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# Investigation on Isobaric Vapor−Liquid Equilibrium for 1-Butanol + Ethylbenzene + *o*-Xylene + *m*-Xylene + *p*-Xylene

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**ABSTRACT:** Isobaric binary vapor−liquid equilibrium (VLE) data for 1-butanol + ethylbenzene, or *o*-, or *m*-, or *p*-xylene and isobaric quinary VLE data for 1-butanol + ethylbenzene + *o*-xylene + *m*-xylene + *p*-xylene are measured at 101.33 kPa using a modified Rose cell with circulation of both phases. The four binary systems of 1-butanol + ethylbenzene, or *o*-, or *m*-, or *p*-xylene exhibit minimum boiling azeotropes, and the composition of the azeotropes are reported. The VLE data for the four binary systems are checked to meet rigorous thermodynamic consistency by Herington method and the point-to-point test of the Fredenslund method. The nonideality in vapor phase of the measured binary systems is analyzed through calculating fugacity coefficients. Combined with the Hayden−O'Connell (HOC) equation, the VLE data for 1-butanol + ethylbenzene, or *o*-, or *m*-, or *p*-xylene are well-correlated by the nonrandom two-liquid (NRTL), universal quasichemical activity coefficient (UNIQUAC), and Wilson equations. The NRTL model parameters obtained from correlation are used to predict the VLE data of the quinary system. According to the average absolute deviation values, the obtained quinary predicted values are in good agreement with the experimental values.

## INTRODUCTION

In the recovery of aromatics from oil fractions a mixture of $C_8$ benzene homologues is obtained which contains mainly *o*-xylene, *m*-xylene, *p*-xylene, and ethylbenzene. Ethylbenzene and xylene isomers are of great importance in the petrochemical industry, since these substances are the main basis for the manufacture of many organic compounds. The demand for every one of these compounds has grown very rapidly, recently, because ethylbenzene is the main raw material used for the synthesis of styrene, and xylene isomers are employed to obtain phthalic anhydride and phthalic acids. For example, *o*-xylene is mainly oxidized to phthalic anhydride which is used to synthesize plasticizers, *m*-xylene is made into isophthalic acid for use in polyesters, and *p*-xylene is converted to terephthalic acid or to dimethyl terephthalate as the first stage in the production of polyester. However, the production of individual components of very high purity from $C_8$ aromatic isomers by distillation is difficult due to the low relative volatilities among these compounds. For example, ethylbenzene can be separated from the remaining isomers by means of a column with more than 300 trays and a high reflux ratio.

As a common separating process, azeotropic distillation can be used in the separation of $C_8$ aromatic isomers. Several solvents,[1] such as 1-butanol, cyclopentanol, and methyl formate, have been reported as agents for the separation of $C_8$ aromatic isomers. It is known that accurate vapor−liquid equilibria (VLE) data are essential in the simulation and design of the distillation process. Unfortunately, there are few VLE data for binary systems of 1-butanol + ethylbenzene, or *o*-, or *m*-, or *p*-xylene in literature. Up to now, the isothermal VLE data[2−4] for the binary systems of 1-butanol + ethylbenzene, or *o*-, or *m*-, or *p*-xylene have been published. The $T-x_1-y_1$ isobaric VLE data for 1-butanol + ethylbenzene (95.8 kPa and 101.33 kPa)[5−7] and 1-butanol + *p*-xylene (97.3 kPa, 101.33 kPa, and 95.1 kPa)[8−10] have also been reported. However, for the binary system of 1-butanol + *m*-xylene, there is only one set of isobaric $T-x_1$ VLE data at 95 kPa and one set of isobaric $x_1-y_1$ VLE data at 99.99 kPa in literature,[11,12] and for the binary system of 1-butanol + *o*-xylene, there is only one set of isobaric $T-x_1$ VLE data at 95 kPa in literature.[13] These isobaric VLE data are obviously not sufficient for the design of the separation processes.

In this work, we use the system of 1-butanol + ethylbenzene as a checking system and determine VLE data at 101.33 kPa for the binary systems 1-butanol + *o*-xylene, 1-butanol + *m*-xylene, and 1-butanol + *p*-xylene and the quinary system 1-butanol + *o*-xylene + *m*-xylene + *p*-xylene + ethylbenzene. The experimental data for these binary systems are tested for thermodynamic consistency considering the nonideality of both phases and verifying their thermodynamic consistency. The Wilson,[14] nonrandom two-liquid (NRTL),[15] and universal quasichemical activity coefficient (UNIQUAC)[16] equations are used to correlate the experimental data of each binary mixture for their correlation parameters, then the obtained NRTL model parameters from binary VLE data are used to predict quinary VLE data of 1-butanol + *o*-xylenel + *m*-xylene + *p*-xylene + ethylbenzene. Meanwhile, we compare the experimental quinary VLE data with the predicted values. These experimental data may be used as basic data to develop the separation processes of mixed xylenes.

## EXPERIMENTAL SECTION

**Materials.** The chemicals used are 1-butanol, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene. 1-Butanol is supplied by Shanghai

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Table 1. Densities ($\rho$), Refractive Index ($n_D$), and Boiling Points of Pure Compounds Compared with Literature Data[18−20]

| | $\rho$/kg·m$^{-3}$ (293.15 K) | | $n_D$ (298.15 K) | | $T_b$/K (101.3 kPa) | |
|---|---|---|---|---|---|---|
| compound | expt. | lit. | expt. | lit. | expt. | lit. |
| 1-butanol | 809.50 | 810.00[a] | 1.3974 | 1.39741[b] | 390.85 | 390.90[a] |
| ethylbenzene | 866.54 | 867.00[a] | 1.5028 | 1.50295[c] | 409.27 | 409.30[a] |
| *o*-xylene | 879.68 | 880.00[a] | 1.4942 | 1.49464[c] | 417.58 | 417.60[a] |
| *m*-xylene | 864.11 | 864.00[a] | 1.4932 | 1.49325[c] | 412.27 | 412.30[a] |
| *p*-xylene | 861.21 | 861.00[a] | 1.4930 | 1.49320[c] | 411.51 | 411.50[a] |

[a] Reference 18. [b] Reference 19. [c] Reference 20.

Table 2. Experimental Vapor−Liquid Equilibrium Data, Activity Coefficients, $\gamma_i$, Gibbs Free Energies, $g^E$, and Fugacity Coefficients, $\check{\phi}_i^V$, for 1-Butanol (1) + Ethylbenzene (2) at 101.33 kPa

