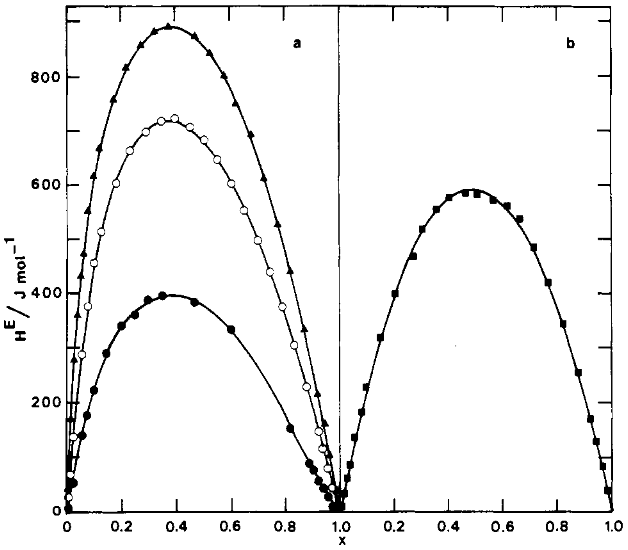

**Figure 1.** Molar excess enthalpies at 298.15 K of 2-butoxyethanol with various solvents vs. the mole fraction, *x*, of the cellosolve. Points are experimental results; curves are smoothed representations by eq 1. Part a: (▲) with *n*-heptane; (○) with di-*n*-butyl ether; (●) with diethyl ether. Part b: (■) with diethylene glycol dimethyl ether.

ference in $H^E_{max}$ between these two mixtures, which is rather large (≃1400 J mol$^{-1}$, see Table I), is reasonably predicted by the theory (*7*).

Excess-enthalpy curves of mixtures containing 2-butoxyethanol indicate that these mixtures behave similarly to mixtures containing an alcohol: i.e., the large and unsymmetric $H^E$ curve with *n*-heptane (Figure 1a), which decreases in magnitude when *n*-alkane is replaced by a more "active" solvent like an ether. When a monoether is replaced by another one, the decrease of $H^E$ corresponds with an increase of the etheric molecular surface fraction $\alpha_e$. As a matter of fact, the change in $H^E$ ($|\Delta H^E_{max}| \simeq 300$ J mol$^{-1}$), observed in Figure 1, is due to the augmentation of OH/O interactions (*1*) between the oxygen and hydroxyl groups between unlike molecules when $\alpha_e$ varies from 0.0464 (di-*n*-butyl ether) to 0.0796 (diethyl ether). When 2-butoxyethanol is mixed with a polyether like diethylene glycol dimethyl ether, we also observe a large decrease of $H^E$ resulting from an increase of the interactions between unlike molecules. However, the symmetry of the $H^E$ curve in this later case (see Figure 1b) shows that the competition of interactions between like and unlike molecules is most probably rather complex. A theoretical interpretation of all of these systems has been tentatively proposed (*7*) and will be given in a forthcoming paper.

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# Isobaric Vapor–Liquid Equilibria of the 1-Octanol–Tetralin System at Subatmospheric Pressures

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**The vapor–liquid equilibria of the 1-octanol–Tetralin system were measured at 50, 100, 200, 400, and 760 mmHg. All of the results could be correlated by the Wilson equation with the parameters at 50 mmHg pressure, up to the atmospheric pressure.**

## Introduction

Knowledge of the effect of pressure on vapor–liquid equilibria is important for the designing of low-pressure distillation units. The vapor–liquid equilibria of the system 1-octanol (1)–Tetralin (1,2,3,4-tetrahydronaphthalene) (2) were measured at 50, 100, 200, 400, and 760 mmHg. The effect of pressure was examined and the results were correlated by the Wilson equation (*1*).

## Experimental Section

The experimental apparatus was the same as the one which was described elsewhere (*2*). The pressures were measured within ±0.4 mmHg by a mercury manometer. The temperatures were measured by a standardized mercury thermometer having an accuracy of 0.02 °C. The compositions of the liquid and vapor phases were determined by the refractive indexes, an Abbe refractometer being used with the sodium lamp at 298.15 K. The compositions were evaluated within an error of ±0.002 mole fraction.

