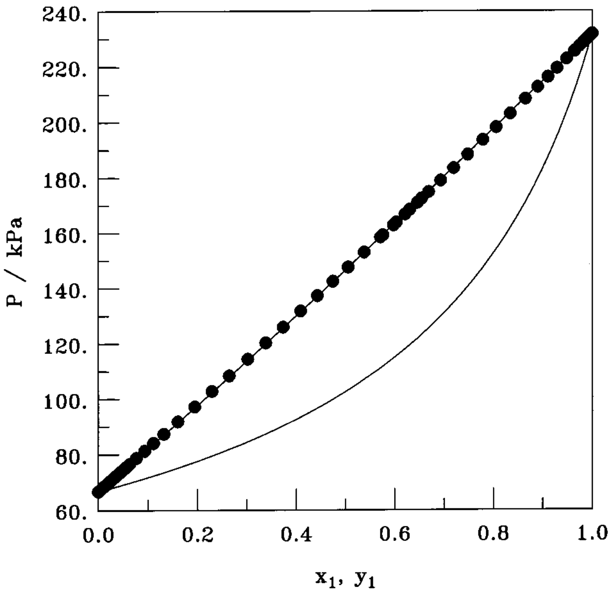

**Figure 1.** Experimental and predicted $P$−$x$($y$) behavior of the system diethyl ether (1) + ethyl *tert*-butyl ether (2) at 333.15 K: experimental (●); UNIQUAC (—).

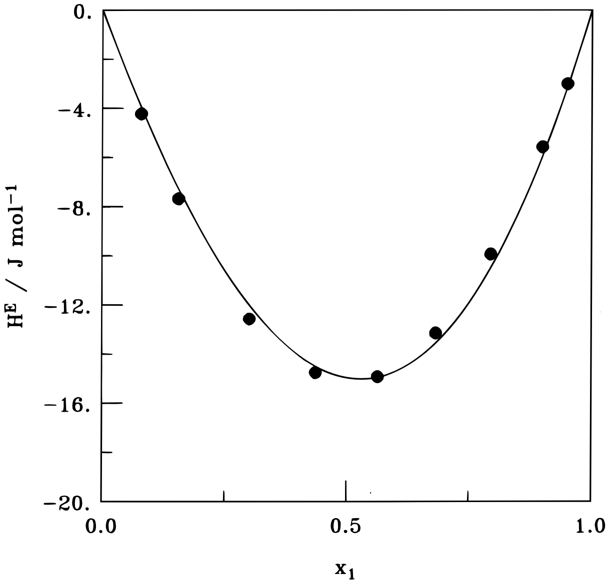

**Figure 2.** Experimental and predicted excess enthalpy data for the system diethyl ether (1) + ethyl *tert*-butyl ether (2) at 333.15 K: experimental (●); UNIQUAC (—).

**Table 7. Experimental $H^E$ Data for the System Propene (1) + 2-Propanol (2) at 333.15 K and 3.1 MPa**

| $x_1$ | $H^E$/(J mol$^{-1}$) | $x_1$ | $H^E$/(J mol$^{-1}$) |
|---|---|---|---|
| 0.0258 | 33.260 | 0.5584 | 776.34 |
| 0.0516 | 79.322 | 0.6081 | 801.83 |
| 0.1031 | 161.21 | 0.6577 | 819.93 |
| 0.1544 | 245.07 | 0.7071 | 810.61 |
| 0.2055 | 329.16 | 0.7563 | 797.05 |
| 0.2564 | 404.83 | 0.8054 | 774.78 |
| 0.3072 | 484.76 | 0.8543 | 734.69 |
| 0.3578 | 559.64 | 0.9030 | 649.33 |
| 0.4082 | 619.06 | 0.9516 | 491.12 |
| 0.4584 | 688.26 | 0.9758 | 350.38 |
| 0.5085 | 733.37 | | |

described previously (Rarey and Gmehling, 1993; Rarey et al., 1998). The experimental uncertainties of this apparatus are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 0.0001$ ($P$/Pa), and $\sigma(x_i) = 0.0001$. For measurement of the system propene + 2-propanol at 298.06 K the static apparatus of Kolbe and Gmehling (1985) was employed. A detailed description of

