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# Isobaric Vapor−Liquid Equilibria for 2,2′-Oxybis[propane] + Cyclohexane

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New isobaric vapor−liquid equilibrium data have been obtained for the system 2,2′-oxybis[propane] (diisopropyl ether) + cyclohexane at 101.3 kPa and compared with previously reported data which appeared to be thermodynamically inconsistent. The system exhibits moderate positive deviations from ideal behavior. The activity coefficients and boiling point of the solution were correlated with its composition by the Redlich−Kister, Margules, and Wisniak−Tamir equations.

The system 2,2′-oxybis[propane] + cyclohexane has been studied at 101.3 kPa by Ramachandran et al. (1975) and at 92.4 kPa by Vijayaraghavan et al. (1965). According to DECHEMA (Gmehling and Onken, 1977), the data of Ramachandran et al. are thermodynamically inconsistent as they fail to pass the area test and the Fredenslund test (Fredenslund et al., 1977). The data published by Vijayaraghavan et al. have not been analyzed by DECHEMA, but they can be shown to be thermodynamically inconsistent because they do not pass the area test (Van Ness and Abbott, 1982) and the L−W test of Wisniak (1993) for thermodynamic consistency. In addition, Vijayaraghavan et al. estimated the Antoine coefficients for 2,2′-oxybis[propane] from an old literature reference which disagree with the data reported by the TRC (1974).

## Experimental Section

***Purity of Materials.*** 2,2′-Oxybis[propane] (99.9+ mol %) was purchased from Aldrich and cyclohexane (99.79+ mol %) from Riedel de Haen. The reagents were used without further purification after gas chromatography failed to show any significant impurities. The properties and purity (as determined by GLC) of the pure components appear in Table 1.

***Apparatus and Procedure.*** An all-glass modified Dvorak and Boublik recirculation still (Boublikova and Lu, 1969) was used in the vapor−liquid equilibrium (VLE) measurements. The experimental features have been described in a previous publication (Wisniak and Tamir, 1975). All analyses were carried out by gas chromatography on a Gow-Mac series 550P apparatus provided with a thermal conductivity detector and a Spectra Physics Model SP 4290 electronic integrator. The column was 3 m long and 0.2 cm in diameter, packed with SE-30 and operated at 333.15 K; injector and detector temperatures were 493.15 and 523.15 K, respectively. Very 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. Concentration measurements were accurate to better than ±0.008 mole fraction unit. The accuracies in the determination of pressure $P$ and temperature $T$ were at least ±0.1 kPa and 0.02 K, respectively. The analytical method used in this work (GLC) is assumed to be more reliable than the refractive index method used by both by Ramachandran et al. (1975) and Vijayaraghavan et al. (1965).

**Table 1. GLC Purities (mol %), Refractive Index $n_D$ at the Na D Line, and Normal Boiling Points $T$ of the Pure Components**

| component (purity/(mol %)) | $n_D$(298.15 K) | $T$/K |
|---|---|---|
| 2,2′-oxybis[propane] (99.9) | 1.3654[a]<br>1.3655[b] | 341.55[a]<br>341.45[b] |
| cyclohexane (99.79) | 1.4233[a]<br>1.42354[b] | 353.84[a]<br>353.888[b] |

[a] Measured. [b] TRC (1974).

