*J. Chem. Eng. Data* **1996,** *41,* 718−723

# VLE Measurements of Binary Mixtures of Methanol, Ethanol, 2-Methoxy-2-methylpropane, and 2-Methoxy-2-methylbutane at 101.32 kPa

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Isobaric vapor−liquid equilibrium data for 2-methoxy-2-methylpropane + methanol, 2-methoxy-2-methylpropane + ethanol, methanol + 2-methoxy-2-methylbutane, ethanol + 2-methoxy-2-methylbutane, and 2-methoxy-2-methylpropane + 2-methoxy-2-methylbutane were determined at 101.32 kPa. Fredenslund *et al.*'s test confirmed the results to be thermodynamically consistent. The VLE data were satisfactorily correlated using the Wilson, NRTL, and UNIQUAC equations for liquid phase activity coefficients and adequately predicted using the ASOG, UNIFAC, UNIFAC−Dortmund, and UNIFAC−Lyngby group contribution methods.

## Introduction

In recent years, increasing use of ethers as oxygenated additives for gasoline has necessitated large increases in worldwide ether production, with important implications for the hydrocarbon processing industry. The ether most widely added to gasoline is 2-methoxy-2-methylpropane (more commonly MTBE, methyl *tert*-butyl ether); an effective but less widely used ether oxygenate is 2-methoxy-2-methylbutane (TAME, *tert*-amyl methyl ether). These ethers are used in combination with methanol and ethanol cosolvents as octane-enhancing agents and antipollutants in gasoline blends. The thermodynamics of ether + alcohol mixtures are thus of some interest. The literature contains vapor−liquid equilibrium (VLE) measurements for MTBE methanol mixtures subjected to the salt effect (Velasco *et al.*, 1990) and TAME + methanol and TAME + ethanol mixtures (Palczewska-Tulinska *et al.*, 1990) and several papers reporting vapor pressures for TAME and MTBE (Krähenbühl and Gmehling, 1994) and mixtures of these ethers with hydrocarbons. In this paper we report VLE data for the binary systems MTBE + methanol, MTBE + ethanol, methanol + TAME, ethanol + TAME, and MTBE TAME. The thermodynamic consistency of the experimental results was checked using the test of Fredenslund *et al.* (1977). The results were correlated using the Wilson (Wilson, 1964), NRTL (Renon and Prausnitz, 1968), and UNIQUAC (Abrams and Prausnitz, 1975) equations and compared with the predictions of the ASOG (Kojima and Tochigi, 1979; Tochigi *et al.*, 1990), UNIFAC (Fredenslund *et al.*, 1977), UNIFAC−Dortmund (Weidlich and Gmehling, 1987; Gmehling *et al.*, 1993), and UNIFAC−Lyngby (Larsen *et al.*, 1987) group contribution methods.

## Experimental Section

***Materials.*** Methanol and ethanol were supplied by Merck with nominal purities >99.7 and >99.5 mass %, respectively; TAME was supplied by Fluka Chemika with nominal purity >98.9 mass %; none was subjected to further purification. MTBE was supplied by Aldrich and was redistilled prior to use, its final purity being >99.7 mass %. Table 1 lists the measured densities, refractive indices, and boiling points of the chemicals used, together with published values.

**Table 1. Densities ($d$), Refractive Indices ($n_D$), and Boiling Points ($T_b$) of the Compounds**

| | $d$(298.15 K)/g·cm$^{-3}$ | | $n_D$ (298.15 K) | | $T_b$ (101.32 kPa)/K | |
|---|---|---|---|---|---|---|
| compd | exp | lit. | exp | lit. | exp | lit. |
| methanol | 0.7866 | 0.786 64[a] | 1.3264 | 1.326 52[a] | 337.65 | 337.696[a] |
| ethanol | 0.7852 | 0.784 93[a] | 1.3592 | 1.359 41[a] | 351.44 | 351.443[a] |
| MTBE | 0.7356 | 0.735 28[c] | 1.3663 | 1.366 3[c] | 328.11 | 328.32[b] |
| TAME | 0.7657 | 0.765 77[d] | 1.3858 | 1.385 8[d] | 359.33 | 359.39[b] |

[a] Riddick *et al.*, 1986. [b] Krähenbühl and Gmehling, 1994. [c] Daubert and Danner, 1989. [d] Linek, 1987.

**Table 2. Composition Dependence at 25 °C of the Densities ($d$) and Refractive Indices ($n_D$) of Some of the Binary Mixtures Studied**

| | TAME (1) + methanol (2) | | TAME (1) + ethanol (2) | | TAME (1) + MTBE (2) | |
|---|---|---|---|---|---|---|
| $x_1$ (m.f.) | $d$/g·cm$^{-3}$ | $n_D$ | $d$/g·cm$^{-3}$ | $n_D$ | $d$/g·cm$^{-3}$ | $n_D$ |
| 0.05 | 0.7850 | 1.3355 | 0.7839 | 1.3624 | 0.7372 | 1.3672 |
| 0.10 | 0.7836 | 1.3430 | 0.7828 | 1.3652 | 0.7389 | 1.3684 |
| 0.15 | 0.7822 | 1.3492 | 0.7817 | 1.3676 | 0.7406 | 1.3695 |
| 0.20 | 0.7810 | 1.3544 | 0.7806 | 1.3698 | 0.7423 | 1.3705 |
| 0.25 | 0.7799 | 1.3588 | 0.7795 | 1.3717 | 0.7440 | 1.3716 |
| 0.30 | 0.7787 | 1.3626 | 0.7785 | 1.3735 | 0.7456 | 1.3727 |
| 0.35 | 0.7777 | 1.3659 | 0.7775 | 1.3750 | 0.7472 | 1.3737 |
| 0.40 | 0.7767 | 1.3687 | 0.7765 | 1.3764 | 0.7488 | 1.3747 |
| 0.45 | 0.7757 | 1.3712 | 0.7755 | 1.3777 | 0.7503 | 1.3757 |
| 0.50 | 0.7747 | 1.3735 | 0.7746 | 1.3788 | 0.7518 | 1.3767 |
| 0.55 | 0.7738 | 1.3754 | 0.7736 | 1.3799 | 0.7533 | 1.3777 |
| 0.60 | 0.7729 | 1.3772 | 0.7728 | 1.3808 | 0.7548 | 1.3786 |
| 0.65 | 0.7720 | 1.3788 | 0.7719 | 1.3817 | 0.7563 | 1.3796 |
| 0.70 | 0.7712 | 1.3802 | 0.7710 | 1.3825 | 0.7577 | 1.3805 |
| 0.75 | 0.7703 | 1.3814 | 0.7702 | 1.3832 | 0.7591 | 1.3814 |
| 0.80 | 0.7695 | 1.3826 | 0.7693 | 1.3839 | 0.7604 | 1.3823 |
| 0.85 | 0.7686 | 1.3836 | 0.7684 | 1.3845 | 0.7618 | 1.3832 |
| 0.90 | 0.7677 | 1.3844 | 0.7676 | 1.3850 | 0.7631 | 1.3841 |
| 0.95 | 0.7667 | 1.3852 | 0.7667 | 1.3854 | 0.7644 | 1.3850 |