**Table 8. UNIQUAC Interaction Parameters Fitted Simultaneously to Isothermal $P-x$ and $H^E$ Data**

| component 1 | component 2 | $a_{12}$/(J mol$^{-1}$) | $a_{21}$/(J mol$^{-1}$) | $b_{12}$/(J mol$^{-1}$ K$^{-1}$) | $b_{21}$/(J mol$^{-1}$ K$^{-1}$) |
|---|---|---|---|---|---|
| diethyl ether | ethyl *tert*-butyl ether | −180.64 | 175.05 | | |
| 1-pentene | methyl acetate | 1681.62 | 143.35 | −2.1512 | −0.4087 |
| propene | 2-propanol | 4735.90 | −1478.35 | −7.6444 | 3.7234 |

**Table 9. Pure Component Parameters:[a] Relative van der Waals Volumes $r_i$, Surfaces $q_i$, and Antoine Coefficients $A_i$, $B_i$, and $C_i$**

| component | $r_i$ | $q_i$ | $A_i$ | $B_i$/K | $C_i$/K |
|---|---|---|---|---|---|
| diethyl ether | 3.3949 | 3.016 | 6.35792[b] | 1241.81 | −22.158 |
| ethyl *tert*-butyl ether | 4.7422 | 4.172 | 5.80161[b] | 1066.84 | −64.910 |
| 1-pentene | 3.5953 | 3.104 | 6.47350[b] | 1337.32 | −3.782 |
| methyl acetate | 2.8042 | 2.576 | 6.19186[b] | 1157.63 | −53.424 |
| propene | 2.2465 | 2.024 | 6.19128[b] | 905.70 | −9.763 |
| 2-propanol | 2.7791 | 2.508 | 7.12798 | 1505.52 | −61.550 |

[a] DDB (1998). [b] Adjusted to the experimental data.

this apparatus was given by Fischer and Gmehling (1994). The experimental uncertainties are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa + 0.0001 ($P$/Pa), and $\sigma(x_i) = 0.0001$. The principle of measurement is the same for both devices. The thermostated, purified, and degassed compounds are filled into the thermostated equilibrium cell by means of precise piston injectors. In the case of the computer operated equipment, the injectors are driven by stepping motors. In the other case manual piston pumps (Model 2200-801, RUSKA) are used for injecting the compounds. When phase equilibrium is reached, the pressure in the equilibrium cell is measured with a pressure sensor (Model 245A, Paroscientific) and a dead weight pressure gage (Desgranges & Huot), respectively. For the temperature measurement a Pt100 resistance thermometer (Model 1506, Hart Scientific, Provo, UT) is used in both cases. The liquid phase compositions can be obtained from exactly known amounts of liquids injected into the cell by solving the mass and volume balance, taking into account the vapor−liquid equilibrium. In the case of all three systems ideal vapor phase behavior was assumed.

For the determination of the excess enthalpy data a commercial isothermal flow calorimeter (Model 7501, Hart) was used. The experimental setup has been described previously (Gmehling, 1993). With this type of calorimeter, the heat effects which occur during mixing are compensated for by means of a pulsed heater. A Peltier cooler allows one to control the required frequency of the pulsed heater so that also exothermic mixing effects can be measured. A back-pressure regulator serves to keep the pressure at a level at which evaporation effects can be prevented. The experimental uncertainties are as follows: $\sigma(T) = 0.03$ K, $\sigma(H^E) = 0.01$ ($H^E$/J mol$^{-1}$), $\sigma(x_i) = 0.0001$.

## Results

The experimental $P-x$ and $H^E$ data for the three binary systems are given in Table 2−7. For all three systems constant or linear temperature dependent parameters for the UNIQUAC model (Abrams and Prausnitz, 1975) were fitted simultaneously to the experimental VLE and $H^E$ data. The obtained parameters are listed in Table 8. The following expression was used to describe the temperature dependence of the interaction parameters:

$$\Delta u_{ij}\,/(\text{J mol}^{-1}) = a_{ij} + b_{ij}(T/\text{K}) \qquad (1)$$

The required van der Waals properties $r_i$ and $q_i$, and the Antoine coefficients $A_i$, $B_i$, and $C_i$ used in the calculations and expressed by the following equation are given in Table 9:

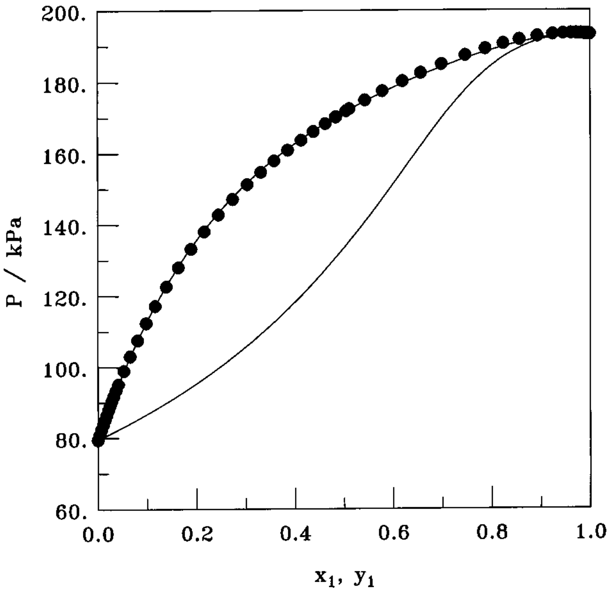

**Figure 3.** Experimental and predicted $P-x(y)$ behavior of the system 1-pentene (1) + methyl acetate (2) at 323.15 K: experimental (●); UNIQUAC (—).

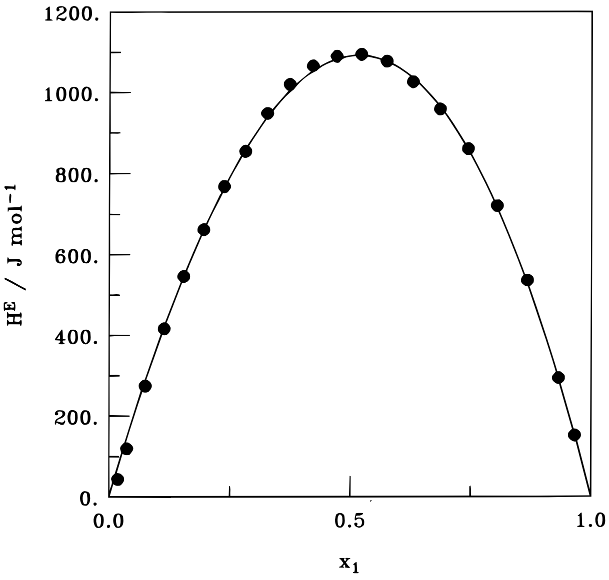

**Figure 4.** Experimental and predicted excess enthalpy data for the system 1-pentene (1) + methyl acetate (2) at 323.15 K: experimental (●); UNIQUAC (—).

$$\log(P_i^s/\text{kPa}) = A_i - \frac{B_i}{C_i + (T/\text{K})} \qquad (2)$$

The Antoine coefficients $A_i$ were adjusted to the experimental pure component vapor pressures $P_i^s$ in order to obtain a correct description of the experimental values. The deviations between experimental data and values calculated with the Antoine coefficients taken from the Dort-

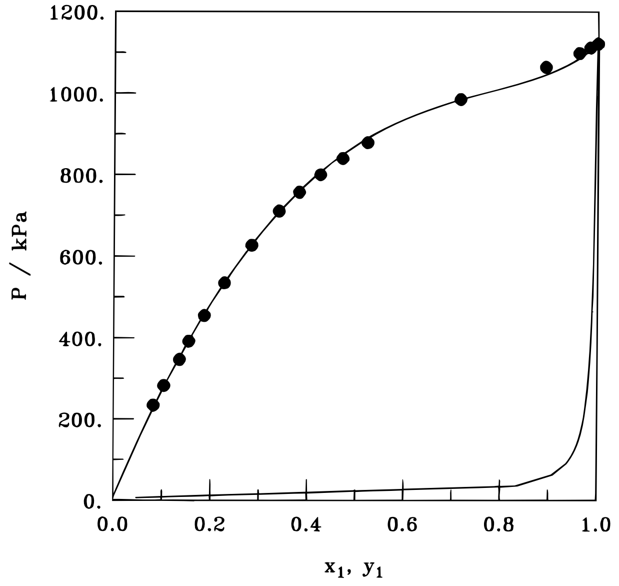

**Figure 5.** Experimental and predicted $P-x(y)$ behavior of the system propene (1) + 2-propanol (2) at 298.06 K: experimental (●); UNIQUAC (—).

