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# Isothermal Vapor−Liquid Equilibria for Binary Mixtures Composed of the Closely Boiling Compounds 1,2-Dimethoxybenzene and 2-Methoxyphenol with an Adducted Agent: *tert*-Butanol or Morpholine

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Isothermal vapor−liquid equilibrium (VLE) data were measured, with a static-type apparatus, for binary systems of 1,2-dimethoxybenzene + 2-methoxyphenol, 1,2-dimethoxybenzene + *tert*-butanol, 2-methoxyphenol + *tert*-butanol, 1,2-dimethoxybenzene + morpholine, and 2-methoxyphenol + morpholine in the temperature range 333.15 K to 443.15 K. No azeotropes were found. While the *tert*-butanol-containing systems exhibited positive deviations from Raoult's law, the morpholine-containing systems showed negative deviations. The VLE data were correlated with the NRTL and the UNIQUAC models. Both models were equally satisfactory in representing the results.

## Introduction

Phenol derivatives are widely used as intermediates for manufacturing a variety of specialty chemicals. Separation of such compounds from product mixtures is usually difficult but plays an important role in the process. In the process of synthesis of 1,2-dimethoxybenzene, it is necessary to separate the closely boiling compounds 2-methoxyphenol and 1,2-dimethoxybenzene. The normal boiling temperatures of these two substances are within the range 475 K to 479 K. Conventional distillation is economically unattractive to separate such compounds. To explore feasible alternatives for separating these mixtures, Lee et al.[1] studied the VLE behavior of binary systems of carbon dioxide with 1,2-methoxybenzene and 2-methoxyphenol at temperatures from 323.15 K to 423.15 K and pressures up to 20 MPa. The experimental results have provided a fundamental basis for the feasibility study of the separation of 1,2-methoxybenzene + 2-methoxyphenol mixtures with supercritical carbon dioxide.

Extractive or adductive crystallization is another alternative method for separating these two closely boiling compounds. The VLE and solid−liquid equilibrium (SLE) data are required in the development of the separation processes. Recently, Lee et al.[2] studied the SLE behavior of the mixtures containing 1,2-dimethoxybenzene and 2-methoxyphenol with diphenylmethane. All three constituent binaries were found to be simply eutectic systems; that is, no complexes were formed in this ternary system. A ternary SLE phase diagram was prepared from the experimental results, and subsequently, a feasible separation sequence of extractive crystallization was suggested. Hwang et al.[3] measured the VLE data for the mixtures composed of 1,2-dimethoxybenzene and 2-methoxyphenol with diphenylmethane. These VLE data can be used in the design of the distillation column to recover diphenylmethane. Weng[4] studied the SLE behavior of the same compounds with two auxiliary agents, *tert*-butanol and morpholine. The experimental liquidus lines revealed that 2-methoxyphenol together with either *tert*-butanol or morpholine formed complexes. It was suggested that adductive crystallization could also be applied to separate the mixtures of 2-methoxyphenol and 1,2-dimethoxybenzene by using *tert*-butanol or morpholine as an adducted agent.

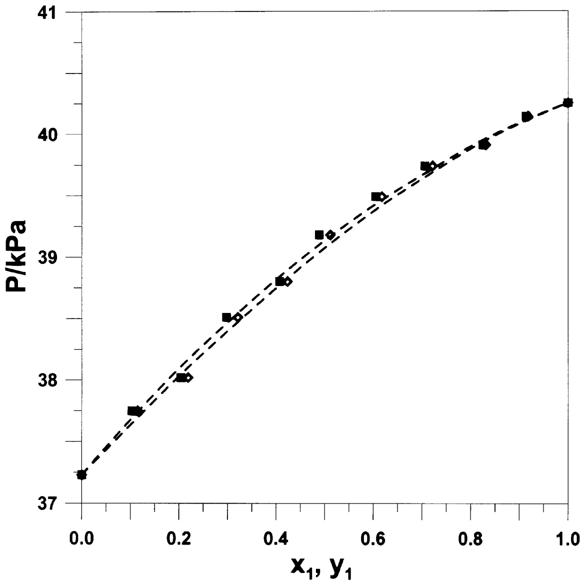

**Figure 1.** Pressure−composition diagram for 2-methoxyphenol (1) + 1,2-dimethoxybenzene (2) at 443.15 K: ■, experimental (liquid phase); ◇, experimental (vapor phase); - - -, calculated (NRTL).