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $g^E$/J·mol$^{-1}$ | $\check{\phi}_1^V$ | $\check{\phi}_2^V$ |
|---|---|---|---|---|---|---|---|
| 390.70 | 0.9820 | 0.9763 | 0.9987 | 2.2430 | −240 | 0.9665 | 0.9513 |
| 390.30 | 0.9450 | 0.9283 | 1.0005 | 2.2411 | −536 | 0.9662 | 0.9511 |
| 389.79 | 0.8966 | 0.8662 | 1.0017 | 2.2509 | −799 | 0.9660 | 0.9509 |
| 389.49 | 0.8415 | 0.8159 | 1.0162 | 2.0334 | −1011 | 0.9658 | 0.9507 |
| 389.38 | 0.7992 | 0.7899 | 1.0401 | 1.8354 | −1134 | 0.9658 | 0.9507 |
| 389.28 | 0.7438 | 0.7410 | 1.0527 | 1.7747 | −1255 | 0.9657 | 0.9506 |
| 389.34 | 0.7031 | 0.7163 | 1.0748 | 1.6727 | −1322 | 0.9657 | 0.9507 |
| 389.49 | 0.6546 | 0.6965 | 1.1171 | 1.5302 | −1382 | 0.9658 | 0.9507 |
| 389.74 | 0.6033 | 0.6647 | 1.1475 | 1.4594 | −1424 | 0.9659 | 0.9509 |
| 390.05 | 0.5732 | 0.6468 | 1.1632 | 1.4150 | −1441 | 0.9661 | 0.9510 |
| 390.30 | 0.4911 | 0.6089 | 1.2682 | 1.3028 | −1450 | 0.9662 | 0.9511 |
| 390.81 | 0.4272 | 0.5764 | 1.3572 | 1.2339 | −1428 | 0.9665 | 0.9514 |
| 392.49 | 0.2862 | 0.4932 | 1.6834 | 1.0974 | −1283 | 0.9674 | 0.9521 |
| 394.27 | 0.2288 | 0.4561 | 1.7897 | 1.0622 | −1182 | 0.9683 | 0.9529 |
| 396.81 | 0.1637 | 0.3804 | 1.9224 | 1.0375 | −1020 | 0.9695 | 0.9541 |
| 399.62 | 0.1118 | 0.3033 | 2.0535 | 1.0155 | −839 | 0.9707 | 0.9552 |
| 402.83 | 0.0635 | 0.2167 | 2.3391 | 0.9920 | −599 | 0.9721 | 0.9565 |
| 404.97 | 0.0386 | 0.1472 | 2.4509 | 0.9935 | −431 | 0.9729 | 0.9574 |

Table 3. Experimental Vapor−Liquid Equilibrium Data, Activity Coefficients, $\gamma_i$, Gibbs Free Energies, $g^E$, and Fugacity Coefficients, $\check{\phi}_i^V$, for 1-Butanol (1) + *o*-Xylene (2) at 101.33 kPa

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $g^E$/J·mol$^{-1}$ | $\check{\phi}_1^V$ | $\check{\phi}_2^V$ |
|---|---|---|---|---|---|---|---|
| 390.41 | 0.9758 | 0.9677 | 1.0061 | 2.8879 | −288 | 0.9663 | 0.9492 |
| 390.37 | 0.9560 | 0.9489 | 1.0085 | 2.5132 | −440 | 0.9663 | 0.9492 |
| 390.31 | 0.9450 | 0.9398 | 1.0125 | 2.3718 | −511 | 0.9663 | 0.9492 |
| 390.25 | 0.9195 | 0.9109 | 1.0108 | 2.3990 | −653 | 0.9662 | 0.9491 |
| 390.19 | 0.8866 | 0.8791 | 1.0140 | 2.3111 | −802 | 0.9662 | 0.9491 |
| 390.09 | 0.8488 | 0.8480 | 1.0255 | 2.1823 | −940 | 0.9661 | 0.9491 |
| 390.05 | 0.8151 | 0.8276 | 1.0438 | 2.0245 | −1041 | 0.9661 | 0.9490 |
| 390.25 | 0.7571 | 0.7964 | 1.0744 | 1.8062 | −1180 | 0.9662 | 0.9491 |
| 390.35 | 0.6808 | 0.7587 | 1.1349 | 1.6212 | −1309 | 0.9663 | 0.9492 |
| 390.71 | 0.6453 | 0.7397 | 1.1534 | 1.5555 | −1354 | 0.9665 | 0.9494 |
| 391.21 | 0.5831 | 0.7155 | 1.2143 | 1.4234 | −1410 | 0.9667 | 0.9496 |
| 392.37 | 0.5303 | 0.6898 | 1.2381 | 1.3291 | −1442 | 0.9673 | 0.9502 |
| 393.70 | 0.4146 | 0.6357 | 1.3971 | 1.2015 | −1439 | 0.9680 | 0.9508 |
| 395.22 | 0.3388 | 0.5942 | 1.5206 | 1.1317 | −1388 | 0.9687 | 0.9515 |
| 397.11 | 0.2493 | 0.5311 | 1.7383 | 1.0882 | −1262 | 0.9696 | 0.9524 |
| 400.16 | 0.1777 | 0.4642 | 1.9347 | 1.0389 | −1097 | 0.9710 | 0.9537 |
| 405.31 | 0.1052 | 0.3426 | 2.0587 | 1.0130 | −839 | 0.9730 | 0.9559 |
| 412.78 | 0.0337 | 0.1449 | 2.1847 | 0.9978 | −404 | 0.9757 | 0.9587 |

Table 4. Experimental Vapor−Liquid Equilibrium Data, Activity Coefficients, $\gamma_i$, Gibbs Free Energies, $g^E$, and Fugacity Coefficients, $\check{\phi}_i^V$, for 1-Butanol (1) + *m*-Xylene (2) at 101.33 kPa

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $g^E$/J·mol$^{-1}$ | $\check{\phi}_1^V$ | $\check{\phi}_2^V$ |
|---|---|---|---|---|---|---|---|
| 390.32 | 0.9582 | 0.9467 | 1.0055 | 2.3882 | −433 | 0.9663 | 0.9505 |
| 390.18 | 0.9444 | 0.9276 | 1.0045 | 2.4465 | −526 | 0.9662 | 0.9505 |
| 390.01 | 0.9250 | 0.9058 | 1.0074 | 2.3690 | −638 | 0.9661 | 0.9504 |
| 389.82 | 0.8972 | 0.8734 | 1.0083 | 2.3321 | −777 | 0.9660 | 0.9503 |
| 389.70 | 0.8709 | 0.8498 | 1.0150 | 2.2085 | −881 | 0.9659 | 0.9502 |
| 389.59 | 0.8315 | 0.8220 | 1.0325 | 2.0091 | −1014 | 0.9659 | 0.9502 |
| 389.55 | 0.7716 | 0.7882 | 1.0688 | 1.7629 | −1169 | 0.9658 | 0.9501 |
| 389.63 | 0.7180 | 0.7435 | 1.0811 | 1.7216 | −1272 | 0.9659 | 0.9502 |
| 389.81 | 0.6597 | 0.7136 | 1.1229 | 1.5824 | −1352 | 0.9660 | 0.9503 |
| 390.09 | 0.6008 | 0.6854 | 1.1735 | 1.4678 | −1407 | 0.9661 | 0.9504 |
| 390.58 | 0.5376 | 0.6530 | 1.2295 | 1.3758 | −1439 | 0.9664 | 0.9506 |
| 391.21 | 0.4974 | 0.6515 | 1.2976 | 1.2478 | −1448 | 0.9667 | 0.9509 |
| 391.58 | 0.4787 | 0.6287 | 1.2854 | 1.2668 | −1448 | 0.9669 | 0.9511 |
| 392.75 | 0.3846 | 0.5968 | 1.4608 | 1.1249 | −1412 | 0.9675 | 0.9516 |
| 393.36 | 0.3112 | 0.5448 | 1.6166 | 1.1129 | −1336 | 0.9678 | 0.9519 |
| 394.63 | 0.2980 | 0.5336 | 1.5853 | 1.0783 | −1323 | 0.9685 | 0.9525 |
| 396.13 | 0.2405 | 0.4990 | 1.7495 | 1.0247 | −1227 | 0.9692 | 0.9532 |
| 398.57 | 0.1487 | 0.3884 | 2.0401 | 1.0393 | −984 | 0.9703 | 0.9542 |
| 407.08 | 0.0367 | 0.1460 | 2.3968 | 1.0146 | −418 | 0.9737 | 0.9577 |