***Apparatus and Procedure.*** Measurements were performed in a Labodest apparatus, recycling both liquid and vapor phases (Fischer Labor und Verfahrenstechnik, Germany), which was equipped with a Fischer digital manometer and a Heraeus QuaT100 quartz thermometer that measured to within ±0.01 kPa and ±0.02 K, respectively. The compositions of vapor and liquid phases were determined by densimetry and refractometry. For the mixtures of methanol and ethanol with MTBE, previously deter-

S0021-9568(95)00323-2 CCC: $12.00

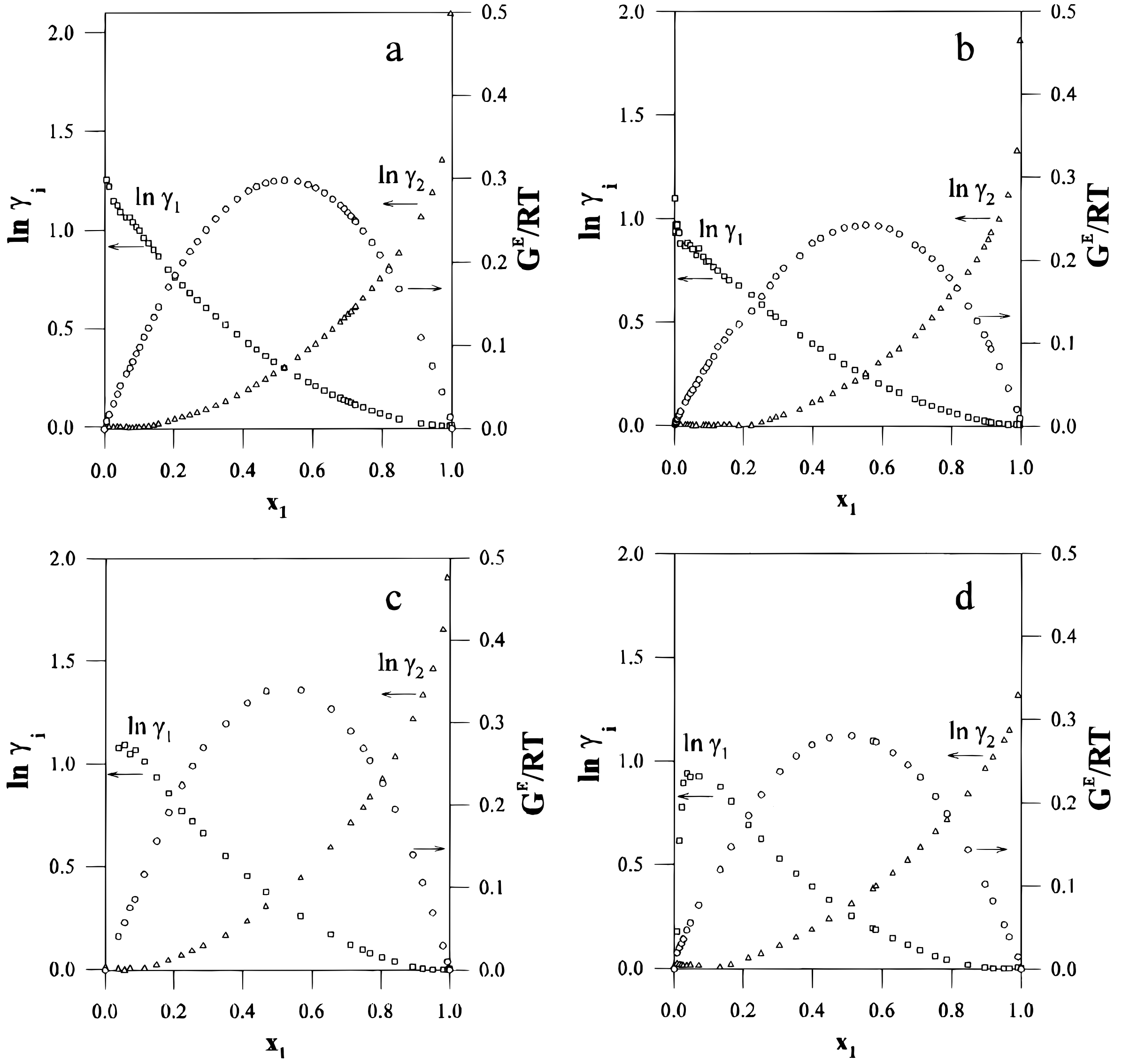

**Figure 1.** Variation of the natural logarithm of the activity coefficient of each component and $G^E/RT$ with liquid phase composition, for mixtures of (a) MTBE (1) + methanol (2), (b) MTBE (1) + ethanol (2), (c) ethanol (1) + TAME (2), and (d) methanol (1) + TAME (2).

mined data for the composition dependence of the densities and refractive indices were used (Arce *et al.*, 1995a, 1995b). For the mixtures with TAME, these data were determined here, measuring the densities to within ±0.0001 $g \cdot cm^{-3}$ in an Anton Paar DSA 48 digital vibrating tube densimeter, and the refractive indices to within ±0.0001 with an ATAGO RX-1000 refractometer (Table 2). The maximum deviation in composition, as estimated by comparison of selected results with those for samples prepared by weighing, was ±0.001 mole fraction.

