tures from 275.65 to 440 K and pressures from 0.5 to 3.2 MPa with the uncertainty of ±0.4% for the data below 420 K, ±0.5% for the data at 430 K, and ±0.8% for the data at 440 K, respectively. These $C_p$ data were correlated as a function of temperature and pressure, and saturated liquid $C_p'$ values were derived from the correlation.

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# Vapor–Liquid Equilibrium Determination by Total Pressure Measurements for Three Binary Systems Made of 1,2-Dimethoxyethane with Toluene, Methylcyclohexane, or (Trifluoromethyl)benzene

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**Total vapor pressures were measured for the three binary systems made of 1,2-dimethoxyethane with toluene, methylcyclohexane, or (trifluoromethyl)benzene (benzotrifluoride) at 350 K. Densities of the mixtures were measured at 298.15 K. The vapor–liquid equilibria were correlated by using the Wilson equation.**

## Introduction

Vapor–liquid equilibria (VLE) are required for engineering use such as in the design and operation of distillation equipment. In the present study, isothermal total pressures $P$ were measured by the ebulliometric method for the three binary systems made of 1,2-dimethoxyethane with toluene, methylcyclohexane, or (trifluoromethyl)benzene (benzotrifluoride) at 350 K. The densities of these mixtures were measured at 298.15 K, and the molar excess volumes $V^E$ were calculated.

## Experimental Section

The experimental apparatus previously reported by Kato et al. (*1*, *2*) was modified in the present study, as shown in Figure 1. The ebulliometer E has been described by Kato et al. (*3*). The liquid volume in the ebulliometer is about 25 cm$^3$.

At the start of an experiment, a solution of desired composition was prepared by mixing each pure substance, which was weighed by use of syringes and an automatic balance, similarly to the procedures of the previous works (*3*, *4*). The reproducibility of the composition was within ±0.001 mole fraction. Cocks $K_1$, $K_2$, and $K_3$ and solenoid valve V were opened, and $K_4$ and $K_5$ were closed. The system pressure was reduced by the vacuum pump near to the total pressure of the desired boiling point temperature. Next, cocks $K_2$ and solenoid valve V were closed, and the temperature was kept constant by use of the Williams (*5*) two-liquid manostat with a precision of ±0.01 mmHg. The upper layer of the manostat is dibutyl phthalate, and the lower layer is ethylene glycol saturated with sodium nitrite. The prepared solution was then boiled. The temperature was controlled to the desired temperature by reducing the pressure.

After attainment of steady state, the total pressure was measured with a Ruska 3850 quartz Bourdon gage with a precision of ±0.02 mmHg. The experimental temperature was measured at 350 K with a Hewlett-Packard 2804A quartz thermometer calibrated at the triple point of water in a reference cell. The reproducibility of the thermometer temperature measurements was ±0.01 K. The densities of the binary liquid mixtures were determined at 298.15 K with an Anton Paar DMA48 digital density meter with a precision of ±0.0001 g/cm$^3$.

Toluene was a special grade reagent supplied by Wako Pure Chemical Industries Ltd. 1,2-Dimethoxyethane, methylcyclohexane, and (trifluoromethyl)benzene were special grade reagents supplied by Tokyo Kasei Kogyo Co., Ltd. Toluene and methylcyclohexane were used without further purification. (Trifluoromethyl)benzene and 1,2-dimethoxyethane were further purified by distillation in an Oldershaw distillation column with 30 plates. The physical properties of the materials used are listed in Table I.

## Results

The experimental total pressures $P$ for the three binary systems at 350 K are given in Table II and Figure 2. The experimental densities $\rho$ for the three binary mixtures at 298.15 K are shown in Table III. Figure 3 shows the molar excess liquid volumes $V^E$ calculated from

$$V^E = V - (x_1V_1 + x_2V_2) \quad (1)$$

and correlated with the following equation:

$$V^E = x_1x_2[\alpha + \beta(x_1 - x_2)] \quad (2)$$

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Table I. Normal Boiling Points $T_b$, Densities $\rho$, and Refractive Indexes $n$ of Materials Used