**Table 2. Experimental Vapor−Liquid Equilibrium Data for 2,2′-Oxybis[propane] (1) + Cyclohexane (2) at 101.3 kPa**

| $T$/K | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ | $-B_{11}$[a] | $-B_{22}$[a] | $-B_{12}$[a] | $G^E/RT$ |
|---|---|---|---|---|---|---|---|---|
| 353.84 | 0 | 0 | 0 | | | | | |
| 352.56 | 0.065 | 0.101 | 1.1172 | 0.9989 | 1257 | 1120 | 1196 | 0.0062 |
| 351.09 | 0.129 | 0.190 | 1.1043 | 1.0086 | 1270 | 1132 | 1208 | 0.0203 |
| 350.50 | 0.168 | 0.241 | 1.0940 | 1.0067 | 1276 | 1137 | 1213 | 0.0206 |
| 350.15 | 0.185 | 0.262 | 1.0910 | 1.0096 | 1279 | 1139 | 1216 | 0.0239 |
| 349.36 | 0.231 | 0.314 | 1.0715 | 1.0182 | 1286 | 1146 | 1223 | 0.0298 |
| 347.95 | 0.336 | 0.429 | 1.0488 | 1.0237 | 1299 | 1157 | 1236 | 0.0316 |
| 346.62 | 0.442 | 0.530 | 1.0244 | 1.0437 | 1312 | 1168 | 1247 | 0.0345 |
| 345.70 | 0.531 | 0.611 | 1.0103 | 1.0569 | 1321 | 1176 | 1256 | 0.0314 |
| 344.95 | 0.594 | 0.669 | 1.0114 | 1.0630 | 1328 | 1182 | 1263 | 0.0315 |
| 344.55 | 0.642 | 0.710 | 1.0051 | 1.0692 | 1332 | 1185 | 1266 | 0.0272 |
| 343.87 | 0.721 | 0.775 | 0.9972 | 1.0870 | 1339 | 1191 | 1273 | 0.0213 |
| 343.50 | 0.759 | 0.808 | 0.9987 | 1.0862 | 1343 | 1194 | 1276 | 0.0189 |
| 343.12 | 0.807 | 0.844 | 0.9926 | 1.1150 | 1346 | 1198 | 1280 | 0.0150 |
| 342.95 | 0.831 | 0.865 | 0.9930 | 1.1078 | 1348 | 1199 | 1281 | 0.0115 |
| 342.69 | 0.855 | 0.885 | 0.9953 | 1.1088 | 1351 | 1201 | 1284 | 0.0109 |
| 342.55 | 0.868 | 0.895 | 0.9954 | 1.1201 | 1352 | 1203 | 1285 | 0.0110 |
| 342.45 | 0.885 | 0.908 | 0.9938 | 1.1268 | 1353 | 1203 | 1286 | 0.0082 |
| 342.29 | 0.895 | 0.916 | 0.996 | 1.1352 | 1355 | 1205 | 1287 | 0.0097 |
| 342.09 | 0.910 | 0.928 | 0.9988 | 1.1396 | 1357 | 1207 | 1289 | 0.0107 |
| 342.05 | 0.932 | 0.946 | 0.9953 | 1.1326 | 1357 | 1207 | 1290 | 0.0041 |
| 341.55 | 1 | 1 | | | | | | |

[a] cm$^3$/mol.

## Results

The temperature $T$ and liquid-phase $x_i$ and vapor-phase $y_i$ mole fraction measurements at $P$ = 101.3 kPa are reported in Table 2 and Figures 1 and 2, together with the activity coefficients $\gamma_i$ that were calculated from the following equation (Van Ness and Abbott, 1982):

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

where $x_i$ and $y_i$ are the equilibrium mole fractions of

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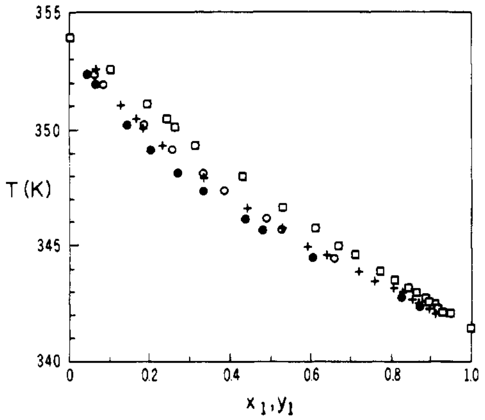

**Figure 1.** Boiling temperature diagram for the system 2,2′-oxybis[propane] (1) + cyclohexane (2) at 101.3 kPa: data of Ramachandran (1975), ●, ○; this work, +, □.