## Experimental Results and Data Treatment

For vapor and liquid phases in equilibrium at pressure $P$ and temperature $T$,

$$y_i \phi_i P = x_i \gamma_i P_i^S \phi_i^S \exp\left[\frac{V_i^L(P - P_i^S)}{RT}\right] \tag{1}$$

where $x_i$ and $y_i$ are the mole fractions of component $i$ in the liquid and vapor phases respectively, $\gamma_i$ is its activity coefficient, $V_i^L$ is its molar volume in the liquid phase, $\phi_i$ and $\phi_i^S$ are its coefficient of fugacity and coefficient of fugacity at saturation, respectively, and $P_i^S$ is its saturated vapor pressure. In this work, $V_i^L$ was calculated from the correlation of Yen and Woods (1966), $\phi_i$ and $\phi_i^S$ from the second virial coefficient by the method of Hayden and O'Connell (1975), and $P_i^S$ from Antoine's equation,

$$\log(P_i^S/\text{kPa}) = A + \frac{B}{T/\text{K} + C} \tag{2}$$

using the coefficients $A$, $B$, and $C$ given in Table 3.

**Table 3. Antoine Coefficients *A*, *B*, and *C* for Equation 2**

| compd | *A* | *B* | *C* |
|---|---|---|---|
| methanol | 7.205 19[a] | −1581.993[a] | −33.439[a] |
| ethanol | 7.168 79[a] | −1552.601[a] | −50.731[a] |
| MTBE | 6.070 34[b] | −1158.912[b] | −43.200[b] |
| TAME | 6.067 82[b] | −1256.258[b] | −50.100[b] |

[a] Riddick *et al.*, 1986. [b] Krähenbühl and Gmehling, 1994.

For each binary system studied, Table 4 lists the experimental values for $x$, $y$, $T$, the activity coefficients, and $G^E/RT$. For the ether + alcohol mixtures, Figure 1 shows the variation of ln $\gamma_i$ and $G^E/RT$ with liquid phase composition ($x_i$). Fredenslund's test for thermodynamic consistency (Fredenslund *et al.*, 1977) was applied to the experimental data, yielding a third-order Legendre polynomial for MTBE + methanol, MTBE + ethanol, methanol + TAME, and MTBE + TAME, and a second-order polynomial for ethanol + TAME. The mean deviations between the experimental and calculated vapor phase mole fraction compositions

**Table 4. Boiling Temperatures ($T$), Liquid and Vapor Mole Fractions ($x_i$, $y_i$), Activity Coefficients ($\gamma_i$), and $G^E/RT$ for the Binary Systems**