| material | $T_b$/K exptl | $T_b$/K lit. | $\rho$(298.15 K)/(g·cm$^{-3}$) exptl | $\rho$(298.15 K)/(g·cm$^{-3}$) lit. | $n_D$(298.15 K) exptl | $n_D$(298.15 K) lit. |
|---|---|---|---|---|---|---|
| 1,2-dimethoxyethane | 358.10 | 358.4 (10) | 0.8612 | 0.8683[a] (10) | 1.3775 | 1.3792[a] (10) |
| toluene | 383.79 | 383.776 (12) | 0.8622 | 0.86232 (12) | 1.4941 | 1.49405 (12) |
| methylcyclohexane | 374.12 | 374.1 (12)<br>374.084 (13) | 0.7649 | 0.76511 (12)<br>0.76506 (13) | 1.4207 | 1.4206 (12)<br>1.42058 (13) |
| (trifluoromethyl)benzene | 375.19 | 375.20 (10)<br>375.200 (13) | 1.1814 | 1.1813 (10)<br>1.18129 (13) | 1.4123 | 1.4114 (10)<br>1.41225 (13) |

[a] At 293.15 K.

Table II. Experimental Total Pressures $P$ and Calculated Vapor-Phase Mole Fraction $y_1$ for the Three Binary Systems[a] at 350 K as a Function of the Liquid-Phase Mole Fraction $x_1$, Wilson Coefficients $\Lambda_{12}$ and $\Lambda_{21}$, Equations 3 and 4, and Standard Relative Deviations $\Delta r(P)$

| | $P$/mmHg | | | $y_1$ | | |
|---|---|---|---|---|---|---|
| $x_1$ | I | II | III | I | II | III |
| 0.000 | 261.10 | 365.25 | 339.54 | 0.000 | 0.000 | 0.000 |
| 0.100 | 292.76 | 426.74 | 352.57 | 0.202 | 0.228 | 0.138 |
| 0.200 | 326.42 | 476.50 | 370.50 | 0.363 | 0.375 | 0.276 |
| 0.300 | 361.71 | 515.98 | 391.74 | 0.494 | 0.480 | 0.408 |
| 0.400 | 395.57 | 544.28 | 412.90 | 0.602 | 0.561 | 0.528 |
| 0.500 | 426.86 | 568.84 | 440.76 | 0.693 | 0.627 | 0.636 |
| 0.600 | 459.04 | 587.17 | 467.78 | 0.771 | 0.687 | 0.731 |
| 0.700 | 491.22 | 595.68 | 494.30 | 0.838 | 0.745 | 0.813 |
| 0.800 | 520.35 | 598.28 | 523.85 | 0.897 | 0.808 | 0.885 |
| 0.900 | 552.33 | 594.53 | 551.90 | 0.950 | 0.886 | 0.947 |
| 1.000 | 581.94 | 581.94 | 581.94 | 1.000 | 1.000 | 1.000 |

[a] Systems: (I) 1,2-dimethoxyethane (1) + toluene (2), $\Lambda_{12}$ = 1.6526, $\Lambda_{21}$ = 0.4762, $\Delta r(P)$ = 0.0018; (II) 1,2-dimethoxyethane (1) + methylcyclohexane (2), $\Lambda_{12}$ = 0.9313, $\Lambda_{21}$ = 0.4591, $\Delta r(P)$ = 0.0023; (III) 1,2-dimethoxyethane (1) + (trifluoromethyl)benzene (2), $\Lambda_{12}$ = 0.5347, $\Lambda_{21}$ = 1.8698, $\Delta r(P)$ = 0.0013.

Table III. Experimental Densities $\rho$ for the Three Binary Systems[a] at 298.15 K as a Function of the Mole Fraction $x_1$ and Coefficients $\alpha$ and $\beta$, Equation 2

| | $\rho$/(g·cm$^{-3}$) | | |
|---|---|---|---|
| $x_1$ | I | II | III |
| 0.000 | 0.8622 | 0.7649 | 1.1814 |
| 0.100 | 0.8624 | 0.7705 | 1.1538 |
| 0.200 | 0.8626 | 0.7768 | 1.1254 |
| 0.300 | 0.8628 | 0.7841 | 1.0962 |
| 0.400 | 0.8628 | 0.7922 | 1.0659 |
| 0.500 | 0.8627 | 0.8012 | 1.0346 |
| 0.600 | 0.8626 | 0.8110 | 1.0022 |
| 0.700 | 0.8624 | 0.8219 | 0.9688 |
| 0.800 | 0.8621 | 0.8338 | 0.9341 |
| 0.900 | 0.8617 | 0.8468 | 0.8983 |
| 1.000 | 0.8612 | 0.8612 | 0.8612 |