Shenbo Chemical Co., Ltd., with a minimum mass fraction purity of 99.0 %. Ethylbenzene (AR grade, ≥ 98.5 % mass fraction) is purchased from Sinopharm Chemical Reagent Co., Ltd. The *o*-xylene (AR grade, ≥ 99.0 % mass fraction), *m*-xylene (AR grade, ≥ 99.0 % mass fraction), and *p*-xylene (AR grade, ≥ 99.0 % mass fraction) are bought from Aladdin Chemistry Co., Ltd. All of the solvents are dried over 0.4 nm molecular sieves and then distilled and degassed as described by Fischer and Gmehling.[17] The purity of the materials is checked by gas chromatography and found to be greater than 0.998 mass fraction. The density, refractive indices, and normal boiling points for the pure compounds are shown in the Table 1 along with their literature values.[18−20]

**Apparatus and Procedure.** In this work, isobaric VLE data are obtained in a modified Rose equilibrium still[21,22] with recirculation of both liquid and vapor phases. The equilibrium still and experimental procedure are described in detail in our previous work.[22] A given liquid solution is charged into the equilibrium still and heated in the boiler to boil with the help of electrical heating. The vapor is condensed in the condenser by the circulation of cooling water to form droplets which are collected in the vapor−phase sample reservoir. The condensed vapor mixes with the liquid phase coming from the liquid−phase

Table 5. Experimental Vapor−Liquid Equilibrium Data, Activity Coefficients, $\gamma_i$, Gibbs Free Energies, $g^E$, and Fugacity Coefficients, $\check{\phi}_i^V$, for 1-Butanol (1) + *p*-Xylene (2) at 101.33 kPa

| $T$ / K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $g^E$ / $J \cdot mol^{-1}$ | $\check{\phi}_1^V$ | $\check{\phi}_2^V$ |
|---|---|---|---|---|---|---|---|
| 390.70 | 0.9819 | 0.9738 | 0.9963 | 2.6230 | −235 | 0.9665 | 0.9514 |
| 390.37 | 0.9557 | 0.9434 | 1.0029 | 2.3340 | −449 | 0.9663 | 0.9513 |
| 390.15 | 0.9356 | 0.9163 | 1.0027 | 2.3864 | −575 | 0.9661 | 0.9511 |
| 389.98 | 0.9179 | 0.9005 | 1.0104 | 2.2346 | −671 | 0.9662 | 0.9512 |
| 389.34 | 0.8891 | 0.8717 | 1.0324 | 2.1708 | −800 | 0.9657 | 0.9508 |
| 389.13 | 0.8548 | 0.8374 | 1.0394 | 2.1108 | −927 | 0.9656 | 0.9507 |
| 388.94 | 0.8030 | 0.8009 | 1.0656 | 1.9125 | −1076 | 0.9655 | 0.9506 |
| 388.95 | 0.7733 | 0.7771 | 1.0736 | 1.8580 | −1145 | 0.9655 | 0.9506 |
| 388.98 | 0.7203 | 0.7439 | 1.1027 | 1.7261 | −1242 | 0.9655 | 0.9506 |
| 389.13 | 0.6580 | 0.7083 | 1.1440 | 1.5983 | −1322 | 0.9656 | 0.9507 |
| 389.18 | 0.5931 | 0.6738 | 1.2061 | 1.4979 | −1371 | 0.9656 | 0.9507 |
| 389.94 | 0.5108 | 0.6319 | 1.2804 | 1.3726 | −1404 | 0.9660 | 0.9511 |
| 390.72 | 0.4358 | 0.6006 | 1.3898 | 1.2607 | −1395 | 0.9665 | 0.9514 |
| 391.21 | 0.3826 | 0.5714 | 1.4821 | 1.2175 | −1367 | 0.9667 | 0.9517 |
| 393.68 | 0.2981 | 0.5315 | 1.6293 | 1.0886 | −1294 | 0.9680 | 0.9528 |
| 395.31 | 0.2292 | 0.4769 | 1.8036 | 1.0550 | −1182 | 0.9688 | 0.9535 |
| 397.41 | 0.1610 | 0.3939 | 1.9839 | 1.0566 | −1014 | 0.9698 | 0.9544 |
| 400.44 | 0.1211 | 0.3359 | 2.0431 | 1.0153 | −885 | 0.9711 | 0.9556 |
| 407.14 | 0.0386 | 0.1443 | 2.2480 | 0.9973 | −439 | 0.9737 | 0.9582 |

Table 6. Experimental VLE Data for the Quinary System of 1-Butanol (1) + *o*-Xylene (2) + *m*-Xylene (3) + *p*-Xylene (4) + Ethylbenzene (5) at 101.33 kPa

| $T$/K | $x_1$ | $x_2$ | $x_3$ | $x_4$ | $y_1$ | $y_2$ | $y_3$ | $y_4$ |
|---|---|---|---|---|---|---|---|---|
| 402.11 | 0.1382 | 0.1908 | 0.0462 | 0.0667 | 0.3674 | 0.1641 | 0.0389 | 0.0577 |
| 410.85 | 0.0079 | 0.5060 | 0.1132 | 0.0374 | 0.0331 | 0.5320 | 0.1172 | 0.0445 |
| 409.28 | 0.0189 | 0.0696 | 0.5618 | 0.2412 | 0.0845 | 0.0733 | 0.5191 | 0.2154 |
| 410.49 | 0.0090 | 0.0586 | 0.3979 | 0.4952 | 0.0457 | 0.0633 | 0.3847 | 0.4546 |
| 389.57 | 0.8893 | 0.0214 | 0.0357 | 0.0465 | 0.8568 | 0.0282 | 0.0458 | 0.0616 |
| 389.47 | 0.7836 | 0.0196 | 0.1018 | 0.0450 | 0.7775 | 0.0212 | 0.1117 | 0.0462 |
| 389.58 | 0.6867 | 0.0482 | 0.1881 | 0.0378 | 0.7183 | 0.0432 | 0.1772 | 0.0308 |
| 392.53 | 0.3281 | 0.4378 | 0.0415 | 0.0900 | 0.5330 | 0.3236 | 0.0301 | 0.0650 |
| 389.50 | 0.7011 | 0.0088 | 0.0394 | 0.2336 | 0.7390 | 0.0081 | 0.0354 | 0.2038 |
| 389.63 | 0.6671 | 0.0078 | 0.0665 | 0.2175 | 0.7241 | 0.0065 | 0.0548 | 0.1868 |
| 389.98 | 0.6090 | 0.0062 | 0.1148 | 0.2167 | 0.6951 | 0.0056 | 0.0914 | 0.1684 |
| 390.50 | 0.5468 | 0.0065 | 0.1609 | 0.2073 | 0.6731 | 0.0055 | 0.1190 | 0.1524 |
| 391.06 | 0.4921 | 0.0061 | 0.2039 | 0.1938 | 0.6381 | 0.0048 | 0.1511 | 0.1416 |
| 392.08 | 0.4124 | 0.0052 | 0.2627 | 0.1842 | 0.6107 | 0.0040 | 0.1813 | 0.1247 |
| 392.40 | 0.3830 | 0.0204 | 0.3210 | 0.1594 | 0.5841 | 0.0155 | 0.2235 | 0.1104 |
| 394.74 | 0.2599 | 0.0412 | 0.4232 | 0.1568 | 0.5108 | 0.0308 | 0.2869 | 0.1031 |
| 397.17 | 0.1799 | 0.0657 | 0.5051 | 0.1407 | 0.4413 | 0.0480 | 0.3515 | 0.0957 |
| 401.14 | 0.0999 | 0.0972 | 0.5837 | 0.1243 | 0.3163 | 0.0807 | 0.4407 | 0.0883 |
| 404.74 | 0.0352 | 0.7944 | 0.0913 | 0.0397 | 0.1505 | 0.7115 | 0.0773 | 0.0326 |
| 399.86 | 0.0923 | 0.7302 | 0.0831 | 0.0357 | 0.2820 | 0.5881 | 0.0640 | 0.0268 |
| 397.52 | 0.1331 | 0.6687 | 0.0768 | 0.0641 | 0.3785 | 0.4921 | 0.0536 | 0.0428 |
| 395.57 | 0.1848 | 0.6065 | 0.0698 | 0.0597 | 0.4417 | 0.4294 | 0.0464 | 0.0384 |