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $G^E/RT$ | $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $G^E/RT$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Methanol (1) + TAME (2) | | | | | | |
| 353.66 | 0.0383 | 0.1934 | 2.9412 | 1.0000 | 0.0413 | 336.00 | 0.5662 | 0.6838 | 1.2959 | 1.5583 | 0.3392 |
| 351.27 | 0.0565 | 0.2674 | 2.9787 | 0.9958 | 0.0577 | 335.59 | 0.6546 | 0.7128 | 1.1855 | 1.8074 | 0.3158 |
| 349.79 | 0.0714 | 0.3078 | 2.8497 | 1.0009 | 0.0756 | 335.43 | 0.7114 | 0.7326 | 1.1273 | 2.0287 | 0.2894 |
| 348.06 | 0.0872 | 0.3614 | 2.9021 | 0.9923 | 0.0858 | 335.34 | 0.7481 | 0.7494 | 1.0997 | 2.1884 | 0.2684 |
| 345.96 | 0.1135 | 0.4150 | 2.7506 | 1.0013 | 0.1160 | 335.35 | 0.7678 | 0.7569 | 1.0816 | 2.3039 | 0.2540 |
| 343.75 | 0.1495 | 0.4683 | 2.5446 | 1.0199 | 0.1564 | 335.36 | 0.8038 | 0.7755 | 1.0575 | 2.5217 | 0.2264 |
| 342.18 | 0.1847 | 0.5061 | 2.3526 | 1.0415 | 0.1912 | 335.42 | 0.8401 | 0.7967 | 1.0365 | 2.8020 | 0.1949 |
| 340.96 | 0.2223 | 0.5357 | 2.1608 | 1.0699 | 0.2238 | 335.70 | 0.8928 | 0.8353 | 1.0108 | 3.3667 | 0.1397 |
| 340.00 | 0.2527 | 0.5595 | 2.0548 | 1.0918 | 0.2476 | 335.98 | 0.9217 | 0.8641 | 1.0016 | 3.7782 | 0.1056 |
| 339.25 | 0.2844 | 0.5779 | 1.9376 | 1.1213 | 0.2700 | 336.39 | 0.9512 | 0.9028 | 0.9978 | 4.2932 | 0.0690 |
| 338.19 | 0.3492 | 0.6119 | 1.7358 | 1.1772 | 0.2987 | 337.00 | 0.9809 | 0.9532 | 0.9978 | 5.2014 | 0.0294 |
| 337.35 | 0.4122 | 0.6358 | 1.5755 | 1.2604 | 0.3234 | 337.38 | 0.9936 | 0.9796 | 0.9978 | 6.6993 | 0.0100 |
| 336.76 | 0.4672 | 0.6526 | 1.4579 | 1.3549 | 0.3380 | | | | | | |
| | | | | | Ethanol (1) + TAME (2) | | | | | | |
| 358.88 | 0.0087 | 0.0133 | 1.1942 | 1.0184 | 0.0197 | 346.92 | 0.5124 | 0.5494 | 1.2874 | 1.3640 | 0.2808 |
| 358.37 | 0.0154 | 0.0359 | 1.8531 | 1.0166 | 0.0257 | 346.83 | 0.5728 | 0.5774 | 1.2136 | 1.4659 | 0.2743 |
| 357.88 | 0.0211 | 0.0567 | 2.1723 | 1.0146 | 0.0306 | 346.81 | 0.5820 | 0.5820 | 1.2047 | 1.4831 | 0.2731 |
| 357.31 | 0.0269 | 0.0797 | 2.4429 | 1.0123 | 0.0359 | 346.85 | 0.6302 | 0.6060 | 1.1557 | 1.5798 | 0.2603 |
| 356.46 | 0.0369 | 0.1115 | 2.5667 | 1.0122 | 0.0465 | 346.92 | 0.6732 | 0.6292 | 1.1195 | 1.6805 | 0.2456 |
| 355.83 | 0.0471 | 0.1365 | 2.5168 | 1.0128 | 0.0556 | 347.00 | 0.7087 | 0.6476 | 1.0905 | 1.7888 | 0.2308 |
| 354.31 | 0.0714 | 0.1967 | 2.5248 | 1.0114 | 0.0767 | 347.21 | 0.7525 | 0.6752 | 1.0613 | 1.9304 | 0.2075 |
| 351.56 | 0.1331 | 0.3156 | 2.3987 | 1.0037 | 0.1197 | 347.45 | 0.7858 | 0.7000 | 1.0431 | 2.0474 | 0.1867 |
| 350.59 | 0.1642 | 0.3509 | 2.2405 | 1.0175 | 0.1470 | 348.02 | 0.8457 | 0.7516 | 1.0166 | 2.3183 | 0.1437 |
| 349.53 | 0.2143 | 0.3920 | 1.9947 | 1.0482 | 0.1849 | 348.72 | 0.8958 | 0.8072 | 1.0021 | 2.6154 | 0.1021 |
| 348.85 | 0.2513 | 0.4196 | 1.8675 | 1.0730 | 0.2097 | 349.13 | 0.9181 | 0.8380 | 0.9987 | 2.7657 | 0.0821 |
| 348.19 | 0.3045 | 0.4512 | 1.6985 | 1.1156 | 0.2374 | 349.82 | 0.9502 | 0.8913 | 0.9987 | 2.9973 | 0.0535 |
| 347.73 | 0.3520 | 0.4764 | 1.5781 | 1.1598 | 0.2566 | 350.22 | 0.9655 | 0.9203 | 0.9992 | 3.1392 | 0.0387 |
| 347.39 | 0.3976 | 0.4996 | 1.4836 | 1.2059 | 0.2696 | 350.93 | 0.9901 | 0.9724 | 1.0016 | 3.7195 | 0.0146 |
| 347.14 | 0.4468 | 0.5210 | 1.3893 | 1.2678 | 0.2782 | | | | | | |
| | | | | | MTBE (1) + Methanol (2) | | | | | | |
| 337.05 | 0.0071 | 0.0310 | 3.5056 | 1.0001 | 0.0090 | 325.26 | 0.4373 | 0.5815 | 1.4810 | 1.2358 | 0.2909 |
| 336.48 | 0.0141 | 0.0587 | 3.3921 | 0.9999 | 0.0171 | 325.08 | 0.4638 | 0.5936 | 1.4329 | 1.2699 | 0.2950 |
| 335.58 | 0.0276 | 0.1041 | 3.1455 | 0.9988 | 0.0305 | 324.94 | 0.4874 | 0.6038 | 1.3925 | 1.3036 | 0.2973 |
| 334.85 | 0.0383 | 0.1386 | 3.0767 | 0.9989 | 0.0420 | 324.79 | 0.5169 | 0.6166 | 1.3466 | 1.3481 | 0.2981 |
| 334.33 | 0.0468 | 0.1618 | 2.9806 | 1.0008 | 0.0519 | 324.61 | 0.5561 | 0.6327 | 1.2909 | 1.4179 | 0.2970 |
| 333.39 | 0.0637 | 0.2086 | 2.8947 | 0.9984 | 0.0662 | 324.51 | 0.5859 | 0.6453 | 1.2529 | 1.4753 | 0.2932 |
| 332.82 | 0.0737 | 0.2380 | 2.8983 | 0.9941 | 0.0729 | 324.45 | 0.6073 | 0.6550 | 1.2288 | 1.5182 | 0.2891 |
| 332.42 | 0.0824 | 0.2570 | 2.8298 | 0.9943 | 0.0805 | 324.40 | 0.6327 | 0.6657 | 1.2002 | 1.5775 | 0.2829 |
| 331.96 | 0.0920 | 0.2765 | 2.7618 | 0.9967 | 0.0905 | 324.37 | 0.6560 | 0.6763 | 1.1766 | 1.6344 | 0.2757 |
| 331.52 | 0.1020 | 0.2976 | 2.7137 | 0.9961 | 0.0983 | 324.33 | 0.6789 | 0.6869 | 1.1557 | 1.6980 | 0.2683 |
| 331.07 | 0.1143 | 0.3167 | 2.6098 | 1.0006 | 0.1102 | 324.32 | 0.6906 | 0.6925 | 1.1455 | 1.7323 | 0.2638 |