Commercial-grade 1-octanol and Tetralin were distilled in a wetted wall column with 1-m length and 10-mm i.d. at 10 mmHg. The refractive indexes of each distillate were read by the Abbe refractometer with an error of ±0.0002 refractive units. The intermediate distillates with refractive indexes close to the values reported in the literature were used for this work. The purity of both compounds was estimated to be 99.8% by gas chromatography at 230 °C, using a column of 2.2-m length and 3-mm i.d. with Porapak-s. The physical properties of the compounds are summarized in Table I.

After each of the pure compounds was heated in an equilibrium still at atmospheric pressure for 3 h, we determined whether the refractive indexes of the contents had changed. No change of refractive index was found in either compound, but the color of the Tetralin in the still turned to brown during the heating. It was found that 1.5 wt % of the Tetralin was

**Table I. Physical Properties of Chemicals**

| | density, g/cm³ | | $n_D$[a] | | | bp, °C | |
|---|---|---|---|---|---|---|---|
| temp, °C | exptl | lit. | exptl | lit. | press., mmHg | exptl | lit. |
| | | | 1-Octanol | | | | |
| 20.0 | 0.8247 | 0.825 55[b] | 1.4285 | 1.429 13[b] | 162.61 | 147.57 | 147.224[c] |
| | | | | | 274.93 | 161.98 | 161.868[c] |
| | | | | | 408.60 | 173.97 | 173.981[c] |
| | | | | | 558.87 | 184.13 | 184.300[c] |
| | | | | | 755.7 | 194.95 | 194.99[c,f] |
| 25.0 | 0.9636 | 0.963 24[d] | 1.5383 | 1.539 19[e] | 118.0 | 140.50 | 140.0[e] |
| | | | | | 216.0 | 150.23 | 150.0[e] |
| | | | | | 273.0 | 167.47 | 167.5[e] |
| | | | | | 758.85 | 207.21 | 207.2[e,f] |

[a] Refractive index. [b] Reference *4*. [c] Reference *3*. [d] Reference *6*. [e] Reference *5*. [f] Interpolated.