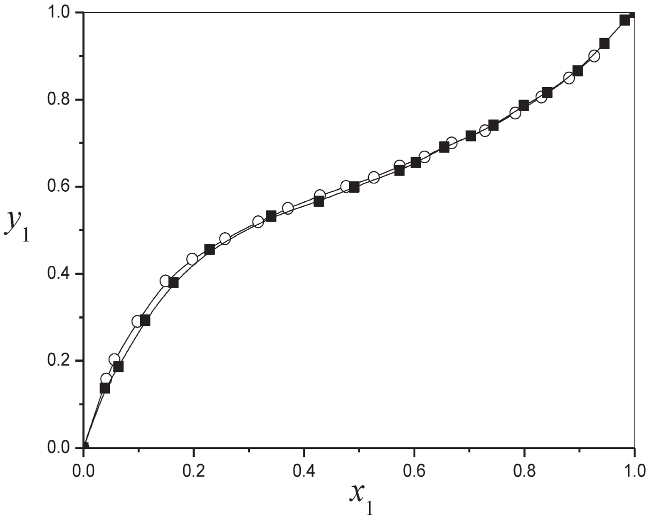

**Figure 1.** Comparison between experimental data and literature data for the 1-butanol (1) + ethylbenzene (2) system at 101.33 kPa: ■, experimental data; ○, ref 6.

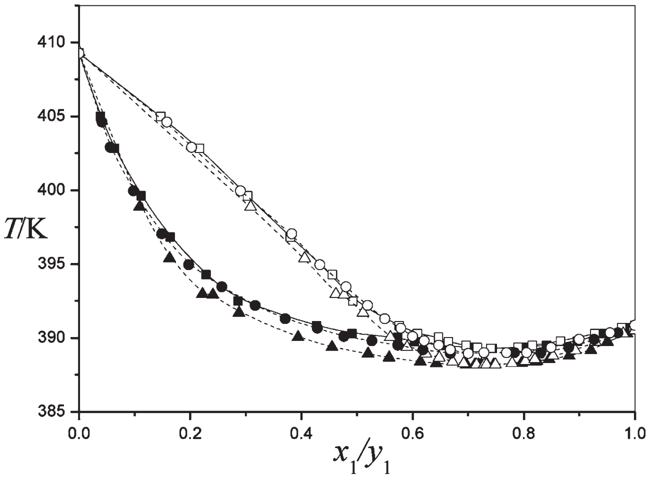

**Figure 2.** Comparison between experimental data and literature data of the 1-butanol (1) + ethylbenzene (2) system at 101.33 kPa: ■, $T-x_1$ and □, $T-y_1$, this work; ●, $T-x_1$ and ○, $T-y_1$, ref 6; ▲, $T-x_1$ and △, $T-y_1$, ref 7.

sample reservoir in the vapor−liquid phases mixing chamber, and then the mixed solution is returned to the boiler for recirculation. It takes approximately 2 h for the circulation in a Rose cell to achieve VLE when temperature is kept constant. Samples of the equilibrium phases are taken out from the vapor and liquid sampling port and analyzed, respectively.

The temperature is measured with the help of a standard mercury thermometer, and the error of temperature measurement is less than 0.1 K. The pressure is established and kept at (101.33 ± 0.04) kPa by using a pressure control system reported in detail in our previous work.[21]

**Sample Analysis.** Compositions of samples of the equilibrium phases are analyzed using a gas chromatograph (GC) SP6890A with a flame ionization detector (FID) produced by Shandong Lunan Ruihong Chemical Instruments Co., Ltd. The response is treated with a dual-channel chromatography workstation N-2000 which is supplied by Zhejiang Zhida Information Engineering Co., Ltd. The GC is calibrated with a set of gravimetrically prepared standard solutions. The relationship between the peak

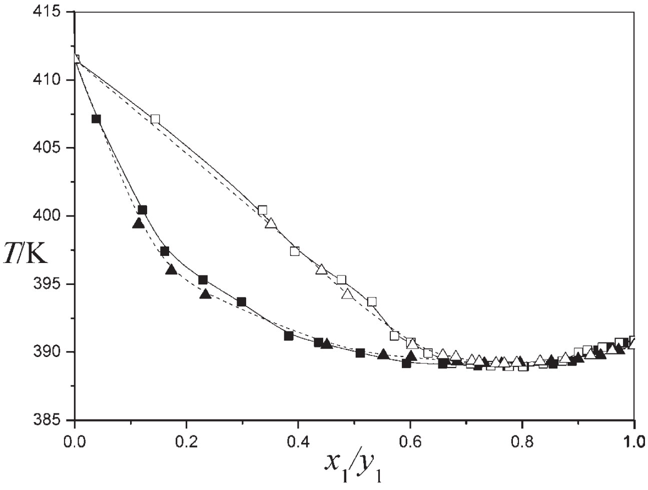

**Figure 3.** Comparison between experimental data and literature data of the 1-butanol (1) + *p*-xylene (2) system at 101.33 kPa: ■, $T-x_1$ and □, $T-y_1$, this work; ▲, $T-x_1$ and △, $T-y_1$, ref 9.

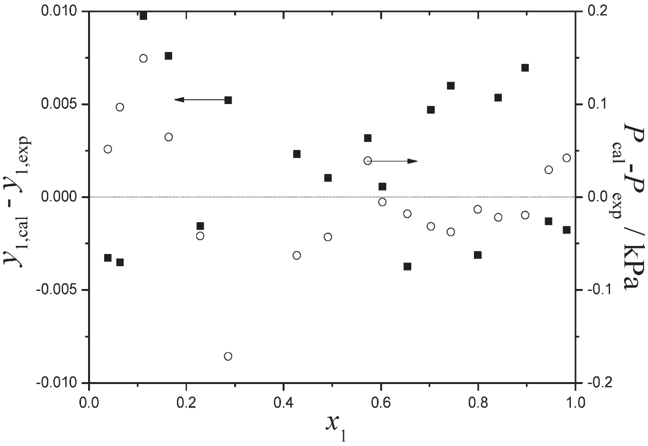

**Figure 4.** Result of thermodynamic consistency test for VLE data of the 1-butanol (1) + ethylbenzene (2) system using the Fredenslund method. ■, $y_{1,cal}-y_{1,exp}$; ○, $P_{cal}-P_{exp}$.

area and the composition is determined for each mixture. The GC column is a B-34 capillary column (30 m × 0.25 mm × 0.3 $\mu$m). The carrier gas is nitrogen with a purity of 99.999 % and a flow rate of 30 $cm^3$ $min^{-1}$. The oven temperature is kept at 363 K. Both the injector and the detector temperatures are 433 K. The retention times of 1-butanol, ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene are 5.065 min, 8.415 min, 8.707 min, 9.148 min, and 9.615 min, respectively. The uncertainty of the equilibrium mixture composition is 0.001 mole fraction.

