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ISOBARIC VAPOR–LIQUID EQUILIBRIA AND DENSITIES FOR THE SYSTEM METHYL 1,1-DIMETHYLETHYL ETHER + 2-PROPANOL

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Vapor–liquid equilibrium data at 50, 75 and 94 kPa have been determined for the binary system methyl 1,1-dimethylethyl ether + 2-propanol, in the temperature range 308–344 K. The measurements were made in an equilibrium still with circulation of both the vapor and liquid phases. Excess volumes have been also determined from density measurements using a vibrating tube densimeter at 298.15 K. The system exhibits positive deviation from ideal behavior and does not present azeotropy within the range of pressures studied. The excess volume of the system is negative over the whole mole fraction range. The activity coefficients and boiling points of the solutions were well correlated with the mole fraction by the Wohl, Wilson, UNIQUAC, and NRTL equations. Excess volume data were correlated using the Redlich–Kister expansion.

Keywords: Vapor–liquid equilibrium; Fuel oxygenating additive; Unleaded gasoline; Ether; MTBE

INTRODUCTION

Amendments of the U.S. Clean Air in 1990 have mandated that new gasoline formulations, with oxygenated gasolines being supplied

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particularly during the winter. Methyl 1,1-dimethylethyl ether (MTBE) has been largely used for high-performance premium gasolines and, in recent years, mixtures of ethers with alcohols have been considered for blending with gasoline. In general, additives like ethers and alcohols have an appropriate antiknock capability and are considered environmental protection substances. However, MTBE is being phased out because of the evidence that it accumulates in surface and underground water. There is still need to investigate the phase equilibrium properties of oxygenated mixtures that may comply with the environmental legislation.

Complete vapor–liquid equilibrium (VLE) data have not been reported for the system MTBE + 2-propanol, only the limiting activity coefficient γ_i^∞ for MTBE in 2-propanol at 323.15 K has been measured by Delcros *et al.* [1], using the comparative ebulliometry technique. According to their results, the system under consideration deviates positively from ideal behavior, when concentrated in ether, yielding $\gamma_i^\infty \sim 2.56$. Delcros *et al.*, also predicted γ_i^∞ of 2-propanol in MTBE with the DISQUAC [2,3] ($\gamma_i^\infty \sim 2.30$) and the UNIFAC-Dortmund [4] ($\gamma_i^\infty \sim 1.86$) methods. Nagata and Tamura [5] have measured the excess enthalpy of the system in question, obtaining positive values for the whole range of concentrations, and with a maximum value of 800 J mol^{-1} .

VLE data of oxygenated mixtures are important for predicting the vapor phase concentration that would be in equilibrium with hydrocarbon mixtures. In addition, the VLE data of ethers and alcohols is also important for the dehydration of alcohols by means of azeotropic distillation technologies. The present work was undertaken to measure isobaric VLE data and densities for the title system for which no complete VLE data are available.

EXPERIMENTAL SECTION

Purity of Materials

MTBE (99.9 mass%) was purchased from Aldrich and 2-propanol (99.9 mass%) was purchased from Merck. 2-propanol was used after a small quantity of water was removed with 3A molecular sieves. Then, both reagents were used without further purification, after gas

TABLE I Mole% GLC purities (mass%), refractive index n_D at Na D line, and normal boiling points T_b of pure components

| Component (purity/mass%) | n_D (293.15 K) | | Density (g cm^{-3}) (298.15 K) | | T_b (101.3 kPa)/K | |
|-----------------------------|----------------------|----------------------|--|----------------------|------------------------|---------------------|
| | <i>exptl.</i> | <i>lit.</i> | <i>exptl.</i> | <i>lit.</i> | <i>exptl.</i> | <i>lit.</i> |
| | MTBE (99.7+) | 1.36912 ^a | 1.3690 ^b | 0.73555 ^a | 0.73528 ^c | 328.18 ^a |
| 2-propanol (99.9+) | 1.37731 ^a | 1.3772 ^c | 0.78107 ^a | 0.78126 ^c | 355.40 ^a | 355.39 ^f |

^aMeasured; ^bTRC Tables, a-6040 [21]; ^cRiddick *et al.* [22]; ^dAucejo *et al.* [7]; ^eBallard and van Winkle [23]; ^fAmbrose and Sprake [8].

chromatography failed to show any significant impurity. The properties and purity of the pure components, as determined by GLC, appear in Table I. Appropriate precautions were taken when handling MTBE in order to avoid peroxide formation.

Apparatus and Procedure

An all-glass (VLE) apparatus model 601, manufactured by Fischer Labor und Verfahrenstechnik (Germany), was used in the equilibrium determinations. In this circulation-method apparatus, the mixture is heated to its boiling point by a 250 W immersion heater. The vapor–liquid mixture flows through an extended contact line (Cottrell pump) that guarantees an intense phase exchange and then enters to a separation chamber whose construction prevents an entrainment of liquid particles into the vapor phase. The separated gas and liquid phases are condensed and returned to a mixing chamber, where they are stirred by a magnetic stirrer, and returned again to the immersion heater. The temperature in the VLE still has been determined with a Systemtechnik S1224 digital temperature meter, and a Pt 100 Ω probe calibrated at the Swedish Statens Provningsanstält. The accuracy is estimated as ± 0.02 K. The total pressure of the system is controlled by a vacuum pump capable of work under vacuum up to 0.25 kPa. The pressure has been measured with a Fischer pressure transducer calibrated against an absolute mercury-in-glass manometer (22-mm diameter precision tubing with cathetometer reading), the overall accuracy is estimated as ± 0.03 kPa. On the average the system reaches equilibrium conditions after 2–3 h operation. Samples, taken by syringing 1.0 μL after the system had

achieved equilibrium, were analyzed by gas chromatography on a Varian 3400 apparatus provided with a thermal conductivity detector and a Thermo Separation Products model SP4400 electronic integrator. The column was 3 m long and 0.3 cm in diameter, packed with SE-30. Column, injector and detector temperatures were (323.15, 383.15, 473.15) K respectively. Good separation was achieved under these conditions, and calibration analyses were carried out to convert the peak ratio to the mass composition of the sample. The pertinent polynomial fit had a correlation coefficient R^2 better than 0.99. At least three analyses were made of each sample. Concentration measurements were accurate to better than ± 0.001 in mole fraction.