In the present study, isothermal VLE data were measured for the binary mixtures composed of 2-methoxyphenol and 1,2-dimethoxybenzene with the potential adducted agents, *tert*-butanol and morpholine, at temperatures ranging from 333.15 K to 443.15 K. No VLE data were available in the literature for these binary systems, except for 2-methoxyphenol + 1,2-dimethoxybenzene at 433.15 K,

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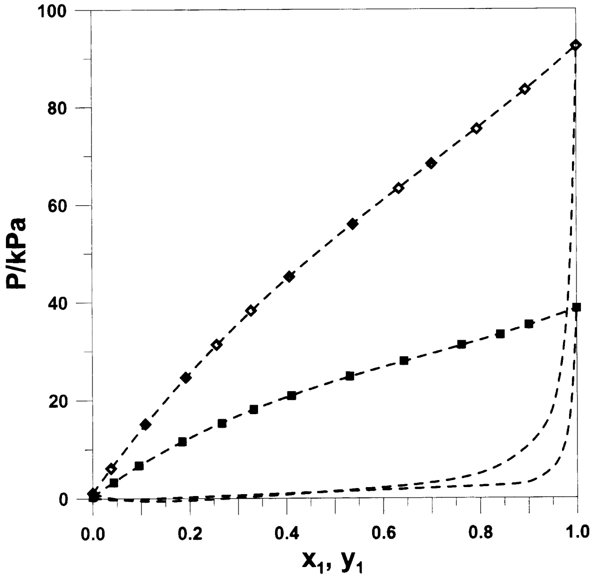

**Figure 2.** Pressure−composition diagram for *tert*-butanol (1) + 2-methoxyphenol (2): ■, experimental (333.15 K); ◇, experimental (353.15 K); - - -, calculated (NRTL).

**Table 1. VLE Properties for 2-Methoxyphenol (1) + 1,2-Dimethoxybenzene (2)**

| $T$/K | $P$/kPa | $x_1$ | $y_1$ |
|---|---|---|---|
| 413.15 | 13.7 | 0.0 | 0.0 |
| 413.15 | 13.9 | 0.102 | 0.117 |
| 413.15 | 14.1 | 0.199 | 0.217 |
| 413.15 | 14.3 | 0.302 | 0.331 |
| 413.15 | 14.5 | 0.402 | 0.433 |
| 413.15 | 14.6 | 0.496 | 0.519 |
| 413.15 | 14.7 | 0.604 | 0.625 |
| 413.15 | 14.9 | 0.704 | 0.726 |
| 413.15 | 15.0 | 0.819 | 0.829 |
| 413.15 | 15.1 | 0.914 | 0.921 |
| 413.15 | 15.2 | 1.0 | 1.0 |
| 428.15 | 23.1 | 0.0 | 0.0 |
| 428.15 | 23.3 | 0.104 | 0.115 |
| 428.15 | 23.7 | 0.202 | 0.215 |
| 428.15 | 23.8 | 0.300 | 0.325 |
| 428.15 | 24.1 | 0.405 | 0.426 |
| 428.15 | 24.4 | 0.490 | 0.519 |
| 428.15 | 24.6 | 0.606 | 0.630 |
| 428.15 | 24.7 | 0.703 | 0.716 |
| 428.15 | 24.9 | 0.824 | 0.837 |
| 428.15 | 25.2 | 0.916 | 0.921 |
| 428.15 | 25.3 | 1.0 | 1.0 |
| 443.15 | 37.2 | 0.0 | 0.0 |
| 443.15 | 37.8 | 0.103 | 0.115 |
| 443.15 | 38.0 | 0.204 | 0.218 |
| 443.15 | 38.5 | 0.298 | 0.321 |
| 443.15 | 38.8 | 0.407 | 0.423 |
| 443.15 | 39.2 | 0.489 | 0.512 |
| 443.15 | 39.5 | 0.605 | 0.618 |
| 443.15 | 39.7 | 0.706 | 0.722 |
| 443.15 | 39.9 | 0.825 | 0.831 |
| 443.15 | 40.1 | 0.914 | 0.918 |
| 443.15 | 40.3 | 1.0 | 1.0 |