## ■ RESULTS AND DISCUSSION

**Experimental Data.** The VLE data for the four binary systems of 1-butanol + ethylbenzene, 1-butanol + *o*-xylene, 1-butanol + *m*-xylene, and 1-butanol + *p*-xylene are measured at 101.33 kPa. The VLE data for the four binary systems are reported in Tables 2 to 5, together with activity coefficients, $\gamma_i$, excess free energies, $g^E$, and fugacity coefficients, $\check{\phi}_i^V$. The VLE data for the quinary system 1-butanol + *o*-xylene + *m*-xylene + *p*-xylene + ethylbenzene are obtained at 101.33 kPa, too, and the results are listed in Table 6.

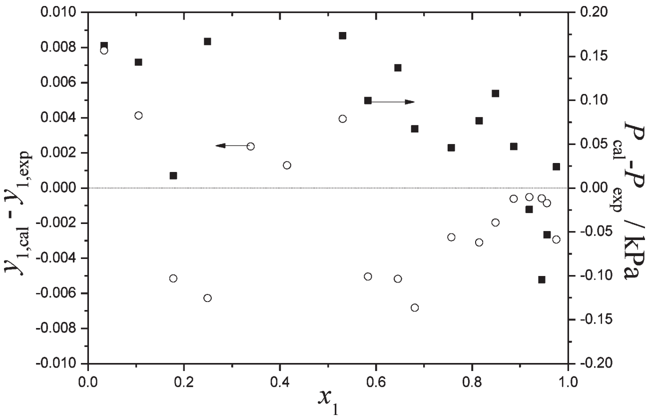

**Figure 5.** Result of thermodynamic consistency test for VLE data of the 1-butanol (1) + *o*-xylene (2) system using the Fredenslund method. ■, $y_{1,cal}-y_{1,exp}$; ○, $P_{cal}-P_{exp}$.

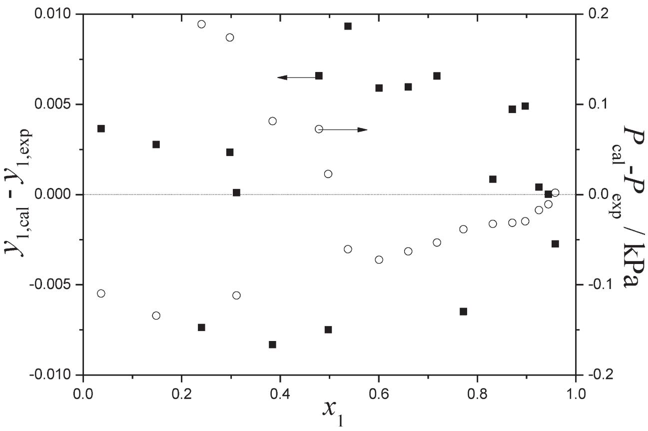

**Figure 6.** Result of thermodynamic consistency test for VLE data of the 1-butanol (1) + *m*-xylene (2) system using the Fredenslund method. ■, $y_{1,cal}-y_{1,exp}$; ○, $P_{cal}-P_{exp}$.

To test the suitability of the equilibria apparatus and experimental procedure, VLE data of 1-butanol + ethylbenzene system are compared with the experimental data presented in the literature.[6] It is found that the experimental data of this work agree well with the published data as can be seen in Figure 1, which illustrates that the recirculating still of modified Rose type and experimental procedure we used are considered satisfactory. Figures 2 and 3 show the comparisons between our experimental data and the literature data of the binary systems of 1-butanol + ethylbenzene and 1-butanol + *p*-xylene.

The experimental data of the binary systems have been tested for thermodynamic consistency by means of the Herington method.[23] According to this method, the necessary condition for experimental data consistency is that the check result $D-J$ is less than 10

$$D = \left| \frac{(\text{area}+) - (\text{area}-)}{(\text{area}+) + (\text{area}-)} \right| \cdot 100 \qquad (1)$$

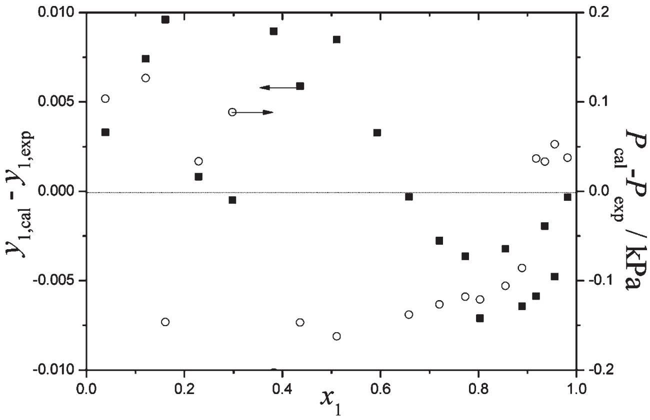

**Figure 7.** Result of thermodynamic consistency test for VLE data of the 1-butanol (1) + *p*-xylene (2) system using the Fredenslund method. ■, $y_{1,\mathrm{cal}}-y_{1,\mathrm{exp}}$; ○, $P_{\mathrm{cal}}-P_{\mathrm{exp}}$.

**Table 7. Experimental Compositions, $x_{1,\mathrm{az}}$, and Boiling Temperatures of the Azeotropic Mixtures, $T_{\mathrm{az}}$, together with Azeotropic Information Given by Literature at 101.33 kPa**

| | $x_{1,\mathrm{az}}$ | | $T_{\mathrm{az}}$/K | |
|---|---|---|---|---|
| system | exptl | lit. | exptl | lit. |
| 1-butanol + ethylbenzene | 0.7221 | 0.7285[a] | 389.26 | 389.00[a] |
| 1-butanol + *o*-xylene | 0.8328 | 0.8280[b] | 390.13 | 390.25[b] |
| 1-butanol + *m*-xylene | 0.7999 | 0.7820[b] | 389.53 | 389.65[b] |
| 1-butanol + *p*-xylene | 0.7779 | 0.7650[c] | 388.93 | 389.15[c] |

[a] Reference 6. [b] Reference 25. [c] Reference 9.

**Table 8. Antoine Equation $[\log p_i^{\mathrm{S}}/\mathrm{kPa} = (A - B)/(C + t/°\mathrm{C})]$ and Parameters[18]**

| compound | A | B | C |
|---|---|---|---|
| 1-butanol | 6.60172 | 1362.390 | 178.720 |
| ethylbenzene | 6.08208 | 1424.255 | 213.060 |
| *o*-xylene | 6.12381 | 1474.679 | 213.686 |
| *m*-xylene | 6.13398 | 1462.266 | 215.105 |
| *p*-xylene | 6.11542 | 1453.430 | 215.307 |

where the values of "area +" and "area−" are from the $\ln(\gamma_1/\gamma_2)-x_1$ diagram.

$$J = 150\frac{(T_{\max} - T_{\min})}{T_{\min}} \tag{2}$$

where $T_{\max}$ and $T_{\min}$ are the maximum and minimum temperatures of each binary system, respectively. For our measured binary systems, $T_{\min}$ is the lowest azeotropic temperature.