For density measurements, the samples were prepared by mass on an analytical balance (Chyo Balance Corp., Japan) with an accuracy of $\pm 10^{-4}$ g. Densities of the pure components and their mixtures were measured using a DMA 5000 densimeter (Anton Paar, Austria) with an accuracy of 5×10^{-6} g cm $^{-3}$. The density determination is based on measuring the period of oscillation of a vibrating U-shaped tube filled with the liquid sample. The temperature of the thermostat, provided with the apparatus, was maintained constant to within ± 0.01 K.

RESULTS

Vapor-Liquid Equilibria

The equilibrium temperature T , liquid-phase x and vapor-phase y mole fraction measurements at $P = 50, 75$ and 94 kPa are reported in Table II-IV and in Figs. 1-4, together with the activity coefficients γ_i that were calculated from the following equation [6]:

$$\ln \gamma_i = \ln \frac{y_i P}{x_i P_i^0} + \frac{(B_{ii} - V_i^L)(P - P_i^0)}{RT} + y_j^2 \frac{\delta_{ij} P}{RT} \quad (1)$$

where P is the total pressure, V_i^L is the molar liquid volume of component i , B_{ii} and B_{jj} are the second virial coefficients of the pure gases, B_{ij} the cross second virial coefficient and

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

TABLE II Experimental VLE data for MTBE (1) + 2-propanol (2) at 50.00 kPa

| T (K) | x_1 | y_1 | γ_1 | γ_2 | $-B_{11}$ ($\text{cm}^3 \text{mol}^{-1}$) | $-B_{22}$ ($\text{cm}^3 \text{mol}^{-1}$) | $-B_{12}$ ($\text{cm}^3 \text{mol}^{-1}$) |
|---------|-------|-------|------------|------------|--|--|--|
| 338.78 | 0.000 | 0.000 | | 1.000 | 1055 | 1324 | 1060 |
| 335.40 | 0.038 | 0.180 | 1.917 | 0.992 | 1081 | 1383 | 1086 |
| 332.58 | 0.074 | 0.301 | 1.792 | 1.000 | 1104 | 1434 | 1108 |
| 329.90 | 0.112 | 0.412 | 1.760 | 0.995 | 1126 | 1487 | 1130 |
| 324.64 | 0.206 | 0.586 | 1.609 | 1.012 | 1173 | 1598 | 1175 |
| 321.95 | 0.260 | 0.663 | 1.576 | 1.012 | 1198 | 1660 | 1200 |
| 320.17 | 0.307 | 0.708 | 1.513 | 1.026 | 1215 | 1704 | 1216 |
| 318.85 | 0.347 | 0.728 | 1.439 | 1.086 | 1228 | 1737 | 1229 |
| 317.64 | 0.387 | 0.758 | 1.400 | 1.097 | 1240 | 1768 | 1240 |
| 316.44 | 0.433 | 0.786 | 1.353 | 1.118 | 1252 | 1800 | 1252 |
| 314.59 | 0.521 | 0.825 | 1.259 | 1.195 | 1271 | 1851 | 1270 |
| 313.79 | 0.566 | 0.843 | 1.218 | 1.236 | 1279 | 1874 | 1279 |
| 312.85 | 0.624 | 0.862 | 1.168 | 1.321 | 1289 | 1901 | 1288 |
| 312.03 | 0.681 | 0.879 | 1.124 | 1.429 | 1298 | 1926 | 1297 |
| 310.72 | 0.782 | 0.912 | 1.065 | 1.636 | 1313 | 1965 | 1310 |
| 310.04 | 0.838 | 0.931 | 1.040 | 1.794 | 1320 | 1987 | 1318 |
| 309.28 | 0.900 | 0.951 | 1.017 | 2.155 | 1329 | 2011 | 1326 |
| 308.80 | 0.945 | 0.969 | 1.004 | 2.549 | 1334 | 2026 | 1331 |
| 308.24 | 1.000 | 1.000 | 1.000 | | 1340 | 2044 | 1337 |