448.15 K, and 463.15 K.[3] The experimental results were correlated with the NRTL[5] and the UNIQUAC[6] models.

**Table 2. VLE Properties for *tert*-Butanol (1) + 2-Methoxyphenol (2)**

| $T$/K | $P$/kPa | $x_1$ | $y_{1,\mathrm{calc}}$ NRTL | $y_{1,\mathrm{calc}}$ UNIQUAC |
|---|---|---|---|---|
| 333.15 | 0.33[a] | 0.0 | 0.0 | 0.0 |
| 333.15 | 3.31 | 0.043 | 0.9061 | 0.9055 |
| 333.15 | 6.70 | 0.095 | 0.9552 | 0.9549 |
| 333.15 | 11.6 | 0.185 | 0.9764 | 0.9763 |
| 333.15 | 15.3 | 0.267 | 0.9837 | 0.9837 |
| 333.15 | 18.1 | 0.332 | 0.9870 | 0.9870 |
| 333.15 | 20.9 | 0.411 | 0.9897 | 0.9897 |
| 333.15 | 24.8 | 0.531 | 0.9925 | 0.9925 |
| 333.15 | 27.9 | 0.643 | 0.9944 | 0.9944 |
| 333.15 | 31.2 | 0.762 | 0.9962 | 0.9962 |
| 333.15 | 33.3 | 0.842 | 0.9974 | 0.9974 |
| 333.15 | 35.3 | 0.901 | 0.9983 | 0.9983 |
| 333.15 | 38.6 | 1.0 | 1.0 | 1.0 |
| 343.15 | 0.61[a] | 0.0 | 0.0 | 0.0 |
| 343.15 | 4.49 | 0.040 | 0.8692 | 0.8702 |
| 343.15 | 10.4 | 0.105 | 0.9467 | 0.9470 |
| 343.15 | 17.0 | 0.189 | 0.9704 | 0.9705 |
| 343.15 | 22.4 | 0.263 | 0.9791 | 0.9791 |
| 343.15 | 26.4 | 0.328 | 0.9836 | 0.9836 |
| 343.15 | 31.2 | 0.409 | 0.9874 | 0.9873 |
| 343.15 | 37.5 | 0.531 | 0.9911 | 0.9911 |
| 343.15 | 42.2 | 0.633 | 0.9934 | 0.9934 |
| 343.15 | 48.1 | 0.756 | 0.9957 | 0.9957 |
| 343.15 | 52.0 | 0.838 | 0.9971 | 0.9971 |
| 343.15 | 55.3 | 0.900 | 0.9982 | 0.9982 |
| 343.15 | 60.8 | 1.0 | 1.0 | 1.0 |
| 353.15 | 1.08[a] | 0.0 | 0.0 | 0.0 |
| 353.15 | 6.15 | 0.038 | 0.8305 | 0.8326 |
| 353.15 | 15.2 | 0.109 | 0.9357 | 0.9363 |
| 353.15 | 24.6 | 0.192 | 0.9640 | 0.9641 |
| 353.15 | 31.3 | 0.256 | 0.9736 | 0.9737 |
| 353.15 | 38.3 | 0.328 | 0.9802 | 0.9801 |
| 353.15 | 45.2 | 0.407 | 0.9849 | 0.9848 |
| 353.15 | 55.9 | 0.539 | 0.9900 | 0.9899 |
| 353.15 | 63.3 | 0.634 | 0.9926 | 0.9925 |
| 353.15 | 68.3 | 0.701 | 0.9941 | 0.9941 |
| 353.15 | 75.4 | 0.795 | 0.9961 | 0.9961 |
| 353.15 | 83.4 | 0.895 | 0.9980 | 0.9980 |
| 353.15 | 92.4 | 1.0 | 1.0 | 1.0 |

[a] Estimated from the Antoine equation: $\ln P/\mathrm{kPa} = 13.6745 - 3378.85/[(T/\mathrm{K}) - 104.6302]$. The coefficients were determined from the vapor pressure data of 2-methoxyphenol at temperatures from 373.15 K to 463.15 K.[8]

## Experimental Section

A static apparatus was used in this study to measure the isothermal VLE data. A schematic diagram has been given by Hwang et al.[7] The basis of the apparatus is a blind equilibrium cell, which was placed in a thermostatic bath (model HT-250, stability = ±0.03 K, Neslab, U.S.A.). The bath temperature was measured with a precision thermometer (model-1560, Hart Scientific, U.S.A.) with a platinum RTD probe to an accuracy of ±0.02 K. A pressure transducer (model PDCR-330, Druck, U.K.) connected to a digital readout (model DPI-262, Druck, U.K.) was used to determine the equilibrium pressure to an accuracy of ±0.1 kPa. While the vapor sample was taken with a six-way sampling valve (operable up to 573 K), the liquid sample was collected in a vial through a sampling port that was connected to the liquid circulation loop with a tee. Compositions of both vapor and liquid samples were analyzed by gas chromatography (model 8700, China Chromatography, Taiwan) with a thermal conductivity detector (TCD). A stainless steel column packed with 10% SP-2340 on Chromosorb 80/100 supelcopart (6 m × 0.003175 m) was used in the sample analysis for 2-methoxyphenol + 1,2-dimethoxybenzene, and a stainless steel column packed with Porapak Q, 80/100 mesh (2 m × 0.003175 m), was used for the other binaries. The carrier gas, helium (99.99% purity), was heated to 500 K before entering the vapor-sampling valve to keep the vapor sample from condensation. Four to five samples were replicated for individual phase measurements at each experimental condition. The average area fraction was converted into mole fraction via