In this work, the check result $D-J$ for 1-butanol + ethylbenzene, 1-butanol + *o*-xylene, 1-butanol + *m*-xylene, and 1-butanol + *p*-xylene systems are −4.18, −3.49, −6.41, and −3.99, respectively, indicating that the VLE results for the four systems are thermodynamically consistent.

To reconfirm the validity of experimental data, the point-to-point test of Fredenslund method[24] is also used. According to this test, the molar fractions of vapor phase and total pressure for each data point are calculated. The absolute deviation between measured and calculated values of $y_i$ and $P$ for the four binary systems are shown in Figures 4 to 7. From Figures 4 to 7, we can see that the absolute deviations between $y_{1,\mathrm{exp}}$ and $y_{1,\mathrm{cal}}$ are all smaller than 0.01 and between $P_{\mathrm{exp}}$ and $P_{\mathrm{cal}}$ are all less than 10 mmHg for these systems. The results indicate that the VLE results for the four systems are thermodynamically consistent.

**Table 9. Properties of the Pure Compounds Used in Calculating Fugacity Coefficients[a]**

| | 1-butanol | ethylbenzene | *o*-xylene | *m*-xylene | *p*-xylene |
|---|---|---|---|---|---|
| $T_{\mathrm{c}}{}^{b}$/K | 562.9 | 617.1 | 630.2 | 617.0 | 616.2 |
| $P_{\mathrm{c}}{}^{b}$/MPa | 4.418 | 3.607 | 3.729 | 3.546 | 3.516 |
| $V_{\mathrm{c}}{}^{b}$/cm$^3$·mol$^{-1}$ | 274.0 | 374.0 | 369.0 | 376.0 | 379.0 |
| $Z_{\mathrm{c}}{}^{b}$ | 0.259 | 0.263 | 0.263 | 0.260 | 0.260 |
| $r^{c}$ | 3.45 | 4.60 | 4.66 | 4.66 | 4.66 |
| $q^{c}$ | 3.05 | 3.51 | 3.54 | 3.54 | 3.54 |
| $\mu^{b}$/D | 1.8 | 0.4 | 1.5 | 0.3 | 0.1 |
| $\omega^{b}$ | 0.590 | 0.301 | 0.314 | 0.331 | 0.324 |
| $R_{\mathrm{D}}{}^{c}$/Å | 3.225 | 3.821 | 3.789 | 3.897 | 3.796 |

[a] Critical temperature $T_{\mathrm{c}}$, critical pressure $P_{\mathrm{c}}$, critical volume $V_{\mathrm{c}}$, critical compressibility factor $Z_{\mathrm{c}}$, structure volume parameter for the UNIQUAC equation $r$, structure area parameter for the UNIQUAC equation $q$, dipole moment $\mu$, acentric factor $\omega$, mean gyration radius $R_{\mathrm{D}}$. [b] Reference 18. [c] Reference 28.

The experimental VLE data for the four binary systems show minimum boiling point azeotropes. The azeotropic points are determined from $y_1-x_1$ versus $x_1$ diagrams to determine $x_{1,\mathrm{az}}$ at $y_1-x_1 = 0$ and $T$ versus $x_1$ diagrams where $T_{\mathrm{az}}$ should be minimum at $x_{1,\mathrm{az}}$. The composition and boiling temperature of the azeotropes are summarized in Table 7, together with azeotropic information given in literature.[6,9,25] It can be seen that the composition and boiling temperature of the azeotropes obtained experimentally are close to literature data, which indicates that the experimental binary VLE data are reliable.

**Vapor−Liquid Equilibria Model.** The liquid-phase activity coefficients of the components in the mixtures are calculated from the experimental data taking into consideration the nonideality of the vapor phase using the VLE equation expressed as follows:[26]

$$\check{\phi}_i^{\mathrm{V}} p y_i = \gamma_i x_i p_i^{\mathrm{S}} \varphi_i^{\mathrm{S}} \exp\left[\frac{V_i^{\mathrm{L}}(p - p_i^{\mathrm{S}})}{RT}\right] \tag{3}$$

where $x_i$ and $y_i$ are the mole fraction of component $i$ in the liquid phase and vapor phases, respectively, $\check{\phi}_i^{\mathrm{V}}$ is the fugacity coefficient of component $i$ in the mixture vapor phase, $\phi_i^{\mathrm{S}}$ is the fugacity coefficient of component $i$ of the pure vapor at saturation, $V_i^{\mathrm{L}}$ is the liquid molar volume of pure component $i$, $\gamma_i$ is the activity coefficient of component $i$, $T$ is the system temperature, and $P$ and $p_i^{\mathrm{S}}$ are the total pressure and the saturated vapor pressure of pure component $i$ at system temperature $T$, respectively. The vapor pressures are calculated from the equation given in Table 8.[18]

At low or moderate pressure, $\exp[(V_i^{\mathrm{L}}(p - p_i^{\mathrm{S}})/RT)]$ is close to 1, so eq 3 can be simplified to

$$\check{\phi}_i^{\mathrm{V}} p y_i = \gamma_i x_i p_i^{\mathrm{S}} \varphi_i^{\mathrm{S}} \tag{4}$$

Meanwhile, the vapor-phase fugacity coefficients for system are calculated from a virial equation with the second virial

Table 10. Correlation Parameters and the Average Absolute Deviations for Binary Systems

| | model parameters | | | average absolute deviation | |
|---|---|---|---|---|---|
| model | $A_{12}$/K | $A_{21}$/K | $\alpha_{12}$ | $\Delta y_1$[a] | $\Delta T$[b]/K |
| | 1-Butanol (1) + Ethylbenzene (2) | | | | |
| NRTL[c] | −718.97 | 1931.57 | 0.30 | 0.0040 | 0.14 |
| Wilson[c] | −1608.41 | 109.33 | | 0.0042 | 0.16 |
| UNIQUAC[c] | 350.25 | −847.01 | | 0.0042 | 0.14 |
| | 1-Butanol (1) + *o*-Xylene (2) | | | | |
| NRTL | 301.56 | 131.04 | 0.30 | 0.0052 | 0.22 |
| Wilson | −174.33 | −284.94 | | 0.0053 | 0.22 |
| UNIQUAC | −36.73 | −69.96 | | 0.0052 | 0.22 |
| | 1-Butanol (1) + *m*-Xylene (2) | | | | |
| NRTL | 318.46 | 71.88 | 0.30 | 0.0045 | 0.22 |
| Wilson | −224.38 | −226.79 | | 0.0049 | 0.20 |
| UNIQUAC | 14.98 | −126.45 | | 0.0046 | 0.22 |
| | 1-Butanol (1) + *p*-Xylene (2) | | | | |
| NRTL | −475.97 | 1908.39 | 0.30 | 0.0045 | 0.33 |
| Wilson | −1524.21 | −114.64 | | 0.0044 | 0.35 |
| UNIQUAC | 299.09 | −902.46 | | 0.0044 | 0.33 |
| | Ethylbenzene (1) + *p*-Xylene (2)[d] | | | | |
| NRTL | 55.54 | −41.25 | 0.30 | | |
| | Ethylbenzene (1) + *m*-Xylene (2)[d] | | | | |
| NRTL | 57.38 | −42.26 | 0.30 | | |
| | Ethylbenzene (1) + *o*-Xylene (2)[d] | | | | |
| NRTL | 58.76 | −43.09 | 0.30 | | |
| | *p*-Xylene (1) + *m*-Xylene (2)[e] | | | | |
| NRTL | 15.37 | −16.06 | 0.30 | 0.0009 | |
| | *p*-Xylene (1) + *o*-Xylene (2)[e] | | | | |
| NRTL | −37.98 | 47.52 | 0.30 | 0.0085 | |
| | *m*-Xylene (1) + *o*-Xylene (2)[e] | | | | |
| NRTL | −19.15 | 19.28 | 0.30 | 0.0076 | |