TABLE III Experimental VLE data for MTBE (1) + 2-propanol (2) at 75.00 kPa

| T (K) | x_1 | y_1 | γ_1 | γ_2 | $-B_{11}$ ($\text{cm}^3 \text{mol}^{-1}$) | $-B_{22}$ ($\text{cm}^3 \text{mol}^{-1}$) | $-B_{12}$ ($\text{cm}^3 \text{mol}^{-1}$) |
|---------|-------|-------|------------|------------|--|--|--|
| 348.07 | 0.000 | 0.000 | | 1.000 | 987 | 1182 | 994 |
| 345.39 | 0.033 | 0.142 | 1.938 | 0.991 | 1006 | 1221 | 1013 |
| 342.39 | 0.075 | 0.277 | 1.809 | 0.992 | 1027 | 1266 | 1034 |
| 339.66 | 0.118 | 0.388 | 1.741 | 0.991 | 1048 | 1310 | 1054 |
| 334.87 | 0.209 | 0.553 | 1.613 | 1.000 | 1085 | 1392 | 1090 |
| 332.67 | 0.261 | 0.621 | 1.550 | 1.005 | 1103 | 1433 | 1108 |
| 330.93 | 0.311 | 0.670 | 1.481 | 1.018 | 1118 | 1466 | 1122 |
| 329.65 | 0.348 | 0.697 | 1.432 | 1.049 | 1129 | 1492 | 1132 |
| 328.44 | 0.388 | 0.727 | 1.392 | 1.068 | 1139 | 1516 | 1143 |
| 326.58 | 0.468 | 0.771 | 1.298 | 1.128 | 1155 | 1556 | 1159 |
| 324.83 | 0.522 | 0.803 | 1.282 | 1.177 | 1171 | 1594 | 1174 |
| 324.64 | 0.567 | 0.818 | 1.210 | 1.212 | 1173 | 1598 | 1175 |
| 323.56 | 0.627 | 0.841 | 1.165 | 1.297 | 1183 | 1623 | 1185 |
| 322.59 | 0.680 | 0.862 | 1.137 | 1.379 | 1192 | 1645 | 1194 |
| 322.15 | 0.726 | 0.877 | 1.099 | 1.468 | 1196 | 1656 | 1198 |
| 321.65 | 0.778 | 0.896 | 1.066 | 1.572 | 1201 | 1668 | 1202 |
| 320.93 | 0.839 | 0.922 | 1.041 | 1.687 | 1208 | 1685 | 1209 |
| 320.24 | 0.902 | 0.945 | 1.016 | 2.026 | 1214 | 1702 | 1216 |
| 319.77 | 0.950 | 0.967 | 1.003 | 2.442 | 1219 | 1714 | 1220 |
| 319.33 | 1.000 | 1.000 | 1.000 | | 1223 | 1725 | 1224 |

TABLE IV Experimental VLE data for MTBE (1) + 2-propanol (2) at 94.00 kPa

| T (K) | x_1 | y_1 | γ_1 | γ_2 | $-B_{11}$ ($\text{cm}^3\text{mol}^{-1}$) | $-B_{22}$ ($\text{cm}^3\text{mol}^{-1}$) | $-B_{12}$ ($\text{cm}^3\text{mol}^{-1}$) |
|---------|-------|-------|------------|------------|---|---|---|
| 353.53 | 0.000 | 0.000 | | 1.000 | 951 | 1110 | 958 |
| 351.05 | 0.031 | 0.121 | 1.877 | 1.001 | 967 | 1142 | 974 |
| 347.93 | 0.079 | 0.272 | 1.799 | 0.989 | 988 | 1184 | 995 |
| 345.54 | 0.121 | 0.373 | 1.720 | 0.986 | 1005 | 1218 | 1012 |
| 343.70 | 0.152 | 0.435 | 1.680 | 0.995 | 1018 | 1246 | 1024 |
| 340.85 | 0.211 | 0.531 | 1.601 | 1.003 | 1039 | 1290 | 1045 |
| 336.96 | 0.308 | 0.642 | 1.485 | 1.037 | 1069 | 1355 | 1074 |
| 335.84 | 0.350 | 0.677 | 1.424 | 1.047 | 1077 | 1375 | 1083 |
| 334.63 | 0.397 | 0.712 | 1.369 | 1.064 | 1087 | 1396 | 1092 |
| 332.14 | 0.477 | 0.758 | 1.308 | 1.156 | 1108 | 1443 | 1112 |
| 331.14 | 0.530 | 0.787 | 1.260 | 1.187 | 1116 | 1462 | 1120 |
| 330.29 | 0.573 | 0.806 | 1.226 | 1.239 | 1123 | 1479 | 1127 |
| 329.49 | 0.626 | 0.828 | 1.182 | 1.303 | 1130 | 1495 | 1134 |
| 328.28 | 0.722 | 0.866 | 1.113 | 1.448 | 1140 | 1520 | 1144 |
| 328.26 | 0.726 | 0.868 | 1.110 | 1.448 | 1141 | 1520 | 1144 |
| 327.93 | 0.778 | 0.889 | 1.072 | 1.528 | 1143 | 1527 | 1147 |
| 327.37 | 0.839 | 0.912 | 1.038 | 1.717 | 1148 | 1539 | 1152 |
| 326.73 | 0.903 | 0.944 | 1.019 | 1.872 | 1154 | 1552 | 1157 |
| 326.29 | 0.950 | 0.966 | 1.005 | 2.254 | 1158 | 1562 | 1161 |
| 325.92 | 1.000 | 1.000 | 1.000 | | 1161 | 1570 | 1164 |

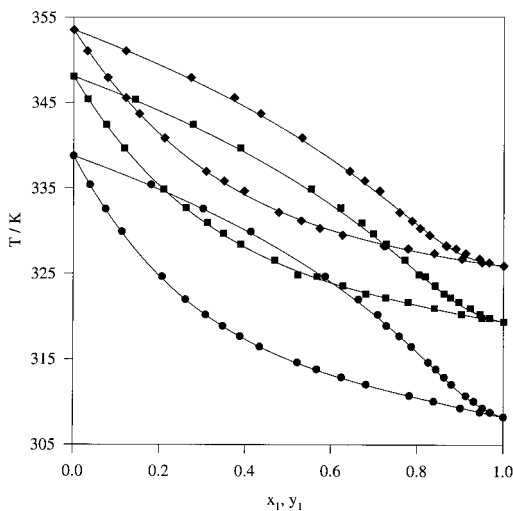


FIGURE 1 Boiling temperature diagram for the system MTBE (1) + 2-propanol (2). Experimental data at (●) 50.00 kPa, (■) 75.00 kPa and (◆) 94.00 kPa; (—) smoothed by the NRTL model, with the parameters given in Table VIII.