| 330.58 | 0.1274 | 0.3389 | 2.5401 | 1.0026 | 0.1210 | 324.32 | 0.7008 | 0.6973 | 1.1365 | 1.7641 | 0.2595 |
| 330.07 | 0.1423 | 0.3609 | 2.4569 | 1.0071 | 0.1339 | 324.33 | 0.7092 | 0.7016 | 1.1294 | 1.7892 | 0.2555 |
| 329.62 | 0.1565 | 0.3796 | 2.3800 | 1.0128 | 0.1464 | 324.34 | 0.7203 | 0.7070 | 1.1200 | 1.8267 | 0.2501 |
| 328.87 | 0.1845 | 0.4097 | 2.2265 | 1.0284 | 0.1705 | 324.35 | 0.7230 | 0.7081 | 1.1171 | 1.8369 | 0.2485 |
| 328.43 | 0.2037 | 0.4286 | 2.1366 | 1.0385 | 0.1847 | 324.37 | 0.7443 | 0.7194 | 1.1013 | 1.9133 | 0.2377 |
| 327.94 | 0.2257 | 0.4499 | 2.0530 | 1.0498 | 0.2000 | 324.41 | 0.7696 | 0.7341 | 1.0849 | 2.0115 | 0.2237 |
| 327.54 | 0.2467 | 0.4677 | 1.9754 | 1.0622 | 0.2134 | 9324.50 | 0.7928 | 0.7484 | 1.0701 | 2.1113 | 0.2085 |
| 327.18 | 0.2683 | 0.4851 | 1.9036 | 1.0744 | 0.2252 | 324.61 | 0.8189 | 0.7652 | 1.0549 | 2.2475 | 0.1904 |
| 326.77 | 0.2933 | 0.5035 | 1.8292 | 1.0918 | 0.2392 | 324.82 | 0.8473 | 0.7862 | 1.0399 | 2.4108 | 0.1675 |
| 326.39 | 0.3207 | 0.5217 | 1.7528 | 1.1125 | 0.2524 | 325.54 | 0.9114 | 0.8472 | 1.0165 | 2.8994 | 0.1092 |
| 326.05 | 0.3489 | 0.5392 | 1.6818 | 1.1352 | 0.2639 | 326.15 | 0.9441 | 0.8891 | 1.0093 | 3.2661 | 0.0749 |
| 325.72 | 0.3824 | 0.5563 | 1.5985 | 1.1694 | 0.2760 | 326.83 | 0.9717 | 0.9322 | 1.0057 | 3.8523 | 0.0437 |
| 325.45 | 0.4142 | 0.5705 | 1.5255 | 1.2079 | 0.2856 | 327.57 | 0.9953 | 0.9757 | 1.0037 | 8.1021 | 0.0135 |
| | | | | | MTBE (1) + Ethanol (2) | | | | | | |
| 351.34 | 0.0006 | 0.0034 | 3.0006 | 1.0011 | 0.0018 | 335.69 | 0.2929 | 0.6160 | 1.6891 | 1.0390 | 0.1806 |
| 351.21 | 0.0019 | 0.0091 | 2.5442 | 1.0017 | 0.0034 | 335.13 | 0.3149 | 0.6324 | 1.6393 | 1.0524 | 0.1906 |
| 351.18 | 0.0020 | 0.0099 | 2.6315 | 1.0021 | 0.0040 | 334.09 | 0.3623 | 0.6655 | 1.5455 | 1.0778 | 0.2055 |
| 351.05 | 0.0034 | 0.0163 | 2.5567 | 1.0020 | 0.0052 | 333.33 | 0.3976 | 0.6847 | 1.4818 | 1.1127 | 0.2207 |
| 350.86 | 0.0048 | 0.0237 | 2.6456 | 1.0032 | 0.0078 | 332.85 | 0.4218 | 0.6991 | 1.4466 | 1.1306 | 0.2267 |
| 350.73 | 0.0062 | 0.0305 | 2.6442 | 1.0026 | 0.0086 | 332.29 | 0.4568 | 0.7161 | 1.3912 | 1.1648 | 0.2337 |
| 350.59 | 0.0077 | 0.0376 | 2.6337 | 1.0021 | 0.0095 | 331.79 | 0.4907 | 0.7308 | 1.3416 | 1.2052 | 0.2393 |
| 350.33 | 0.0105 | 0.0492 | 2.5435 | 1.0028 | 0.0126 | 331.35 | 0.5211 | 0.7455 | 1.3058 | 1.2366 | 0.2407 |
| 350.11 | 0.0131 | 0.0610 | 2.5412 | 1.0015 | 0.0137 | 330.95 | 0.5521 | 0.7579 | 1.2682 | 1.2813 | 0.2422 |
| 349.81 | 0.0170 | 0.0745 | 2.4094 | 1.0026 | 0.0175 | 330.56 | 0.5883 | 0.7702 | 1.2238 | 1.3473 | 0.2415 |
| 348.59 | 0.0311 | 0.1308 | 2.3837 | 1.0019 | 0.0288 | 330.18 | 0.6207 | 0.7838 | 1.1940 | 1.4006 | 0.2378 |
| 347.97 | 0.0376 | 0.1578 | 2.4162 | 1.0014 | 0.0346 | 329.89 | 0.6489 | 0.7963 | 1.1706 | 1.4454 | 0.2315 |
| 347.40 | 0.0449 | 0.1838 | 2.3910 | 1.0003 | 0.0394 | 329.49 | 0.6943 | 0.8150 | 1.1334 | 1.5368 | 0.2183 |
| 346.90 | 0.0522 | 0.2071 | 2.3470 | 0.9989 | 0.0435 | 329.28 | 0.7161 | 0.8225 | 1.1161 | 1.6036 | 0.2127 |
| 346.24 | 0.0624 | 0.2361 | 2.2765 | 0.9989 | 0.0503 | 329.06 | 0.7431 | 0.8338 | 1.0977 | 1.6771 | 0.2021 |
| 345.47 | 0.0698 | 0.2677 | 2.3541 | 0.9957 | 0.0557 | 328.90 | 0.7677 | 0.8439 | 1.0806 | 1.7559 | 0.1903 |
| 344.65 | 0.0833 | 0.3002 | 2.2602 | 0.9982 | 0.0662 | 328.68 | 0.7930 | 0.8545 | 1.0664 | 1.8564 | 0.1791 |
| 344.26 | 0.0908 | 0.3168 | 2.2107 | 0.9983 | 0.0705 | 328.54 | 0.8153 | 0.8653 | 1.0548 | 1.9398 | 0.1659 |
| 343.68 | 0.0986 | 0.3393 | 2.2142 | 0.9972 | 0.0759 | 328.37 | 0.8477 | 0.8812 | 1.0385 | 2.0932 | 0.1445 |
| 342.92 | 0.1129 | 0.3701 | 2.1524 | 0.9969 | 0.0838 | 328.24 | 0.8728 | 0.8952 | 1.0287 | 2.2263 | 0.1265 |
| 342.18 | 0.1246 | 0.3937 | 2.1167 | 1.0027 | 0.0958 | 328.15 | 0.8942 | 0.9079 | 1.0211 | 2.3640 | 0.1097 |
| 341.28 | 0.1434 | 0.4300 | 2.0583 | 1.0004 | 0.1039 | 328.12 | 0.9063 | 0.9156 | 1.0169 | 2.4509 | 0.0992 |
| 340.56 | 0.1578 | 0.4548 | 2.0178 | 1.0032 | 0.1135 | 328.11 | 0.9136 | 0.9196 | 1.0135 | 2.5339 | 0.0926 |
| 339.30 | 0.1855 | 0.5037 | 1.9682 | 0.9965 | 0.1228 | 328.06 | 0.9368 | 0.9374 | 1.0090 | 2.7068 | 0.0714 |
| 337.86 | 0.2224 | 0.5543 | 1.8809 | 0.9975 | 0.1386 | 328.06 | 0.9625 | 0.9584 | 1.0040 | 3.0363 | 0.0455 |
| 336.94 | 0.2518 | 0.5815 | 1.7891 | 1.0131 | 0.1562 | 328.06 | 0.9876 | 0.9830 | 1.0035 | 3.7596 | 0.0199 |
| 336.24 | 0.2766 | 0.6021 | 1.7206 | 1.0273 | 0.1696 | 328.09 | 0.9965 | 0.9918 | 1.0025 | 6.4204 | 0.0090 |