[a] $\Delta y = (1/N)\Sigma|y_{\text{cal}} - y_{\text{exp}}|$; $N$: number of data points; $y_{\text{cal}}$: calculated vapor-phase mole fraction from the model; $y_{\text{exp}}$: experimental vapor-phase mole fraction. [b] $\Delta T = (1/N)\Sigma|T_{\text{cal}} - T_{\text{exp}}|$; $N$: number of data points; $T_{\text{cal}}$: calculated bubbling-point temperature from the model, K; $T_{\text{exp}}$: experimental boiling point temperature, K. [c] Wilson: $A_{12} = (\lambda_{12} - \lambda_{11})/R$, $A_{21} = (\lambda_{21} - \lambda_{22})/R$; NRTL: $A_{12} = (g_{12} - g_{22})/R$, $A_{21} = (g_{21} - g_{11})/R$; UNIQUAC: $A_{12} = (U_{12} - U_{22})/R$, $A_{21} = (U_{21} - U_{11})/R$. [d] Reference 25. [e] Reference 26.

coefficient, which is given by

$$\ln \check{\phi}_i = \frac{p}{RT}\left[2 \sum_{j=1}^{N} (y_j B_{ij} - B_m)\right] \tag{5}$$

where

$$B_m = \sum_{i=1}^{N} \sum_{j=1}^{N} y_i y_j B_{ij} \tag{6}$$

where $B_{ii}$ and $B_{jj}$ are the second virial coefficients of the pure components and $B_{ij}$ is the cross second virial coefficient. The Hayden−O'Connell (HOC) equation[27] is used for the estimation

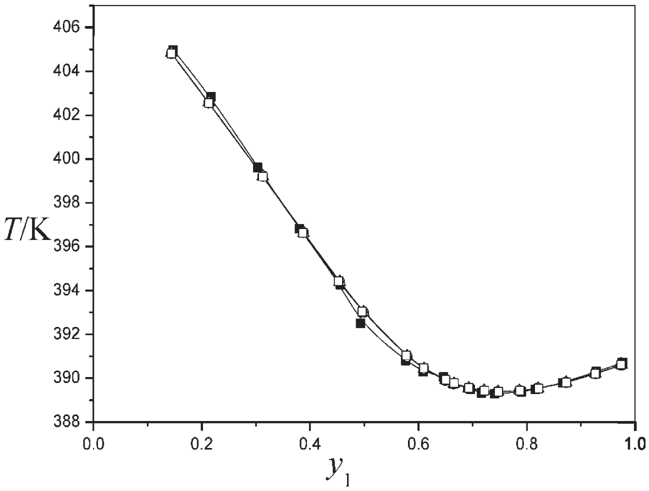

**Figure 8.** Experimental and calculated $T-y_1$ diagram for 1-butanol (1) + ethylbenzene (2) at 101.33 kPa: ■, $T-y_1$ experimental; ○, $T-y_1$ calculated (calculation based on the NRTL model); △, $T-y_1$ calculated (calculation based on the UNIQUAC model); □, $T-y_1$ calculated (calculation based on the Wilson model).

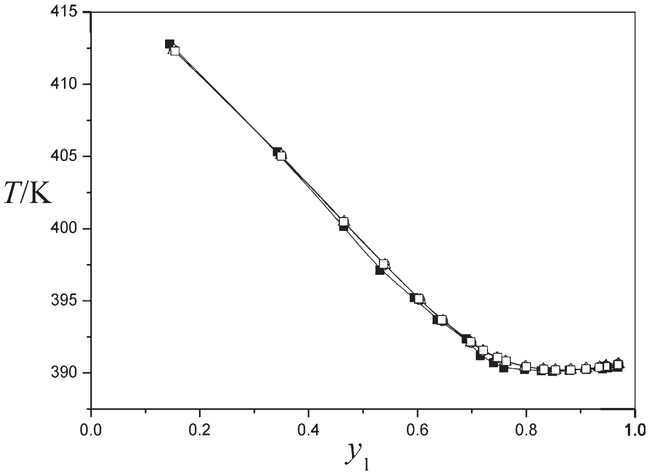

**Figure 9.** Experimental and calculated $T-y_1$ diagram for 1-butanol (1) + *o*-xylene (2) at 101.33 kPa: ■, $T-y_1$ experimental; ○, $T-y_1$ calculated-(calculation based on the NRTL model); △, $T-y_1$ calculated (calculation based on the UNIQUAC model); □, $T-y_1$ calculated (calculation based on the Wilson model).

of second virial coefficients. The physical properties of the pure components required in this calculation are given in Table 9.[18,28] The calculated fugacity coefficients are summarized in Tables 2 to 5.

The liquid-phase activity coefficients of the four binary systems are calculated by using the Wilson, NRTL, and UNIQUAC equations. The calculated $\gamma_i$ are reported in Tables 2 to 5. It can be seen that all of the binary systems present positive deviations from ideality. Meanwhile, the Gibbs free energies are also calculated from activity coefficients, and their values are all negative in the overall range of mole fraction for these binary systems. The absolute value of $g^{\text{E}}$ is maximized at an equimolar fraction in four binary systems.

**Correlation of Binary Vapor−Liquid Equilibrium.** During the simulation of distillation separation for the system of $C_8$

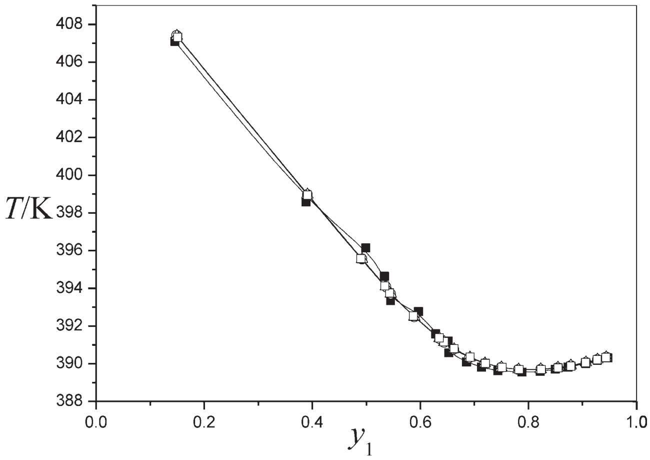

**Figure 10.** Experimental and calculated $T-y_1$ diagram for 1-butanol (1) + *m*-xylene (2) at 101.33 kPa: ■, $T-y_1$ experimental; ○, $T-y_1$ calculated (calculation based on the NRTL model); △, $T-y_1$ calculated (calculation based on the UNIQUAC model); □, $T-y_1$ calculated (calculation based on the Wilson model).