**Table 3. VLE Properties for *tert*-Butanol (1) + 1,2-Dimethoxybenzene (2)**

| | | | $y_{1,\mathrm{calc}}$ | |
|---|---|---|---|---|
| $T$/K | $P$/kPa | $x_1$ | NRTL | UNIQUAC |
| 333.15 | 0.32[a] | 0.0 | 0.0 | 0.0 |
| 333.15 | 4.43 | 0.033 | 0.9296 | 0.9292 |
| 333.15 | 7.49 | 0.061 | 0.9601 | 0.9599 |
| 333.15 | 12.0 | 0.113 | 0.9766 | 0.9766 |
| 333.15 | 18.7 | 0.210 | 0.9859 | 0.9859 |
| 333.15 | 21.6 | 0.276 | 0.9885 | 0.9885 |
| 333.15 | 24.9 | 0.366 | 0.9906 | 0.9906 |
| 333.15 | 27.8 | 0.499 | 0.9923 | 0.9923 |
| 333.15 | 29.4 | 0.592 | 0.9932 | 0.9932 |
| 333.15 | 30.7 | 0.654 | 0.9938 | 0.9938 |
| 333.15 | 31.5 | 0.712 | 0.9944 | 0.9944 |
| 333.15 | 33.5 | 0.808 | 0.9956 | 0.9956 |
| 333.15 | 35.7 | 0.906 | 0.9973 | 0.9973 |
| 333.15 | 38.6 | 1.0 | 1.0 | 1.0 |
| 343.15 | 0.57[a] | 0.0 | 0.0 | 0.0 |
| 343.15 | 6.65 | 0.036 | 0.9178 | 0.9174 |
| 343.15 | 12.4 | 0.074 | 0.9572 | 0.9570 |
| 343.15 | 16.4 | 0.105 | 0.9684 | 0.9684 |
| 343.15 | 26.6 | 0.209 | 0.9822 | 0.9822 |
| 343.15 | 30.7 | 0.263 | 0.9851 | 0.9852 |
| 343.15 | 35.7 | 0.354 | 0.9881 | 0.9881 |
| 343.15 | 40.7 | 0.477 | 0.9906 | 0.9906 |
| 343.15 | 44.4 | 0.590 | 0.9922 | 0.9922 |
| 343.15 | 46.5 | 0.652 | 0.9931 | 0.9930 |
| 343.15 | 49.1 | 0.725 | 0.9941 | 0.9941 |
| 343.15 | 52.1 | 0.819 | 0.9956 | 0.9956 |
| 343.15 | 56.2 | 0.913 | 0.9976 | 0.9976 |
| 343.15 | 60.8 | 1.0 | 1.0 | 1.0 |
| 353.15 | 0.99[a] | 0.0 | 0.0 | 0.0 |
| 353.15 | 9.38 | 0.037 | 0.8991 | 0.8993 |
| 353.15 | 17.2 | 0.075 | 0.9466 | 0.9467 |
| 353.15 | 24.6 | 0.117 | 0.9640 | 0.9641 |
| 353.15 | 36.7 | 0.202 | 0.9777 | 0.9777 |
| 353.15 | 45.7 | 0.282 | 0.9832 | 0.9832 |
| 353.15 | 53.0 | 0.367 | 0.9866 | 0.9866 |
| 353.15 | 61.2 | 0.491 | 0.9896 | 0.9896 |
| 353.15 | 66.8 | 0.591 | 0.9914 | 0.9914 |
| 353.15 | 70.1 | 0.654 | 0.9925 | 0.9924 |
| 353.15 | 74.8 | 0.742 | 0.9939 | 0.9939 |
| 353.15 | 78.7 | 0.812 | 0.9952 | 0.9952 |
| 353.15 | 85.3 | 0.913 | 0.9975 | 0.9975 |
| 353.15 | 92.4 | 1.0 | 1.0 | 1.0 |

[a] Estimated from the Antoine equation: $\ln P/\mathrm{kPa} = 15.0418 - 4271.711/[(T/\mathrm{K}) - 69.3365]$. The coefficients were determined from the vapor pressure data of 1,2-dimethoxybenzene at temperatures from 373.15 K to 468.15 K.[8]

**Table 4. VLE Properties for Morpholine (1) + 2-Methoxyphenol (2)**

| | | | $y_{1,\mathrm{calc}}$ | |
|---|---|---|---|---|
| $T$/K | $P$/kPa | $x_1$ | NRTL | UNIQUAC |
| 373.15 | 2.98 | 0.0 | 0.0 | 0.0 |
| 373.15 | 3.64 | 0.133 | 0.3434 | 0.3612 |
| 373.15 | 5.17 | 0.216 | 0.6083 | 0.6253 |
| 373.15 | 8.23 | 0.321 | 0.8172 | 0.8111 |
| 373.15 | 10.5 | 0.377 | 0.8784 | 0.8696 |
| 373.15 | 15.1 | 0.473 | 0.9375 | 0.9301 |
| 373.15 | 16.5 | 0.503 | 0.9491 | 0.9427 |
| 373.15 | 20.8 | 0.583 | 0.9698 | 0.9657 |
| 373.15 | 24.6 | 0.656 | 0.9811 | 0.9786 |
| 373.15 | 29.0 | 0.736 | 0.9890 | 0.9878 |
| 373.15 | 31.3 | 0.786 | 0.9923 | 0.9916 |
| 373.15 | 35.4 | 0.867 | 0.9962 | 0.9959 |
| 373.15 | 38.0 | 0.929 | 0.9982 | 0.9982 |
| 373.15 | 41.0 | 1.0 | 1.0 | 1.0 |
| 383.15 | 4.69 | 0.0 | 0.0 | 0.0 |
| 383.15 | 5.52 | 0.123 | 0.2836 | 0.2750 |
| 383.15 | 7.26 | 0.214 | 0.5551 | 0.5546 |
| 383.15 | 11.2 | 0.324 | 0.7842 | 0.7874 |
| 383.15 | 13.9 | 0.378 | 0.8519 | 0.8547 |
| 383.15 | 19.5 | 0.467 | 0.9201 | 0.9219 |
| 383.15 | 22.7 | 0.515 | 0.9426 | 0.9439 |
| 383.15 | 27.9 | 0.584 | 0.9644 | 0.9651 |
| 383.15 | 33.6 | 0.656 | 0.9785 | 0.9789 |
| 383.15 | 39.0 | 0.728 | 0.9873 | 0.9875 |
| 383.15 | 43.8 | 0.791 | 0.9922 | 0.9923 |
| 383.15 | 49.4 | 0.868 | 0.9962 | 0.9963 |
| 383.15 | 53.4 | 0.931 | 0.9984 | 0.9984 |
| 383.15 | 57.6 | 1.0 | 1.0 | 1.0 |
| 393.15 | 7.08 | 0.0 | 0.0 | 0.0 |
| 393.15 | 8.20 | 0.122 | 0.2756 | 0.2727 |
| 393.15 | 10.8 | 0.215 | 0.5445 | 0.5456 |
| 393.15 | 15.6 | 0.315 | 0.7576 | 0.7596 |
| 393.15 | 20.0 | 0.379 | 0.8416 | 0.8431 |
| 393.15 | 28.0 | 0.472 | 0.9157 | 0.9164 |
| 393.15 | 31.8 | 0.514 | 0.9364 | 0.9369 |
| 393.15 | 38.5 | 0.581 | 0.9593 | 0.9595 |
| 393.15 | 46.1 | 0.654 | 0.9754 | 0.9755 |
| 393.15 | 53.8 | 0.728 | 0.9854 | 0.9855 |
| 393.15 | 60.2 | 0.792 | 0.9911 | 0.9912 |
| 393.15 | 67.4 | 0.864 | 0.9955 | 0.9955 |
| 393.15 | 73.3 | 0.930 | 0.9981 | 0.9981 |
| 393.15 | 79.0 | 1.0 | 1.0 | 1.0 |