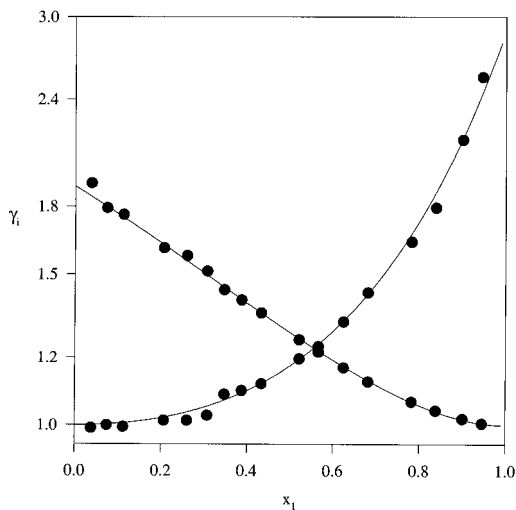


FIGURE 2 Activity coefficients for the system MTBE (1) +2-propanol (2) at 50.00 kPa. (●) experimental data; (—) smoothed by the NRTL model, with the parameters given in Table VIII.

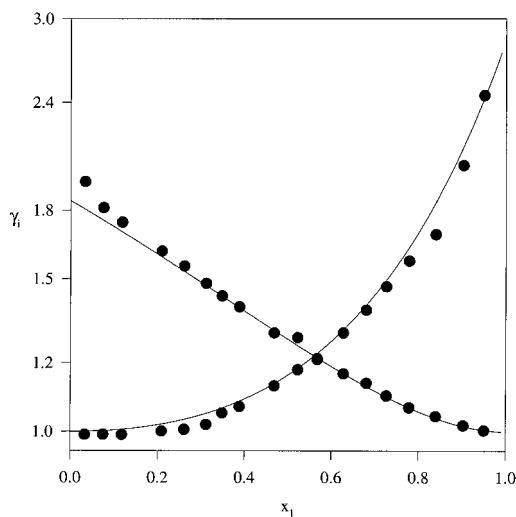


FIGURE 3 Activity coefficients for the system MTBE (1) +2-propanol (2) at 75.00 kPa. (●) experimental data; (—) smoothed by the NRTL model, with the parameters given in Table VIII.

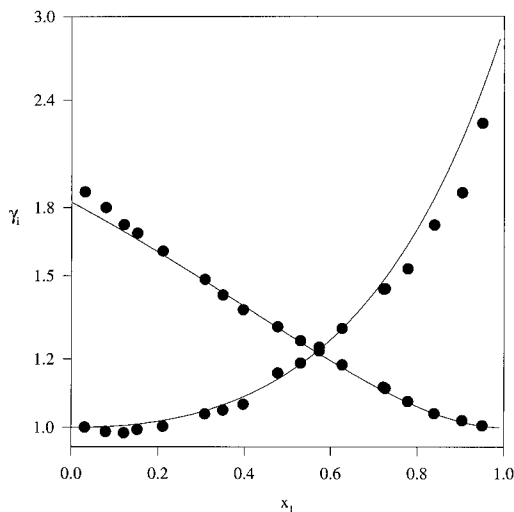


FIGURE 4 Activity coefficient for the system MTBE (1) + 2-propanol (2) at 94.00 kPa. (●) experimental data; (—) smoothed by the NRTL model, with the parameters given in Table VIII.

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. Equation (1) is valid from low to moderate pressure, when the virial equation of state truncated after the second coefficient is adequate to describe the vapor phase of the pure components and their mixtures, and liquid volumes of the pure components are incompressible over the pressure range under consideration. The pure component vapor pressures P_i^0 for MTBE and 2-propanol were determined experimentally in the same still used for VLE determinations and pertinent results are presented in Table V. The measured vapor pressures were then correlated using the Antoine equation:

$$\log(P_i^0/kPa) = A_i - \frac{B_i}{(T/K) - C_i} \quad (3)$$

where the Antoine constants A_i , B_i , and C_i are reported in Table VI. The experimental vapor pressures were fitted with an average percentage deviation [$MADP$] of 0.03% for MTBE and 2-propanol. In addition, the parameters presented in Table VI predict very well the

TABLE V Experimental vapor pressure data for pure components

| <i>MTBE</i> | | <i>2-propanol</i> | |
|--------------|---------------|-------------------|---------------|
| <i>T</i> (K) | P_1^0 (kPa) | <i>T</i> (K) | P_2^0 (kPa) |
| 299.89 | 36.00 | 321.71 | 21.95 |
| 303.44 | 41.52 | 325.76 | 26.93 |
| 306.60 | 46.99 | 329.82 | 32.90 |
| 309.39 | 52.24 | 333.40 | 39.01 |
| 312.01 | 57.60 | 336.35 | 44.75 |
| 314.17 | 62.37 | 338.85 | 50.17 |
| 316.30 | 67.35 | 340.95 | 55.07 |
| 318.46 | 72.73 | 342.99 | 60.27 |
| 320.67 | 78.61 | 345.16 | 66.24 |
| 322.50 | 83.73 | 347.13 | 72.08 |
| 324.30 | 88.99 | 349.00 | 78.02 |
| 325.92 | 94.00 | 350.50 | 83.04 |
| 328.18 | 101.33 | 352.22 | 89.13 |
| | | 353.54 | 94.01 |
| | | 355.40 | 101.33 |