[a] Systems: (I) 1,2-dimethoxyethane (1) + toluene (2), $\alpha$ = −0.50, $\beta$ = −0.1; (II) 1,2-dimethoxyethane (1) + methylcyclohexane (2), $\alpha$ = 4.12, $\beta$ = −0.3; (III) 1,2-dimethoxyethane (1) + (trifluoromethyl)benzene (2), $\alpha$ = 0.05, $\beta$ = 0.0.

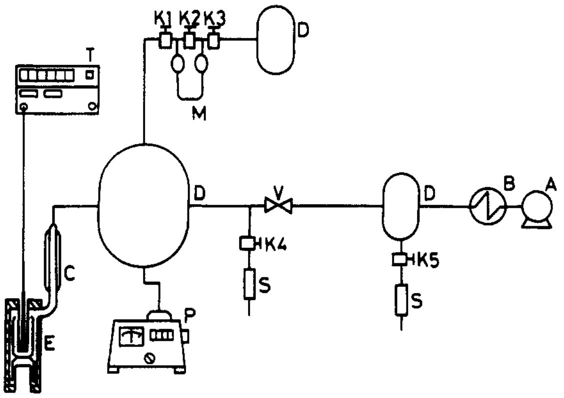

Figure 1. Experimental apparatus for measuring isothermal total pressures: (A) vacuum pump; (B) trap; (C) condenser; (D) reservoir; (E) ebulliometer; (K) cock; (M) manostat; (P) pressure gage; (S) silica gel; (T) thermometer; (V) solenoid valve.

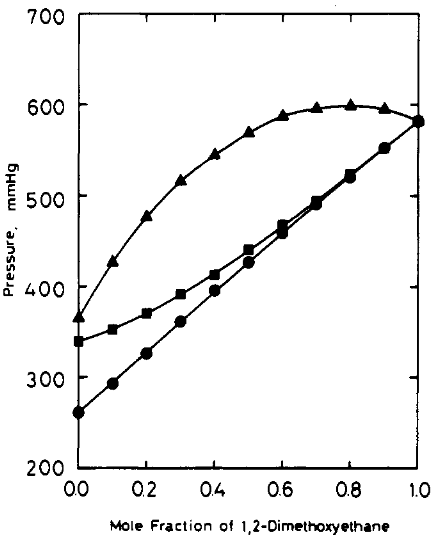

Figure 2. Experimental total pressure $P$ curves at 350 K: (-●-) 1,2-dimethoxyethane + toluene; (-▲-) 1,2-dimethoxyethane + methylcyclohexane; (-■-) 1,2-dimethoxyethane + (trifluoromethyl)benzene.

The vapor-phase corrections in terms of the second molar virial coefficients $B_{ij}$ were estimated by the Hayden and O'Connell (*6*) method, using the parameters (*7–10*) shown in Table IV. The liquid volume change with pressure was neglected in the present study.

Table IV. Parameters Used to Calculate the Second Molar Virial Coefficients $B_{ij}$ by the Method of Hayden–O'Connell (*6*): Critical Pressure $P_c$, Critical Temperature $T_c$, Mean Radius of Gyration $R'$, Molecular Dipole Moment $\mu$, and Association Factor $\eta$

| material | $P_c$/atm | $T_c$/K | $R'$/Å | $\mu$/D | $\eta$ | $B_{ii}$/(cm$^3$·mol$^{-1}$) | $B_{ij}$/(cm$^3$·mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| 1,2-dimethoxyethane | 38.2 (9) | 536 (9) | 3.361[b] | 1.79 (10) | 0.00[c] | −1145 | |
| toluene | 41.6 (7) | 592.0 (7) | 3.443 (7) | 0.36 (7) | 0.00 (7) | −1499 | −1251 |
| methylcyclohexane | 34.3 (9) | 572.1 (9) | 3.823[b] | 0.00 (9) | 0.00 (8) | −1682 | −1316 |
| (trifluoromethyl)benzene | 31.73[a] | 557.84[a] | 4.830[b] | 2.56 (10) | 0.00[c] | −1900 | −1452 |

[a] Estimated from the Lydersen method. [b] Estimated from parachor. [c] Assumed.