**Table 4 (Continued)**

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $G^E/RT$ | $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $G^E/RT$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | MTBE (1) + TAME (2) | | | | | | |
| 358.31 | 0.0180 | 0.0531 | 1.2758 | 0.9940 | −0.0015 | 341.22 | 0.4738 | 0.7064 | 1.0152 | 0.9745 | −0.0065 |
| 357.16 | 0.0438 | 0.1110 | 1.1279 | 0.9910 | −0.0034 | 340.23 | 0.5074 | 0.7365 | 1.0166 | 0.9652 | −0.0091 |
| 356.12 | 0.0670 | 0.1569 | 1.0699 | 0.9930 | −0.0020 | 339.44 | 0.5301 | 0.7521 | 1.0164 | 0.9772 | −0.0022 |
| 354.91 | 0.0950 | 0.2134 | 1.0583 | 0.9899 | −0.0038 | 338.73 | 0.5559 | 0.7709 | 1.0140 | 0.9785 | −0.0019 |
| 353.39 | 0.1287 | 0.2778 | 1.0574 | 0.9878 | −0.0035 | 337.57 | 0.5979 | 0.8016 | 1.0139 | 0.9730 | −0.0028 |
| 351.97 | 0.1650 | 0.3327 | 1.0248 | 0.9941 | −0.0009 | 336.94 | 0.6225 | 0.8159 | 1.0096 | 0.9824 | −0.0007 |
| 350.23 | 0.2068 | 0.4010 | 1.0316 | 0.9906 | −0.0010 | 336.09 | 0.6531 | 0.8381 | 1.0135 | 0.9678 | −0.0026 |
| 348.90 | 0.2440 | 0.4524 | 1.0219 | 0.9900 | −0.0023 | 334.85 | 0.7052 | 0.8707 | 1.0116 | 0.9490 | −0.0073 |
| 347.59 | 0.2799 | 0.5021 | 1.0241 | 0.9844 | −0.0046 | 333.78 | 0.7478 | 0.8937 | 1.0110 | 0.9463 | −0.0058 |
| 346.38 | 0.3126 | 0.5432 | 1.0251 | 0.9828 | −0.0041 | 332.83 | 0.7884 | 0.9140 | 1.0092 | 0.9432 | −0.0052 |
| 345.29 | 0.3443 | 0.5815 | 1.0265 | 0.9772 | −0.0061 | 331.79 | 0.8340 | 0.9346 | 1.0068 | 0.9482 | −0.0032 |
| 344.33 | 0.3735 | 0.6119 | 1.0225 | 0.9780 | −0.0056 | 330.89 | 0.8728 | 0.9512 | 1.0064 | 0.9532 | −0.0005 |
| 343.40 | 0.4024 | 0.6418 | 1.0214 | 0.9751 | −0.0065 | 329.59 | 0.9341 | 0.9753 | 1.0037 | 0.9754 | 0.0018 |
| 342.46 | 0.4321 | 0.6676 | 1.0158 | 0.9816 | −0.0037 | 328.84 | 0.9696 | 0.9882 | 1.0028 | 1.0376 | 0.0038 |