TABLE VI Antoine Coefficients, Eq. (3)

| <i>Compound</i> | A_i | B_i | C_i |
|-------------------------|---------|-----------|--------|
| MTBE ^a | 6.07009 | 1155.1624 | 43.965 |
| 2-propanol ^a | 6.90592 | 1382.0250 | 73.362 |

^aparameters calculated from the experimental data presented in Table V.

experimental vapor pressures reported by Aucejo *et al.* [7] for MTBE [$MADP=0.18\%$] and by Ambrose and Sprake [8] for 2-propanol [$MADP=0.03\%$], as can be confirmed in Fig. 5. The molar virial coefficients B_{ii} and B_{ij} were estimated by the method of Hayden and O'Connell [9] using the molecular parameters suggested by the authors and assuming the association parameter η to be zero. Physical properties of all components were taken from *DIPPR* [10]. The last two terms in Eq. (1), particularly the second one that expresses the correction due to the non-ideal behavior of the vapor phase, contributed less than 1% to activity coefficients. In general, their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Tables II–IV and are estimated accurate to within $\pm 2\%$. The result reported in these tables indicate that for the range of pressure studied, the system MTBE (1) + 2-propanol (2) deviates positively from ideal behavior and does not exhibit azeotropic

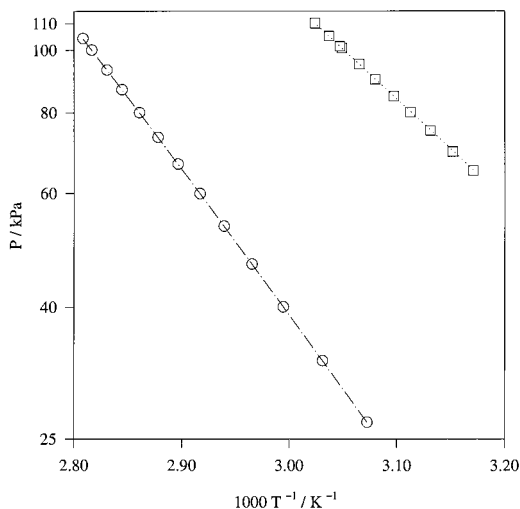


FIGURE 5 Comparison of correlated vapor pressure with other references. (\square) experimental data reported by Aucejo *et al.* [7] for MTBE; (\circ) experimental data reported by Ambrose and Sprake [8] for 2-propanol. Predicted by Eq. 3 and parameters given in Table VI for MTBE (...) and for 2-propanol (-.-).

behavior. However, inspection of Fig. 1 in the range of concentrated MTBE suggests that an azeotrope may appear at higher pressures. The possibility of azeotropic behavior has not been confirmed yet in this research due to the limitations of our apparatus for operating at superatmospheric pressures.

The VLE data reported in Table II–IV, were found to be thermodynamically consistent by the point-to-point method of Van Ness *et al.* [11] as modified by Fredenslund *et al.* [12] ($\Delta y < 0.01$). In all cases, the consistency criteria were met by fitting the data to a three-parameter Legendre polynomial. Pertinent consistency statistics are presented in Table VII.

The VLE data were also correlated with the Wohl, NRTL, Wilson, and UNIQUAC equation [13] and predicted by the UNIFAC group contribution method [12,14]. The parameters of these models were obtained by minimizing the following objective function (*OF*):

$$OF = \sum_{i=1}^N \left(\left| \frac{P_i^{\text{exptl}} - P_i^{\text{calc}}}{P_i^{\text{exptl}}} + \left| y_i^{\text{exptl}} - y_i^{\text{calc}} \right| \right)^2 \quad (5)$$

TABLE VII Consistency test statistics for the binary system MTBE (1) + 2-propanol (2)

| Pressure level (kPa) | N_p ^a | $100 \times \Delta y$ ^b | ΔP ^c (kPa) |
|----------------------|--------------------|------------------------------------|-------------------------------|
| 50.00 | 3 | 0.3 | 0.10 |
| 75.00 | 3 | 0.4 | 0.34 |
| 94.00 | 3 | 0.5 | 0.47 |

^aNumber of parameters for the Legendre polynomial used in consistency; ^bAverage absolute deviation in vapor phase mole fractions $\Delta y = 1/N \sum_{i=1}^N |y_i^{\text{exptl}} - y_i^{\text{calc}}|$ (N : number of data points); ^cAverage absolute deviation in pressure $\Delta P = 1/N \sum_{i=1}^N |P_i^{\text{exptl}} - P_i^{\text{calc}}|$.