an equation determined by calibration on mixtures of known mole fraction prepared by mass. The uncertainties of the reported mole fractions for the liquid and vapor phases are within ±0.002 and ±0.005, respectively.

2-Methoxyphenol (99+ mass %), 1,2-dimethoxybenzene (99+ mass %), *tert*-butanol (99.5+ mass %), and morpholine (99+ mass %) were purchased from Arcos, U.S.A. No impurity peaks were detected from chromatographic analysis. All the chemicals were used without further purification.

## Results and Discussion

The isothermal VLE results are listed in Tables 1−5 for the binary systems 2-methoxyphenol + 1,2-dimethoxybenzene, *tert*-butanol + 2-methoxyphenol, *tert*-butanol + 1,2-dimethoxybenzene, morpholine + 2-methoxyphenol, and morpholine + 1,2-dimethoxybenzene, respectively. $P-T-x_i-y_i$ data were measured for 2-methoxyphenol + 1,2-dimethoxybenzene. Because the volatilities of the adducted agents are appreciably higher than those of 2-methoxyphenol and 1,2-dimethoxybenzene, the heavy components in the vapor phase are so minor that the compositions of the vapor phase cannot be determined accurately. Only $P-T-x_i$ data are, thus, reported for the other four binary systems. Table 6 presents the results of the thermodynamic consistency tests for 2-methoxyphenol + 1,2-dimethoxybenzene. These VLE data passed the point, the area, and the infinite dilution tests. The methods of the consistency tests have been detailed in refs 9 and 10.

Figure 1 shows the VLE phase diagram for 2-methoxyphenol + 1,2-dimethoxybenzene. Similar to the results of Hwang et al.,[3] this binary system exhibits positive deviations from Raoult's law. Although no azeotropes form in the system, the compositions of liquid and vapor phases are apparently too close to be separated efficiently by conventional distillation. Figures 2−5 illustrate the pressure−composition diagrams for *tert*-butanol + 2-methoxyphenol, *tert*-butanol + 1,2-dimethoxybenzene, morpholine + 2-methoxyphenol, and morpholine + 1,2-dimethoxybenzene, respectively. While positive deviations from Raoult's law are illustrated in Figures 2 and 3 for the systems containing *tert*-butanol, negative deviations are shown in Figures 4 and 5 for the mixtures containing morpholine. Moreover, no azeotropes were found in all binaries. It is suggested that the adducted agents, both *tert*-butanol and morpholine, could be recovered by a distillation column. These two auxiliary agents are potent to facilitate the separation of

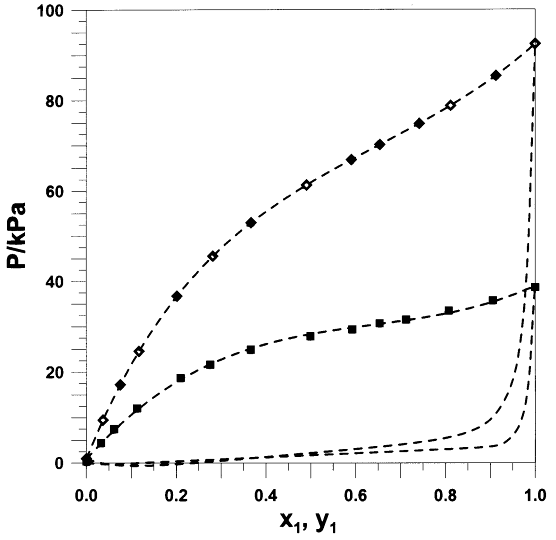

**Figure 3.** Pressure–composition diagram for *tert*-butanol (1) + 1,2-dimethoxybenzene (2): ■, experimental (333.15 K); ◇, experimental (353.15 K); - - -, calculated (NRTL).