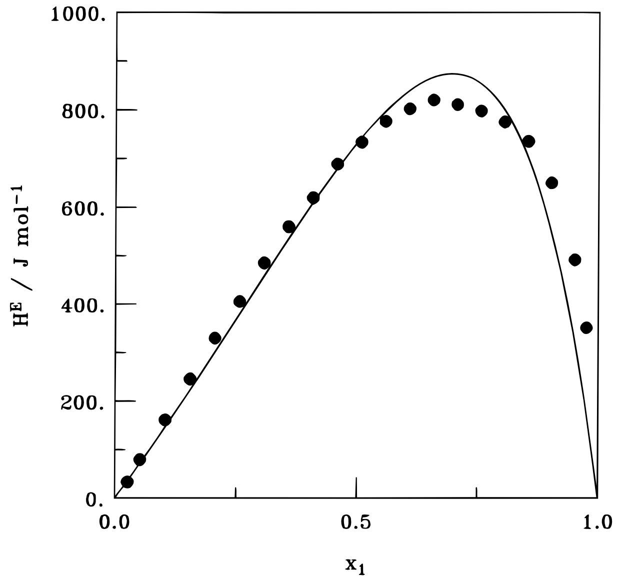

**Figure 6.** Experimental and predicted excess enthalpy data for the system propene (1) + 2-propanol (2) at 333.15 K: experimental (●); UNIQUAC (—).

mund Data Bank (DDB 1998) are smaller than 0.5% except for the system propene + 2-propanol. For 2-propanol, no experimental pure component vapor pressure was determined and the experimental value for propene is about 1.5% smaller than the calculated one.

A graphical representation of the experimental VLE and $H^E$ data is given in Figures 1−6 together with the results of the UNIQUAC model using the parameters given in Table 8. As can be seen from the different diagrams, good agreement is obtained between experimental and calculated results. The results from this work were compared with data from other authors. Figure 7 shows two isothermal $P-x$ data sets from Zabaloy et al. (1993) for the system propene + 2-propanol which were not included in the data regression and results predicted with the listed UNIQUAC parameters.

While for the system diethyl ether + ethyl *tert*-butyl ether nearly ideal VLE behavior and small excess enthalpy data are observed, the other systems (1-pentene + methyl acetate, propene + 2-propanol) show positive deviation from Raoults law. For the system 1-pentene + methyl acetate the azeotropic composition was derived graphically from the experimental $P-x$ data. It is given in Table 10 together with one value from literature.

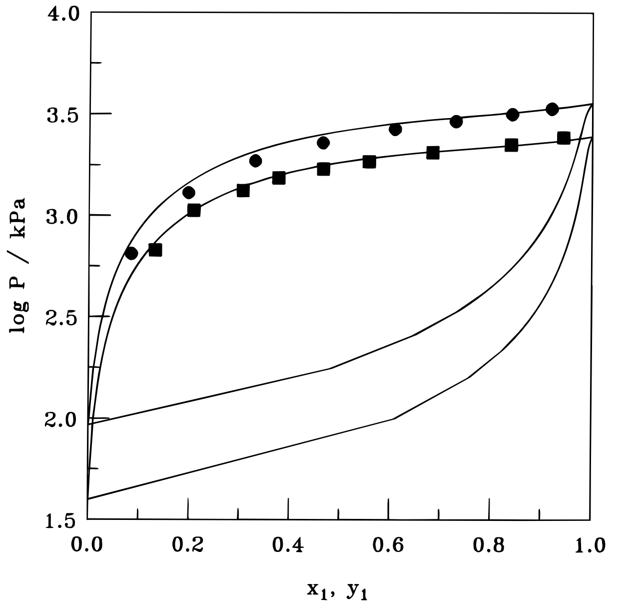

**Figure 7.** Experimental and predicted VLE behavior of the system propene (1) + 2-propanol (2); experimental data from Zabaloy et al. (1993): (■) 333.1 K, (●) 353.1 K; UNIQUAC (—).

**Table 10. Azeotropic Condition of the System 1-Pentene (1) + Methyl Acetate (2)**

| $T$/K | $y_{az,1}$ | $P_{az}$/kPa | source |
|---|---|---|---|
| 303.15 | 0.968 | 101.32 | Koch and van Raay (1954) |
| 323.15 | 0.965 | 193.55 | this work |

## Conclusions

$P-x$ and $H^E$ data for the three binary systems diethyl ether + ethyl *tert*-butyl ether, 1-pentene + methyl acetate, and propene + 2-propanol have been measured using the static technique and isothermal flow calorimetry, respectively. Constant or temperature-dependent UNIQUAC parameters have been fitted to the experimental data. With the help of these parameters good agreement is obtained with the experimental $P-x$ and $H^E$ data from this work and other authors.

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