 TABLE VIII Parameters and prediction statistics for different G^E models

| Model | P (kPa) | A_{12} | A_{21} | α_{12} | Bubble-point pressures | | Dew-point pressures | |
|------------------------|-----------|----------|----------|--------------------|-----------------------------|-------------------------|---------------------|-------------------------|
| | | | | | ΔP (%) ^f | $100 \times \Delta y_i$ | ΔP (%) | $100 \times \Delta x_i$ |
| Wohl | 94.00 | 0.603 | 1.007 | 0.396 ^e | 0.48 | 0.4 | 0.78 | 0.6 |
| | 75.00 | 0.612 | 0.980 | 0.396 ^e | 0.43 | 0.4 | 0.77 | 0.6 |
| | 50.00 | 0.637 | 0.953 | 0.396 ^e | 0.24 | 0.3 | 0.50 | 0.4 |
| NRTL ^a | 94.00 | 3744.81 | -783.80 | 0.3 | 0.50 | 0.4 | 0.81 | 0.7 |
| | 75.00 | 3446.86 | -636.86 | 0.3 | 0.37 | 0.5 | 0.84 | 0.7 |
| | 50.00 | 3220.90 | -475.55 | 0.3 | 0.20 | 0.2 | 0.53 | 0.3 |
| Wilson ^{a,b} | 94.00 | -1480.72 | 4499.72 | | 0.60 | 0.4 | 0.91 | 0.6 |
| | 75.00 | -1368.54 | 4221.17 | | 0.32 | 0.4 | 0.81 | 0.6 |
| | 50.00 | -1230.46 | 4094.36 | | 0.36 | 0.2 | 0.57 | 0.4 |
| UNIQUAC ^{a,c} | 94.00 | 2278.35 | -1103.18 | | 0.55 | 0.4 | 0.86 | 0.6 |
| | 75.00 | 2116.75 | -1022.10 | | 0.30 | 0.4 | 0.76 | 0.6 |
| | 50.00 | 1956.98 | -915.89 | | 0.25 | 0.2 | 0.52 | 0.3 |
| UNIFAC ^d | 94.00 | | | | 1.81 | 0.9 | 1.89 | 1.7 |
| | 75.00 | | | | 2.05 | 0.8 | 2.46 | 1.6 |
| | 50.00 | | | | 2.20 | 0.7 | 2.07 | 1.1 |

^aparameters in J mol^{-1} , ^bliquid volumes have been estimated from the Rackett equation [20]; ^cmolecular parameters are those calculated from UNIFAC [12]; ^dcalculations based on original UNIFAC [12,14]; ^e q parameter for the Wohl's model; ^f $\Delta P = 100/N \sum_{i=1}^N |P_i^{\text{exptl}} - P_i^{\text{calc}}|/P_i^{\text{exptl}}$.

and are reported in Table VIII, together with the relative deviation of the vapor phase mole fraction. Inspection of the results given in Table VIII shows that all four models gave a reasonable fit of the binary systems, the best fit corresponding to the NRTL and UNIQUAC models. The capability of predicting simultaneously the vapor phase mole fraction and the equilibrium pressure was been used as the ranking factor. Table VIII shows also that the UNIFAC [14] model

does not predict accurately the VLE data of the systems reported in this work.

Excess Volume Data

The density ρ measurements at $T = 298.15$ K are reported in Table IX, together with the excess volumes V^E that were calculated from the following equation

$$V^E = \frac{1}{\rho} \sum_{i=1}^2 x_i M_i - \sum_{i=1}^2 x_i \frac{M_i}{\rho_i} \quad (6)$$

where ρ is the density of the mixture, ρ_i corresponds to the density of pure components, and M_i is the molecular weight. M_i values were taken from *DIPPR* [10]. The calculated excess volumes reported in Table IX are estimated accurate to within $\pm 10^{-3} \text{ cm}^3 \text{ mol}^{-1}$ and compared well with the data previously reported by Blanco *et al.* [15]. Table IX and Fig. 6 indicate that the excess volumes of the system MTBE (1) + 2-propanol (2) are negative, behavior that may be explained in terms of cross association between components, as

TABLE IX Densities and excess volumes for the binary system MTBE (1) + 2-propanol (2) at 298.15 K

| x_1 | ρ (g cm ⁻³) | $10^3 V^E$ (cm ³ mol ⁻¹) |
|--------|------------------------------|---|
| 0.0174 | 0.78005 | -20 |
| 0.0323 | 0.77918 | -36 |
| 0.0480 | 0.77825 | -50 |
| 0.0827 | 0.77625 | -81 |
| 0.1175 | 0.77434 | -115 |
| 0.1503 | 0.77257 | -143 |
| 0.2008 | 0.76988 | -179 |
| 0.2318 | 0.76828 | -199 |
| 0.2835 | 0.76564 | -224 |
| 0.3346 | 0.76309 | -241 |
| 0.4341 | 0.75838 | -264 |
| 0.4676 | 0.75683 | -264 |
| 0.5697 | 0.75233 | -258 |
| 0.6279 | 0.74987 | -246 |
| 0.6969 | 0.74705 | -225 |
| 0.7398 | 0.74533 | -204 |
| 0.8037 | 0.74286 | -171 |
| 0.8928 | 0.73949 | -107 |
| 0.9616 | 0.73697 | -45 |

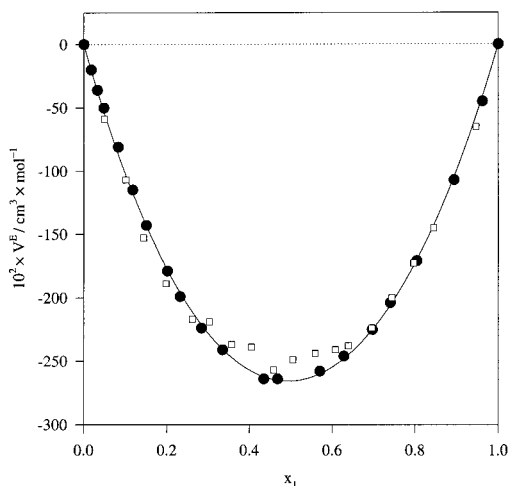
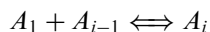


FIGURE 6

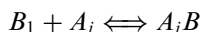
expected for specific interactions between the polar alkanol and the aprotic aliphatic ether.