**Table 5. VLE Properties for Morpholine (1) + 1,2-Dimethoxybenzene (2)**

| | | | $y_{1,\mathrm{calc}}$ | |
|---|---|---|---|---|
| *T*/K | *P*/kPa | $x_1$ | NRTL | UNIQUAC |
| 373.15 | 2.66 | 0.0 | 0.0 | 0.0 |
| 373.15 | 5.72 | 0.056 | 0.5640 | 0.5601 |
| 373.15 | 8.05 | 0.103 | 0.6989 | 0.6976 |
| 373.15 | 11.5 | 0.186 | 0.8054 | 0.8059 |
| 373.15 | 12.1 | 0.206 | 0.8216 | 0.8223 |
| 373.15 | 15.4 | 0.296 | 0.8726 | 0.8734 |
| 373.15 | 18.9 | 0.396 | 0.9088 | 0.9092 |
| 373.15 | 22.3 | 0.490 | 0.9330 | 0.9331 |
| 373.15 | 25.3 | 0.576 | 0.9502 | 0.9501 |
| 373.15 | 28.4 | 0.658 | 0.9635 | 0.9634 |
| 373.15 | 31.5 | 0.752 | 0.9762 | 0.9761 |
| 373.15 | 33.9 | 0.810 | 0.9828 | 0.9827 |
| 373.15 | 36.6 | 0.881 | 0.9899 | 0.9900 |
| 373.15 | 41.0 | 1.0 | 1.0 | 1.0 |
| 383.15 | 4.15 | 0.0 | 0.0 | 0.0 |
| 383.15 | 7.95 | 0.054 | 0.5075 | 0.5030 |
| 383.15 | 11.3 | 0.106 | 0.6679 | 0.6665 |
| 383.15 | 15.8 | 0.187 | 0.7820 | 0.7827 |
| 383.15 | 16.2 | 0.193 | 0.7876 | 0.7884 |
| 383.15 | 21.8 | 0.305 | 0.8614 | 0.8624 |
| 383.15 | 26.1 | 0.394 | 0.8979 | 0.8984 |
| 383.15 | 31.5 | 0.502 | 0.9292 | 0.9292 |
| 383.15 | 35.4 | 0.578 | 0.9461 | 0.9460 |
| 383.15 | 39.5 | 0.656 | 0.9602 | 0.9601 |
| 383.15 | 44.3 | 0.754 | 0.9747 | 0.9746 |
| 383.15 | 47.1 | 0.803 | 0.9809 | 0.9808 |
| 383.15 | 51.6 | 0.884 | 0.9897 | 0.9897 |
| 383.15 | 57.6 | 1.0 | 1.0 | 1.0 |
| 393.15 | 6.40 | 0.0 | 0.0 | 0.0 |
| 393.15 | 11.2 | 0.052 | 0.4583 | 0.4661 |
| 393.15 | 15.8 | 0.110 | 0.6380 | 0.6447 |
| 393.15 | 21.4 | 0.185 | 0.7520 | 0.7567 |
| 393.15 | 22.3 | 0.197 | 0.7647 | 0.7691 |
| 393.15 | 29.3 | 0.298 | 0.8406 | 0.8431 |
| 393.15 | 35.6 | 0.395 | 0.8861 | 0.8872 |
| 393.15 | 42.7 | 0.495 | 0.9195 | 0.9197 |
| 393.15 | 48.6 | 0.582 | 0.9413 | 0.9411 |
| 393.15 | 53.9 | 0.657 | 0.9565 | 0.9560 |
| 393.15 | 60.0 | 0.739 | 0.9703 | 0.9697 |
| 393.15 | 63.7 | 0.791 | 0.9778 | 0.9773 |
| 393.15 | 70.7 | 0.885 | 0.9890 | 0.9886 |
| 393.15 | 79.0 | 1.0 | 1.0 | 1.0 |

the closely boiling mixtures of 2-methoxyphenol + 1,2-dimethoxybenzene via an adductive crystallization method.

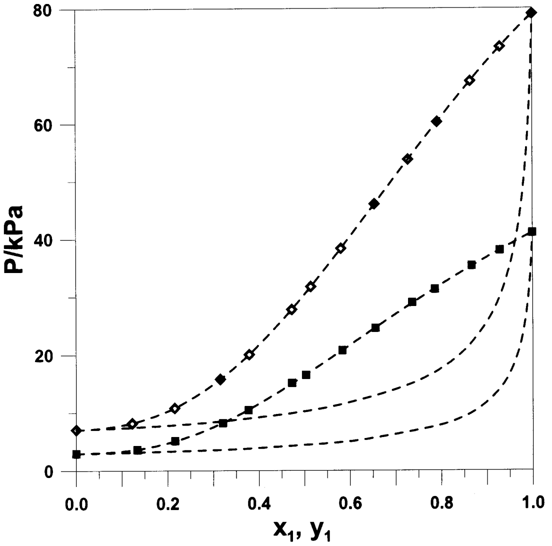

**Figure 4.** Pressure–composition diagram for morpholine (1) + 2-methoxyphenol (2): ■, experimental (373.15 K); ◇, experimental (393.15 K); - - -, calculated (NRTL).