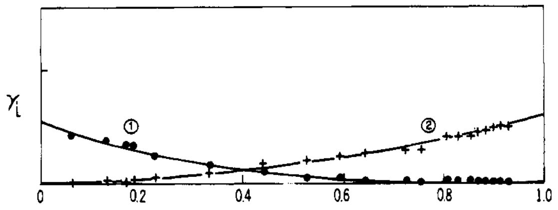

**Figure 2.** Activity coefficients for the system 2,2′-oxybis[propane] (1) + cyclohexane (2) at 101.3 kPa.

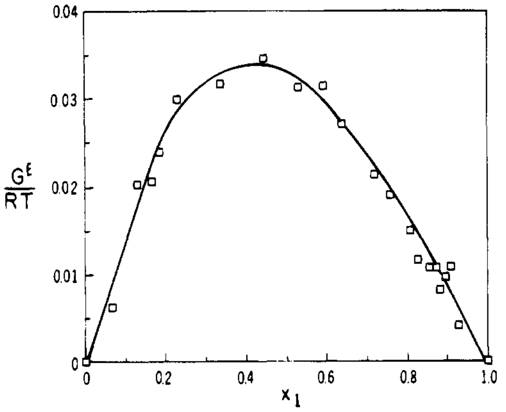

**Figure 3.** Variation of $G^E/RT$ with composition.

component $i$ in the liquid and vapor phases, respectively, $T$ and $P$ are the boiling point and 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, $B_{ij}$ is the cross second virial coefficient, and

$$\delta_{ij} = 2B_{ij} - B_{jj} - B_{ii} \tag{2}$$

The standard state for calculation of activity coefficients is the pure component at the pressure and temperature of the solution. The pure component vapor pressures $P_i°$ were calculated according to the Antoine equation:

$$\log(P_i°/\text{kPa}) = A_i - \frac{B_i}{(T/\text{K}) - C_i} \tag{3}$$

where the constants $A_i$, $B_i$, and $C_i$ are reported in Table 3. The molar virial coefficients $B_{ii}$ and $B_{ij}$ were estimated by the method of O'Connell and Prausnitz (1967) using the molecular parameters suggested by the authors and assuming the association parameter $\eta$ to be zero. The last two terms in eq 1 contributed less than 2% to the activity coefficients, and their influence was important only at very dilute concentrations. The calculated activity coefficients are reported in Table 2 and are estimated accurate to within ±3%.

**Table 3. Antoine Coefficients, Eq 3**

| compound | $A_i$ | $B_i$ | $C_i$ |
|---|---|---|---|
| 2,2′-oxybis[propane][a] | 6.222 00 | 1257.60 | 43.14 |
| cyclohexane[b] | 5.964 07 | 1200.310 | 50.65 |

[a] Yaws (1992). [b] TRC (1974).

The vapor–liquid equilibrium data reported in Table 1 were found to be thermodynamically consistent by the Redlich–Kister area test (1948) and by the L–W point-to-point and area method of Wisniak (1993). From Figure 2 it is seen that the system presents moderate positive deviations from ideality. The excess Gibbs function of the system is presented in Figure 3 as the variation of the Gibbs number $g = G^E/RT$ with composition; the value of $G^E$ at $x = 0.5$ is 2.88 kJ/mol.

The activity coefficients were correlated by the Redlich–Kister equation (1948) as follows:

$$\log(\gamma_1/\gamma_2) = B(x_2 - x_1) + C(6x_1x_2 - 1) \tag{4}$$

where $B = 0.0654$ and $C = -0.0041$. The average percent deviation was 1.8%, and the root mean square deviation (rmsd) was 0.004.

The activity coefficients were also correlated with the Margules equation (Van Ness and Abbott, 1982):

$$\log \gamma_1 = x_2^{\,2}(2B - A) + 2x_2^{\,3}(A - B) \tag{5}$$

$$\log \gamma_2 = x_2^{\,1}(2A - B) + 2x_1^{\,3}(B - A) \tag{6}$$

where $A = 0.071\,52$ and $B = 0.037\,24$. The average percent deviation was 0.6% for $\gamma_1$ and 1.8% for $\gamma_2$. The overall root mean square deviation (rmsd) was 0.006.

The boiling point of the solution was correlated with its composition by the equation proposed by Wisniak and Tamir (1976):

$$T/\text{K} = x_1T_1° + x_2T_2° + x_1x_2\sum_{k=1}^{m} C_k(x_1 - x_2)^k \tag{7}$$

In this equation, $T_i°/\text{K}$ is the boiling point of the pure component $i$ and $m$ is the number of terms in the series expansion of $x_1 - x_2$. The values of the constants in eq 7 were obtained by multilinear regression and are $C_1 = -7.060\,76$ and $C_2 = 3.323\,72$. Equation 7 predicts the boiling points with an average percent deviation of 0.08% and rmsd of 0.015 K.

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