An Association Approach to the Data

As follows from the chemical theory [16], positive deviations from ideal behavior, as observed in the present VLE data, may be explained in terms of dominant self association of 2-propanol. In addition, cross association between the components of the mixture may be expected for the functional groups of ether and alcohol. According to the association theory of Nath and Bender [17], it is possible to predict that the equilibrium association constants for 2-propanol and MTBE, at 323.15 K, are in the ratio 47:2. Consequently, the self-association of MTBE may be neglected. Considering the association theory of Nath and Bender [18], when a molecule A (for example, 2-propanol) self-associates according to the following scheme



and cross-associates with a non-associating molecule B (in this case, MTBE) according to



the chemical contribution to activity coefficients is given by the following relations

$$\ln \gamma_A^{\text{chem}} = \ln \left(\frac{\phi_{A_1}}{x_A \phi_{A_1}^0} \right) - \frac{v_A}{v_{AB}} + \frac{v_A}{v_A^0} \quad (7)$$

$$\ln \gamma_B^{\text{chem}} = \ln \left(\frac{\phi_{0B}}{x_B} \right) + 1 - \frac{v_B}{v_{AB}} \quad (8)$$

where v_i is the apparent molar volume of component i ; ϕ_{A_1} , ϕ_{0B} are the volume fractions of the monomer A_1 and of the unreacted component B , respectively. In Eqs. (7) and (8) V_{AB} corresponds to the molar volume of the solution which, in turn, may be calculated from

$$\frac{1}{v_{AB}} = \frac{\phi_{A_1}}{v_A(1 - K_A \phi_{A_1})} + \frac{\phi_{0B}}{v_B} \left[\frac{1 - (K_A - K_{AB})\phi_{A_1}}{1 - K_A \phi_{A_1}} \right] \quad (9)$$

where $\phi_{A_1}^0$ and V_A^0 are the volume fraction and the molar volume of pure component A present as the monomer, given as function of the self association equilibrium constant K_A as

$$\phi_{A_1}^0 = [(2K_A + 1) - (1 + 4K_A)^{1/2}] / 2K_A^2 \quad (10)$$

$$\frac{1}{v_A^0} = \frac{\phi_{A_1}^0}{v_A(1 - K_A \phi_{A_1}^0)} \quad (11)$$

ϕ_{A_1} , ϕ_{0B} can be calculated by solving simultaneously the following relations

$$\phi_A = [\phi_{A_1} / (1 - K_A \phi_{A_1})^2] \times [1 + K_{AB} \phi_{0B} v_A / v_B] \quad (12)$$

$$\phi_B = \phi_{0B} [1 - (K_A - K_{AB}) \phi_{A_1}] \times [1 - K_A \phi_{A_1}]^{-1} \quad (13)$$

where ϕ_A and ϕ_B are apparent volume fractions defined as

$$\phi_i = \frac{x_i v_i}{x_A v_A + x_B v_B} \quad (i = A, B) \quad (14)$$

K_A and K_{AB} are equilibrium constants for self and cross association, respectively, and in the approach of Nath and Bender, they depend

on temperature as follows

$$K_i = K_i^{323K} \exp \left[-\frac{h_i}{R} \left(\frac{1}{T/K} - \frac{1}{323.15} \right) \right] \quad (i = A, AB) \quad (15)$$

where h_i is the association enthalpy and K_i^{323K} corresponds to the equilibrium association constant, normalized to 323.15 K. The approach of Nath and Bender [17] provides a predictive scheme for calculating association enthalpies and equilibrium constants for pure fluids that self associate. In the case of cross association, both enthalpy and the normalized equilibrium constant must be calculated from VLE data. Once activity coefficients have been calculated from Eqs. (7) to (15), the chemical contribution to the excess energy may be evaluated as

$$\left(\frac{G^E}{RT} \right)^{\text{chem}} = x_A \ln \gamma_A^{\text{chem}} + x_B \ln \gamma_B^{\text{chem}} \quad (16)$$

while the excess Gibbs energy, including physical contributions, is given by

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT} \right)^{\text{phys}} + \left(\frac{G^E}{RT} \right)^{\text{chem}} \quad (17)$$

According to *DIPPR* [10], the critical volumes of 2-propanol and MTBE are in the ratio 1:1.5, indicating that molecular size may affect the excess energy of the system. The intrinsic excess model associated to the van der Waals equation of state, which is able to take into account size effects in phase equilibria, is the van Laar equation [19]

$$\left(\frac{G^E}{RT} \right)^{\text{phys}} = \frac{A_{ij}A_{ji}x_i x_j}{A_{ij}x_i + A_{ji}x_j} \quad (18)$$

Equation (18) has been used for modeling the physical contribution in Eq. (17). The association model proposed here depends on four parameters and on pure (apparent) fluid volumes V_A and V_B . The two parameters A_{ij} and A_{ji} are needed for modeling the physical

TABLE X Data treatment for the system MTBE (1) + 2-propanol (2) using the association approach in Eq. (17). Model parameters and correlation statistics

| <i>I. Parameters</i> | | | | | |
|-----------------------------------|-------------------------------|-------------------------|---------------------------------|-------------------------|---------------------|
| K_2^{323K} | h_2 (J mol ⁻¹) | K_{12}^{323K} | h_{12} (J mol ⁻¹) | A_{12} | A_{21} |
| 46.4 ^a | -16936 ^a | 14.240 ^b | -14847 ^b | 0.3898 ^b | 0.3411 ^b |
| <i>II. Correlation statistics</i> | | | | | |
| P (kPa) | <i>Bubble-point pressures</i> | | <i>Dew-point pressures</i> | | |
| | ΔP (%) | $100 \times \Delta y_4$ | ΔP (%) | $100 \times \Delta x_i$ | |
| 50.00 | 0.19 | 0.3 | 0.51 | 0.5 | |
| 75.00 | 0.75 | 0.3 | 0.97 | 0.5 | |
| 94.00 | 0.93 | 0.3 | 0.94 | 0.6 | |

^acalculated according to the approach of Nath and Bender [17] from saturation data.