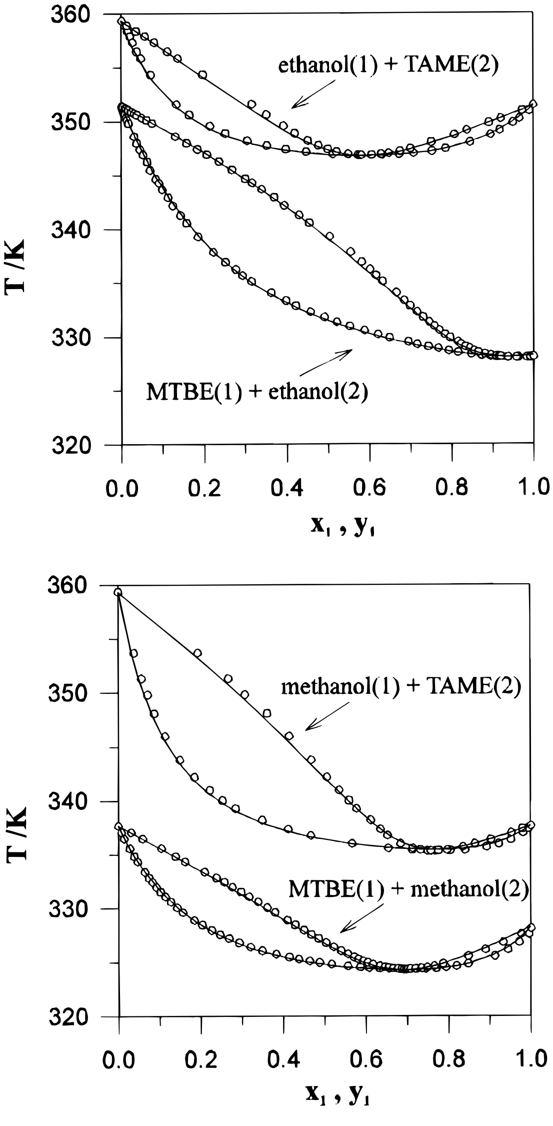

**Figure 2.** For the ether + alcohol systems studied, the experimental vapor−liquid equilibrium data (○) and the corresponding UNIQUAC correlation (—).

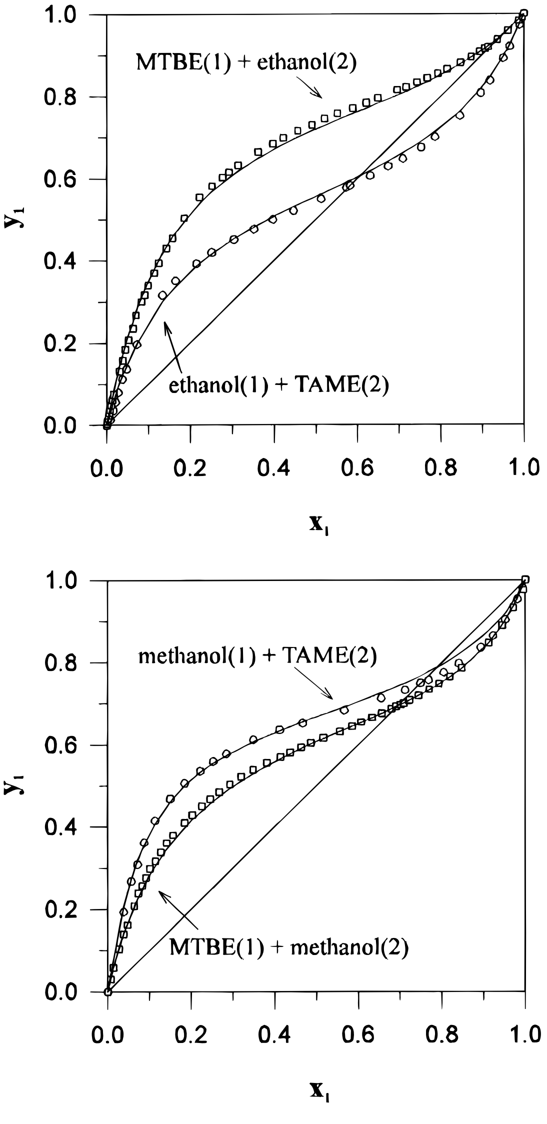

**Figure 3.** For the ether + alcohol systems studied, the experimental vapor−liquid equilibrium data (○, □) and the corresponding UNIFAC−Dortmund prediction (—).

(0.0048 for MTBE + methanol, 0.0053 for MTBE + ethanol, 0.0108 for methanol + TAME, 0.0092 for ethanol + TAME, and 0.0073 for MTBE + TAME) confirm consistency.

All the binary ether + alcohol systems studied formed azeotropes at the minimum boiling point. These boiling points and the corresponding compositions are listed in Table 5.

***Correlation.*** Correlation of the experimental ($P$, $T$, $x$, $y$) results was performed by a nonlinear regression method based on the maximum-likelihood principle using the programs published by Prausnitz *et al.* (1980). The models used for the liquid phase activity coefficients were Wilson's equation (Wilson, 1964), the NRTL equation (Renon and Prausnitz, 1968), setting the nonrandomness parameter $\alpha$ to different values and selecting the value giving the best correlation, and the UNIQUAC equation (Abrams and Prausnitz, 1975) with the area parameter $q'$ set to 0.92 for methanol and to 0.96 for ethanol (Anderson and Prausnitz, 1978). Table 6 lists the model parameters fitted for each system, together with the root mean square deviations in

**Table 5. Compositions (Mole Fraction) and Boiling Points of the Azeotropes Formed by the Binary Ether + Alcohol Systems**

| system | $x_1$ | $T_b$/K |
|---|---|---|
| MTBE (1) + methanol (2) | 0.691 | 324.32 |
| MTBE (1) + ethanol (2) | 0.937 | 328.06 |
| methanol (1) + TAME (2) | 0.749 | 335.34 |
| ethanol (1) + TAME (2) | 0.582 | 346.81 |