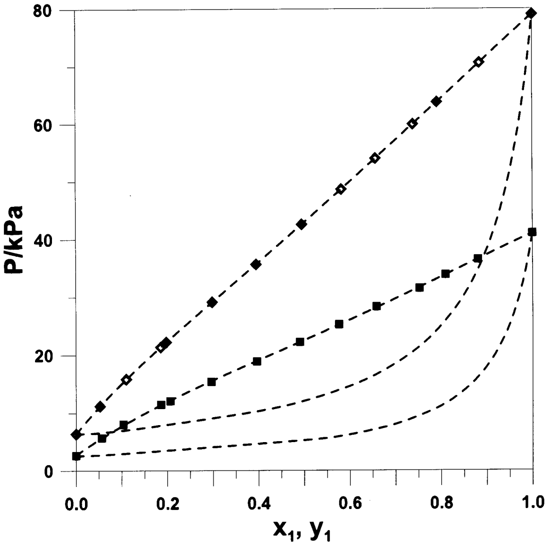

**Figure 5.** Pressure–composition diagram for morpholine (1) + 1,2-dimethoxybenzene (2): ■, experimental (373.15 K); ◇, experimental (393.15 K); - - -, calculated (NRTL).

## VLE Data Correlation

The $\phi-\gamma$ method was used in the present study to correlate the new binary VLE data. The NRTL and UNIQUAC models were employed to represent the nonideality of liquid mixtures, and the vapor mixtures were assumed as ideal due to the low equilibrium pressures of these investigated systems. The optimal values of the binary parameters of 2-methoxyphenol + 1,2-dimethoxybenzene were determined by the minimization of the following objective function $\pi_1$:

$$\pi_1 = \sum_{k=1}^{n} \left\{ \left[ \frac{(P_k^{\mathrm{calc}} - P_k^{\mathrm{expt}})}{\sigma_P} \right]^2 + \left[ \frac{(y_{1,k}^{\mathrm{calc}} - y_{1,k}^{\mathrm{expt}})}{\sigma_{y_1}} \right]^2 \right\} \tag{1}$$

where $\sigma_i$ is the standard deviation of the measured variable *i* and *n* is the number of data points. In the calculation, the values of $\sigma$ were set to 0.1 kPa for pressure and 0.005 for vapor mole fraction, respectively. For the systems

**Table 6. Results of Thermodynamic Consistency Tests**

| | consistency test index[a,b] | | | | $G^E/RT$ coefficient[c] | | | $\ln(\gamma_1/\gamma_2)$ coefficient[d] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $T$/K | $\delta$ | $A$ | $I_1$ | $I_2$ | $C_0$ | $C_1$ | $C_2$ | $D_0$ | $D_1$ | $D_2$ | $D_3$ |
| 413.15 | 0.42 (+) | 0.44 (+) | 27.6 (+) | 11.9 (+) | 0.0444 | −0.0081 | −0.0144 | 0.0044 | 0.0413 | −0.0095 | −0.0025 |
| 428.15 | 0.55 (+) | 0.25 (+) | 17.5 (+) | 23.3 (+) | 0.0273 | 0.0064 | −0.0094 | 0.0025 | 0.0186 | 0.0113 | 0.0041 |
| 443.15 | 1.37 (+) | 0.46 (+) | 29.0 (+) | 18.1 (+) | 0.0426 | 0.0012 | 0.0056 | 0.0046 | 0.0444 | −0.0076 | 0.0097 |

[a] Criteria for passing the thermodynamic consistency tests: $\delta < 5$ (point test); $A < 3$ (area test); $I_1 < 30$; $I_2 < 30$ (infinite dilution test). The definitions of $\delta$, $A$, $I_1$, and $I_2$ have been given in refs 9 and 10. [b] (+): passes the consistency test. [c] $G^E/RT = x_1x_2[C_0 + C_1(x_1 - x_2) + C_2(x_1 - x_2)^2]$. [d] $\ln(\gamma_1/\gamma_2) = D_0 + D_1(x_2 - x_1) + D_2(6x_1x_2 - 1) + D_3(x_2 - x_1)(1 - 8x_1x_2)$.