^bcalculated from the experimental data presented in Tables II–IV.

contribution to the excess energy in Eq. (17). Additional parameters are the cross association enthalpy h_{AB} and the normalized equilibrium constant K_{AB}^{323K} . All these previous parameters have been calculated from the experimental VLE data presented in Tables II and IV, using the objective function indicated in Eq. (5). Pure fluid volumes have been estimated from the equation proposed by Rackett [20] and pure component physical data have been taken from *DIPPR* [10]. Pertinent parameters and statistics are reported in Table X, from which it is possible to conclude a good correlation of the data.

Acknowledgements

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NOMENCLATURE

- A_i Antoine's equation parameter, Eq. (3)
 B_i Antoine's equation parameter, Eq. (3)
 B_{ii} pure component second virial coefficient cm³ mol⁻¹
 B_{ij} cross second virial coefficient cm³ mol⁻¹
 C_i Antoine's equation parameter, Eq. (3)
 G^E excess Gibbs energy J mol⁻¹

| | | |
|-------------|---|-------------------------------|
| h | association enthalpy | J mol^{-1} |
| K | association constant | |
| P | absolute pressure | kPa |
| P° | pure component vapor pressure | kPa |
| R | universal gas constant | J mol K^{-1} |
| T | absolute temperature | K |
| V | volume | $\text{cm}^3 \text{mol}^{-1}$ |
| x, y | mole fractions of the liquid and vapor phases | |

Greek

| | | |
|---------------|------------------------------|-------------------------------|
| δ_{ij} | parameter defined in Eq. (2) | $\text{cm}^3 \text{mol}^{-1}$ |
| γ | activity coefficient | |
| ρ | density | g cm^{-3} |
| ϕ | volume fraction | |

Superscripts

| | |
|------|----------------------------------|
| E | excess property |
| L | pertaining to the liquid phase |
| 0 | reference state (pure component) |
| chem | chemical contribution |
| phys | physical contribution |

Subscripts

| | |
|--------|--------------------------------|
| i, j | component, i, j respectively |
|--------|--------------------------------|

References

- [1] S. Delcros, J.-P.E. Grolier, V. Dohnal and D. Fenclová (1995). *Chem. Engng. Sci.*, **50**, 2957.
- [2] H.V. Kehiaian (1983). *Fluid Phase Equilibria*, **13**, 243.
- [3] H.V. Kehiaian (1985). *Pure Applied Chem.*, **57**, 15.
- [4] U. Weidlich and J. Gmehling (1987). *Ind. Eng. Chem. Res.*, **26**, 1372.
- [5] I. Nagata and K. Tamura (1995). *J. Chem. Thermodynamics*, **27**, 1067.
- [6] H.C. Van Ness and M.M. Abbott (1982). *Classical Thermodynamics of Nonelectrolyte Solutions*. McGraw-Hill Book Co., New York, USA.
- [7] A. Aucejo, S. Loras, R. Muñoz, R. Reich and H. Segura (1998). *J. Chem. Eng. Data*, **43**, 973.

- [8] D. Ambrose and C.H.S. Sprake (1970). *J. Chem. Thermodynamics*, **2**, 631.
- [9] J. Hayden and J.A. O'Connell (1975). *Ind. Eng. Chem. Process Des. Dev.*, **14**, 209.
- [10] T.E. Daubert and R.P. Danner (1989). *Physical and Thermodynamic Properties of Pure Chemicals. Data Compilation*. Taylor & Francis, Bristol, PA.
- [11] H.C. Van Ness, S.M. Byer and R.E. Gibbs (1973). *AIChE J.*, **19**, 238.
- [12] Aa. Fredenslund, J. Gmehling and P. Rasmussen (1977). *Vapor-Liquid Equilibria Using UNIFAC*. Elsevier, Amsterdam.
- [13] S.M. Walas (1985). *Phase Equilibria in Chemical Engineering*. Butterworth Publishers, Boston.
- [14] H.K. Hansen, P. Rasmussen and Aa. Fredenslund (1991). *Ind. Eng. Chem. Res.*, **30**, 2355.
- [15] S.T. Blanco, J. Muñoz Embid and S. Otín (1994). *J. Chem. Thermodynamics*, **26**, 23.
- [16] J.M. Prasunitz, R.N. Lichtenthaler and E. Gomes de Azevedo (1986). *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall, New Jersey.
- [17] A. Nath and E. Bender (1981). *Fluid Phase Equilibria*, **7**, 275.
- [18] A. Nath and E. Bender (1981). *Fluid Phase Equilibria*, **7**, 289.
- [19] P. van Konynenburg and R.L. Scott (1980). *Phil. Trans. Royal Society, London*, **288A**, 495.
- [20] H.G. Rackett (1970). *J. Chem. Eng. Data*, **15**, 514.
- [21] *TRC-Thermodynamic Tables – Non-Hydrocarbons*, a-6040, 1963. Thermodynamics Research Center. The Texas A&M University System, College Station, TX, extant 1996.
- [22] J.A. Riddick, W.B. Bunger and T.K. Sakano (1986). *Organic Solvents Techniques of Chemistry*, 4th Edn., Vol II. Wiley, New York.
- [23] L.H. Ballard and M. Van Winkle (1952). *Ind. Eng. Chem.*, **44**, 2450.