**Table 6. Parameters and Root Mean Square Deviations ($\sigma$) for the Wilson, NRTL, and UNIQUAC Models**

| model | parameters$^a$ | $\sigma(T)$/K | $\sigma(x)$ | $\sigma(y)$ | $\sigma(P)$/kPa |
|---|---|---|---|---|---|
| | Methanol (1) + TAME (2) | | | | |
| Wilson | $\Delta\lambda_{12} = 5399.45$, $\Delta\lambda_{21} = -632.12$ | 0.20 | 0.0038 | 0.0059 | 0.004 |
| NRTL ($\alpha = 0.47$) | $\Delta g_{12} = 2700.18$, $\Delta g_{21} = 1981.29$ | 0.20 | 0.0040 | 0.0059 | 0.004 |
| UNIQUAC | $\Delta u_{12} = -863.07$, $\Delta u_{21} = 6227.17$ | 0.20 | 0.0039 | 0.0060 | 0.004 |
| | Ethanol (1) + TAME (2) | | | | |
| Wilson | $\Delta\lambda_{12} = 4462.73$, $\Delta\lambda_{21} = -590.74$ | 0.12 | 0.0033 | 0.0033 | 0.003 |
| NRTL ($\alpha = 0.1$) | $\Delta g_{12} = 1289.17$, $\Delta g_{21} = 2047.02$ | 0.11 | 0.0032 | 0.0029 | 0.002 |
| UNIQUAC | $\Delta u_{12} = -1546.49$, $\Delta u_{21} = -6445.36$ | 0.12 | 0.0032 | 0.0030 | 0.003 |
| | MTBE (1) + Methanol (2) | | | | |
| Wilson | $\Delta\lambda_{12} = -1492.77$, $\Delta\lambda_{21} = 5505.18$ | 0.10 | 0.0026 | 0.0023 | 0.002 |
| NRTL ($\alpha = 0.47$) | $\Delta g_{12} = 2373.37$, $\Delta g_{21} = 1582.18$ | 0.10 | 0.0030 | 0.0024 | 0.002 |
| UNIQUAC | $\Delta u_{12} = 6067.59$, $\Delta u_{21} = -1066.92$ | 0.09 | 0.0025 | 0.0020 | 0.002 |
| | MTBE (1) + Ethanol (2) | | | | |
| Wilson | $\Delta\lambda_{12} = -1371.85$, $\Delta\lambda_{21} = 4826.28$ | 0.12 | 0.0030 | 0.0027 | 0.002 |
| NRTL ($\alpha = 0.47$) | $\Delta g_{12} = 2594.20$, $\Delta g_{21} = 797.55$ | 0.12 | 0.0032 | 0.0037 | 0.002 |
| UNIQUAC | $\Delta u_{12} = 6437.83$, $\Delta u_{21} = -1703.89$ | 0.10 | 0.0024 | 0.0026 | 0.002 |
| | MTBE (1) + TAME (2) | | | | |
| Wilson | $\Delta\lambda_{12} = -1781.13$, $\Delta\lambda_{21} = 2995.15$ | 0.09 | 0.0029 | 0.0027 | 0.002 |
| NRTL ($\alpha = 0.1$) | $\Delta g_{12} = 7379.27$, $\Delta g_{21} = -5834.62$ | 0.08 | 0.0028 | 0.0024 | 0.002 |
| UNIQUAC | $\Delta u_{12} = 1921.46$, $\Delta u_{21} = -1419.34$ | 0.08 | 0.0028 | 0.0024 | 0.002 |

All energy parameters in J·mol$^{-1}$.

**Table 7. Root Mean Square Deviations ($\sigma$) between the Experimental Boiling Temperatures ($T_b$) and Vapor Phase Compositions ($y$) and Those Calculated by the ASOG, UNIFAC, and Modified UNIFAC Methods**

| | ASOG | | UNIFAC | | UNIFAC−Dortmund | | UNIFAC−Lyngby | |
|---|---|---|---|---|---|---|---|---|
| system | $\sigma$ ($T_b$/K) | $\sigma$ ($y$) | $\sigma$ ($T_b$/K) | $\sigma$ ($y$) | $\sigma$ ($T_b$/K) | $\sigma$ ($y$) | $\sigma$ ($T_b$/K) | $\sigma$ ($y$) |
| methanol (1) + TAME (2) | 1.86 | 0.0262 | 0.67 | 0.0158 | 0.38 | 0.0124 | 0.56 | 0.0095 |
| ethanol (1) + TAME (2) | 0.40 | 0.0104 | 0.23 | 0.0094 | 0.15 | 0.0109 | 0.47 | 0.0108 |
| MTBE (1) + methanol (2) | 1.78 | 0.0300 | 0.48 | 0.0135 | 0.12 | 0.0070 | 0.48 | 0.0068 |
| MTBE (1) + ethanol (2) | 0.44 | 0.0048 | 0.43 | 0.0081 | 0.35 | 0.0100 | 0.75 | 0.0154 |
| MTBE (1) + TAME (2) | 0.23 | 0.0090 | 0.18 | 0.0086 | 0.15 | 0.0083 | 0.16 | 0.0084 |

, $x$, and $y$. Figure 2 compares the UNIQUAC temperature−composition curves with the corresponding experimental data.

***Prediction.*** The VLE data were predicted using the ASOG (Kojima and Tochigi, 1979; Tochigi *et al.*, 1990), UNIFAC (Fredenslund *et al.*, 1977), UNIFAC−Dortmund (Weidlich and Gmehling, 1987; Gmehling *et al.*, 1993), and UNIFAC−Lyngby (Larsen *et al.*, 1987) group contribution methods to calculate the liquid phase activity coefficients. For the UNIFAC method, the structural and group interaction parameters recommended by Gmehling *et al.* (1982) were employed. Table 7 lists the root mean square deviations between the experimental VLE data and those predicted by each model. Figure 3 compares the VLE data predicted using the UNIFAC−Dortmund method with the experimental data for the ether + alcohol mixtures studied.

## Discussion

The VLE data obtained for the binary ether + alcohol systems and the MTBE + TAME system were all shown to be thermodynamically consistent. Nonetheless, the fact that mixtures containing TAME consistently gave higher deviations suggests that revision of some of the molecular parameters for TAME (gyration radius, dipole moment, solvation parameters, etc.) used in our calculations is called for.

The Wilson, NRTL, and UNIQUAC models were adequate for correlation of the VLE data obtained, although, on average, the UNIQUAC model gave very slightly smaller deviations in $T$, $x$, and $y$. Likewise, the VLE data were generally satisfactorily predicted by the ASOG, UNIFAC, and modified UNIFAC group contribution methods, although the ASOG method gave somewhat larger deviations, specially in the equilibrium temperatures for the mixtures containing methanol.

## Acknowledgment

This work was partly financed by the DGICYT (Spain) under Project PB94-0658.

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Received for review December 18, 1995. Accepted March 19, 1996.⊗

JE950323O

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⊗ Abstract published in *Advance ACS Abstracts*, May 1, 1996.