**Table 7. VLE Data Correlation with the NRTL and the UNIQUAC Models**

| | | NRTL | | | | | UNIQUAC[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $T$ | $(g_{12} - g_{22})/R$ | $(g_{21} - g_{11})/R$ | | RMSD[c] | | $(u_{12} - u_{22})/R$ | $(u_{21} - u_{11})/R$ | RMSD[c] | |
| mixture[b] | K | K | K | α | $\Delta P$/kPa | $\Delta y_1$ | K | K | $\Delta P$/kPa | $\Delta y_1$ |
| M1 | 413.15 | 19.44 | −1.53 | 0.3 | 0.02 | 0.0022 | 17.28 | −11.44 | 0.02 | 0.0022 |
| | 428.15 | 14.96 | −3.71 | 0.3 | 0.04 | 0.0030 | 14.05 | −10.03 | 0.04 | 0.0031 |
| | 443.15 | 19.48 | −1.39 | 0.3 | 0.05 | 0.0026 | 16.07 | −10.01 | 0.05 | 0.0027 |
| | 413.15−443.15 | 20.01 | −2.79 | 0.3 | 0.05 | 0.0027 | 15.19 | −9.73 | 0.05 | 0.0028 |
| M2 | 333.15 | 261.00 | 8.44 | 0.3 | 0.07 | | 173.93 | −113.76 | 0.06 | |
| | 343.15 | 227.83 | −9.00 | 0.3 | 0.06 | | 141.75 | −103.66 | 0.05 | |
| | 353.15 | 214.80 | −34.87 | 0.3 | 0.08 | | 141.71 | −113.57 | 0.05 | |
| | 333.15−353.15 | 190.64 | 6.16 | 0.3 | 0.26 | | 75.14 | −57.29 | 0.24 | |
| M3 | 333.15 | 356.89 | 154.28 | 0.3 | 0.10 | | 72.73 | 15.64 | 0.11 | |
| | 343.15 | 278.75 | 166.64 | 0.3 | 0.09 | | 28.46 | 45.35 | 0.10 | |
| | 353.15 | 297.15 | 115.36 | 0.3 | 0.06 | | 43.75 | 21.17 | 0.07 | |
| | 333.15−353.15 | 292.46 | 145.43 | 0.329 | 0.27 | | 60.66 | 10.01 | 0.24 | |
| M4 | 373.15 | −691.32 | 287.88 | 0.3 | 0.07 | | −364.93 | 365.02 | 0.09 | |
| | 383.15 | −550.77 | −7.51 | 0.3 | 0.08 | | −394.15 | 363.57 | 0.09 | |
| | 393.15 | −540.38 | −1.04 | 0.3 | 0.08 | | −370.48 | 308.84 | 0.08 | |
| | 373.15−393.15 | −537.25 | −1.71 | 0.355 | 0.19 | | −365.21 | 306.53 | 0.20 | |
| M5 | 373.15 | −294.53 | 536.28 | 0.3 | 0.07 | | −194.29 | 317.23 | 0.08 | |
| | 383.15 | −332.53 | 568.27 | 0.3 | 0.09 | | −203.47 | 320.98 | 0.10 | |
| | 393.15 | −365.54 | 596.31 | 0.3 | 0.08 | | −210.75 | 322.53 | 0.09 | |
| | 373.15−393.15 | −279.02 | 488.89 | 0.371 | 0.21 | | −195.56 | 299.89 | 0.23 | |

[a] The values of the parameters $r$ and $q$ in the UNIQUAC model are 4.531 and 3.448 for 2-methoxyphenol, 5.146 and 4.016 for 1,2-dimethoxybenzene, 3.923 and 3.744 for *tert*-butanol, and 3.474 and 2.796 for morpholine. These values were estimated from the group-contribution method.[12] [b] M1, 2-methoxyphenol + 1,2-dimethoxybenzene; M2, *tert*-butanol + 2-methoxyphenol; M3, *tert*-butanol + 1,2-dimethoxybenzene; M4, morpholine + 2-methoxyphenol; M5, morpholine + 1,2-dimethoxybenzene. [c] RMSD: root-mean-square deviation, defined as $\mathrm{RMSD}(\Delta P) = [\sum_{k=1}^{n}(P_k^{\mathrm{calc}} - P_k^{\mathrm{expt}})^2/n]^{1/2}$ and $\mathrm{RMSD}(\Delta y_1) = [\sum_{k=1}^{n}(y_{1,k}^{\mathrm{calc}} - y_{1,k}^{\mathrm{expt}})^2/n]^{1/2}$.

without vapor composition data, the objective function was defined as

$$\pi_2 = \sum_{k=1}^{n}(P_k^{\mathrm{calc}} - P_k^{\mathrm{expt}})^2 \qquad (2)$$

The optimization algorithm is similar to that of Prausnitz et al.[11] Table 7 lists the correlated results, indicating that both models correlated the data equally well. The calculated vapor compositions are reported in Tables 2−5. The solid curves in Figures 1−5 represent the calculated results from the NRTL model. The NRTL model with the tabulated parameters, from 413.15 K to 443.15 K, in Table 7 was used to calculate the equilibrium pressures ($P$) and vapor compositions ($y_i$) for 2-methoxyphenol + 1,2-dimethoxybenzene at 433.15 K. In comparison with the experimental results of Hwang et al.,[3] the RMSDs of $P$ and $y_1$ are about 0.1 kPa and 0.005, respectively. The values are within the experimental uncertainties.

## Conclusions

Isothermal VLE data have been determined experimentally with a static apparatus for binary mixtures composed of the closely boiling compounds 2-methoxyphenol and 1,2-dimethoxybenzene with an adducted agent, *tert*-butanol or morpholine, over the temperature range 333.15 K to 443.15 K. No azeotropes were found in these investigated systems. The adducted agents could be recovered from the mother liquor with a distillation column. The NRTL and UNIQUAC models are capable of accurately correlating the VLE data of the investigated systems.

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