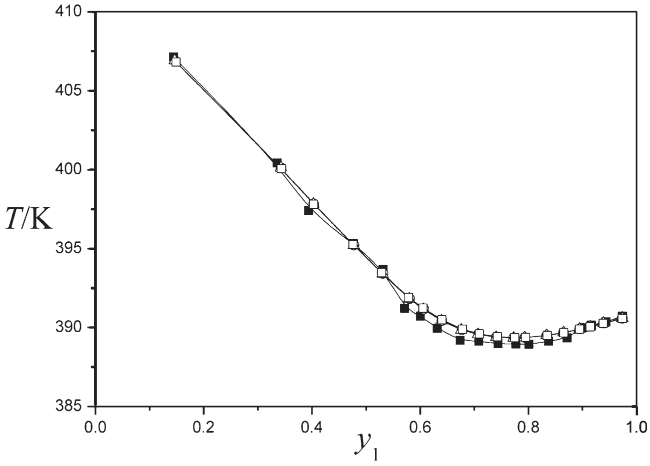

**Figure 11.** Experimental and calculated $T-y_1$ diagram for 1-butanol (1) + *p*-xylene (2) at 101.33 kPa: ■, $T-y_1$ experimental; ○, $T-y_1$ calculated (calculation based on the NRTL model); △, $T-y_1$ calculated (calculation based on the UNIQUAC model); □, $T-y_1$ calculated (calculation based on the Wilson model).

aromatic hydrocarbon isomers + 1-butanol, it is critical to obtain the model parameters of related binary systems. Among these systems, model parameters of 1-butanol + ethylbenzene, 1-butanol + *o*-xylene, 1-butanol + *m*-xylene, and 1-butanol + *p*-xylene systems are correlated from measured VLE data by the minimization of the objective function *F*, while model parameters of ethylbenzene + *p*-xylene, ethylbenzene + *m*-xylene, ethylbenzene + *o*-xylene, *p*-xylene + *m*-xylene, *p*-xylene + *o*-xylene, and *m*-xylene + *o*-xylene systems shown in Table 10 are taken from literature.[29,30] The objective function *F* used in this work can be expressed as:[31]

$$F = \sum_{k=1}^{N} \{(\gamma_1^{\text{exp}} - \gamma_1^{\text{cal}})_k^2 + (\gamma_2^{\text{exp}} - \gamma_2^{\text{cal}})_k^2\} \tag{7}$$

where $\gamma$ is the activity coefficient and *N* denotes the number of experimental data.

**Table 11. Predicted Deviations for the Quinary System**

| $\Delta T$/K | $\Delta y_1$ | $\Delta y_2$ | $\Delta y_3$ | $\Delta y_4$ |
|---|---|---|---|---|
| −0.57 | 0.0221 | −0.0024 | −0.0025 | −0.0067 |
| −0.06 | 0.0049 | −0.0015 | −0.0047 | −0.0082 |
| −0.03 | 0.0054 | −0.0019 | 0.0102 | 0.0067 |
| −0.01 | 0.0006 | −0.0011 | 0.0022 | 0.0171 |
| 0.12 | 0.0085 | −0.0016 | −0.0020 | −0.0053 |
| 0.09 | 0.0129 | −0.0009 | −0.0099 | −0.0019 |
| 0.05 | 0.0119 | 0.0011 | −0.0125 | 0.0017 |
| 0.03 | 0.0157 | −0.0127 | −0.0023 | −0.0062 |
| 0.12 | 0.0005 | 0.0002 | −0.0003 | 0.0008 |
| 0.18 | 0.0020 | 0.0005 | 0.0017 | −0.0051 |
| 0.12 | 0.0052 | −0.0003 | −0.0001 | 0.0005 |
| 0.08 | 0.0019 | −0.0003 | 0.0012 | −0.0007 |
| 0.04 | 0.0148 | −0.0001 | −0.0049 | −0.0057 |
| −0.01 | 0.0064 | −0.0001 | −0.0006 | −0.0009 |
| −0.06 | 0.0144 | −0.0004 | −0.0052 | −0.0046 |
| −0.05 | 0.0071 | −0.0005 | −0.0019 | −0.0002 |
| −0.01 | −0.0005 | 0.0020 | 0.0008 | −0.0001 |
| 0.06 | 0.0046 | 0.0002 | 0.0049 | 0.0042 |
| 0.24 | 0.0007 | −0.0024 | 0.0008 | 0.0007 |
| 0.28 | 0.0172 | −0.0123 | −0.0015 | −0.0005 |
| 0.29 | −0.0099 | 0.0075 | 0.0009 | 0.0016 |
| 0.24 | −0.0088 | 0.0072 | 0.0012 | 0.0013 |

The correlation deviations between the experimental and the calculated values of the vapor-phase composition and equilibrium temperature for each data point are shown in Figures 8 to 11. The fitted model parameters $A_{12}$ and $A_{21}$ along with the average absolute deviations of equilibrium temperature and vapor-phase mole fraction are given in Table 10.

As seen from Figures 8 to 11, the experimental data agree well with data calculated with NRTL, Wilson, or UNIQUAC models. Meanwhile, from Table 10, it can be observed that the three models show a good performance on correlating the activity coefficients for measured systems.

**Prediction of Quinary Vapor−Liquid Equilibrium.** The NRTL model parameters obtained from the binary systems in Table 10 are used to predict the VLE data for the quinary system of 1-butanol + *o*-xylene + *m*-xylene + *p*-xylene + ethylbenzene. The predictive deviations of equilibrium temperatures and vapor-phase compositions for each compound under different temperatures are given in Table 11. From Table 11, it can be deduced that the average absolute deviation (AAD) of the vapor-phase mole fractions of 1-butanol, ethylbenzene, *p*-xylene, and *m*-xylene are 0.0100, 0.0045, 0.0047, and 0.0053 for the quinary system, individually, and the AAD of the equilibrium temperature is 0.18 K. The maximum deviation of the equilibrium temperature is −0.57 K, and the maximum deviations of the vapor-phase mole fractions of 1-butanol, ethylbenzene, *p*-xylene, and *m*-xylene are 0.0221, −0.0127, −0.0125, and 0.0171, respectively. Consequently, from the AAD and maximum deviations, we can conclude that the NRTL model gives a good representation of the experimental data.

## ■ CONCLUSIONS

The isobaric VLE data of 1-butanol + ethylbenzene, 1-butanol + *o*-xylene, 1-butanol + *m*-xylene, 1-butanol + *p*-xylene, and 1-butanol +

*o*-xylene + *m*-xylene + *p*-xylene + ethylbenzene are obtained at 101.33 kPa. The VLE data of all of the measured binary sytems satisfy thermodynamic consistency as validated conducting with the Herington method and Fredenslund method, individually. The four binary systems of 1-butanol + ethylbenzene or *o*-, *m*-, or *p*-xylene present minimum temperature azeotropes. The nonideal behavior of binary systems in the vapor phase is analyzed through calculating fugacity coefficients. The obtained experimental data of binary systems are correlated using the NRTL, Wilson, and UNIQUAC models, respectively. The results show that the correlated deviations of Wilson, NRTL, and UNIQUAC equations are reasonably small, which indicates that the three activity coefficient models are all suitable for correlating the VLE of the measured binary systems. Moreover, the interaction parameters of the three models are obtained from correlation, and the interaction parameters of NRTL model obtained from correlation are employed to predict the VLE data for the quinary system of 1-butanol + *o*-xylene + *m*-xylene + *p*-xylene + ethylbenzene. The predicted values agree well with experimental data, which indicates that the NRTL model is suitable for correlating the VLE of the experimental binary systems. Therefore, the NRTL interaction parameters can represent the VLE for quinary system.

## AUTHOR INFORMATION

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