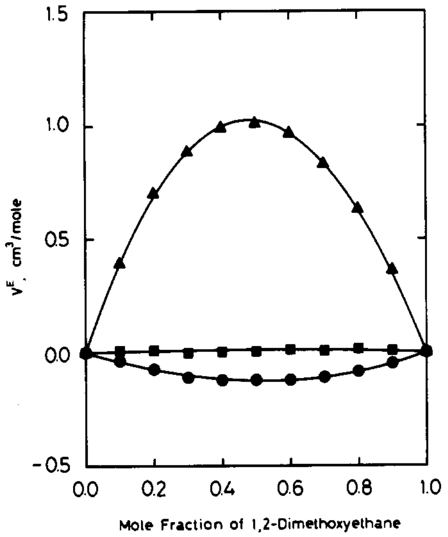

**Figure 3.** Experimental molar excess liquid volumes $V^E$ at 298.15 K: (-●-) 1,2-dimethoxyethane + toluene; (-▲-) 1,2-dimethoxyethane + methylcyclohexane; (-■-) 1,2-dimethoxyethane + (trifluoromethyl)benzene.

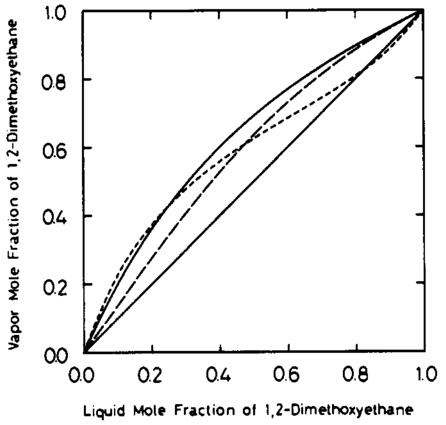

**Figure 4.** Calculated vapor–liquid equilibria at 350 K: (—) 1,2-dimethoxyethane + toluene; (- -) 1,2-dimethoxyethane + methylcyclohexane; (– –) 1,2-dimethoxyethane + (trifluoromethyl)benzene.

The activity coefficients $\gamma_i$ at constant temperature and pressure ($T$ and $P_1$) were correlated with the following Wilson (*11*) equations, almost similar to our previous paper (*2*).

$$\ln \gamma_1 = -\ln (x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right) \quad (3)$$

$$\ln \gamma_2 = -\ln (x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{\Lambda_{12}x_2 + x_1}\right) \quad (4)$$

The Wilson parameters $\Lambda_{12}$ and $\Lambda_{21}$ (Table II) were determined to minimize the sum of squares of deviations in the absolute total pressures for all experimental data points. The calculated vapor phase mole fractions $y_1$ and the mean relative deviations in pressure $\Delta r(P)$ are listed in Table II. Vapor–liquid equilibrium relations are shown in Figure 4. The azeotropic composition of the 1,2-dimethoxyethane (1) + methylcyclohexane (2) system at 350 K is estimated to be $x_1(\mathrm{Az}) = 0.826$.

## Acknowledgment

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## Glossary

| | |
|---|---|
| $P$ | pressure, mmHg |
| $T$ | temperature, K |
| $V$ | molar liquid volume, cm$^3$·mol$^{-1}$ |
| $V^E$ | molar excess liquid volume, eq 1, cm$^3$·mol$^{-1}$ |
| $x$ | liquid mole fraction |
| $y$ | vapor mole fraction |

### *Greek Letters*

| | |
|---|---|
| $\alpha, \beta$ | parameters in eq 2 |
| $\gamma$ | activity coefficient |
| $\Lambda$ | Wilson parameter |
| $\Delta r(P)$ | mean relative deviation, $= \frac{1}{N}\sum \lvert P_{calc} - P_{exp}\rvert / P_{exp}$ ($N$, number of experimental points) |

### *Subscripts*

| | |
|---|---|
| 1 | 1,2-dimethoxyethane |
| 2 | toluene, methylcyclohexane, or (trifluoromethyl)benzene |

**Registry No.** 1,2-dimethoxyethane, 110-71-4; toluene, 108-88-3; methylcyclohexane, 108-87-2; benzotrifluoride, 98-08-8.

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