**Table II. Vapor-Liquid Equilibrium Data for the 1-Octanol (1)-Tetralin (2) System**

| *P*, mmHg | *t*, °C | $x_1$ | $y_1$ | $\gamma_1$ | $\gamma_2$ |
|---|---|---|---|---|---|
| 762.0 | 207.25 | 0.000 | | | |
| 761.0 | 206.32 | 0.012 | 0.047 | 2.060 | 0.989 |
| 755.5 | 203.16 | 0.063 | 0.144 | 1.813 | 0.991 |
| 757.1 | 200.20 | 0.148 | 0.293 | 1.721 | 0.978 |
| 743.3 | 199.10 | 0.168 | 0.322 | 1.685 | 0.969 |
| 761.0 | 199.22 | 0.230 | 0.368 | 1.435 | 0.996 |
| 751.1 | 198.09 | 0.248 | 0.389 | 1.432 | 1.000 |
| 752.1 | 197.13 | 0.294 | 0.449 | 1.432 | 0.985 |
| 746.2 | 195.19 | 0.374 | 0.527 | 1.382 | 0.992 |
| 754.4 | 195.16 | 0.467 | 0.584 | 1.241 | 1.037 |
| 749.1 | 194.41 | 0.550 | 0.643 | 1.176 | 1.066 |
| 757.0 | 194.94 | 0.577 | 0.656 | 1.139 | 1.093 |
| 753.3 | 194.22 | 0.708 | 0.747 | 1.073 | 1.177 |
| 757.1 | 194.22 | 0.731 | 0.762 | 1.066 | 1.207 |
| 752.1 | 194.12 | 0.785 | 0.797 | 1.034 | 1.283 |
| 752.9 | 193.92 | 0.877 | 0.877 | 1.025 | 1.367 |
| 764.1 | 194.69 | 0.913 | 0.913 | 1.018 | 1.361 |
| 754.0 | 194.00 | 0.921 | 0.921 | 1.024 | 1.364 |
| 748.5 | 193.91 | 0.953 | 0.953 | 1.019 | 1.360 |
| 757.7 | 194.70 | 1.000 | | | |
| 400.0 | 181.51 | 0.000 | | | |
| | 177.00 | 0.075 | 0.188 | 2.235 | 0.988 |
| | 174.64 | 0.167 | 0.326 | 1.873 | 0.973 |
| | 173.31 | 0.281 | 0.414 | 1.473 | 1.014 |
| | 172.15 | 0.441 | 0.519 | 1.221 | 1.106 |
| | 171.78 | 0.495 | 0.572 | 1.213 | 1.100 |
| | 171.73 | 0.568 | 0.614 | 1.137 | 1.162 |
| | 171.60 | 0.668 | 0.679 | 1.073 | 1.262 |
| | 171.61 | 0.722 | 0.712 | 1.041 | 1.352 |
| | 171.78 | 0.782 | 0.782 | 1.043 | 1.329 |
| | 172.12 | 0.927 | 0.907 | 1.016 | 1.639 |
| | 172.59 | 0.967 | 0.954 | 1.009 | 1.770 |
| | 172.90 | 1.000 | | | |
| 200.0 | 156.77 | 0.000 | | | |
| | 156.21 | 0.019 | 0.048 | 2.236 | 0.989 |
| | 153.89 | 0.088 | 0.188 | 2.054 | 0.973 |
| | 152.60 | 0.125 | 0.250 | 2.015 | 0.975 |
| | 151.36 | 0.213 | 0.332 | 1.643 | 1.003 |
| | 150.90 | 0.302 | 0.397 | 1.409 | 1.036 |
| | 150.61 | 0.387 | 0.451 | 1.262 | 1.083 |
| | 150.41 | 0.482 | 0.513 | 1.161 | 1.144 |
| | 150.35 | 0.578 | 0.569 | 1.077 | 1.246 |
| | 150.48 | 0.671 | 0.633 | 1.027 | 1.355 |
| | 150.81 | 0.757 | 0.708 | 1.006 | 1.445 |
| | 151.64 | 0.884 | 0.830 | 0.979 | 1.717 |
| | 152.19 | 0.945 | 0.909 | 0.984 | 1.905 |
| | 152.42 | 1.000 | | | |
| 100.0 | 135.30 | 0.000 | | | |
| | 133.91 | 0.020 | 0.056 | 2.915 | 1.005 |
| | 132.31 | 0.056 | 0.139 | 2.684 | 1.010 |
| | 131.09 | 0.148 | 0.253 | 2.004 | 1.008 |
| | 130.09 | 0.225 | 0.323 | 1.741 | 1.033 |
| | 129.89 | 0.270 | 0.347 | 1.586 | 1.073 |
| | 129.61 | 0.418 | 0.429 | 1.282 | 1.188 |
| | 129.59 | 0.502 | 0.472 | 1.175 | 1.285 |
| | 130.05 | 0.584 | 0.520 | 1.091 | 1.376 |
| | 130.54 | 0.675 | 0.579 | 1.029 | 1.519 |
| | 130.90 | 0.772 | 0.661 | 1.012 | 1.722 |
| | 131.91 | 0.867 | 0.782 | 1.021 | 1.831 |
| | 132.91 | 0.937 | 0.878 | 1.017 | 2.091 |
| | 133.76 | 0.984 | 0.964 | 1.026 | 2.360 |
| | 134.42 | 1.000 | | | |
| 50.0 | 116.00 | 0.000 | | | |
| | 115.42 | 0.023 | 0.054 | 2.796 | 0.987 |
| | 114.92 | 0.052 | 0.108 | 2.674 | 0.971 |
| | 114.29 | 0.092 | 0.167 | 2.420 | 0.965 |
| | 113.61 | 0.156 | 0.229 | 1.908 | 0.998 |
| | 113.22 | 0.233 | 0.286 | 1.627 | 1.032 |
| | 113.07 | 0.277 | 0.302 | 1.455 | 1.077 |
| | 112.91 | 0.352 | 0.350 | 1.338 | 1.126 |
| | 112.98 | 0.431 | 0.393 | 1.223 | 1.194 |
| | 113.18 | 0.508 | 0.444 | 1.160 | 1.255 |
| | 113.65 | 0.602 | 0.493 | 1.016 | 1.390 |
| | 114.31 | 0.693 | 0.593 | 1.075 | 1.410 |
| | 115.26 | 0.772 | 0.667 | 1.037 | 1.497 |
| | 117.43 | 0.907 | 0.817 | 0.975 | 1.857 |
| | 118.61 | 0.973 | 0.943 | 0.992 | 1.906 |
| | 119.20 | 1.000 | | | |

**Table III. Azeotrope Data for the 1-Octanol (1)-Tetralin (2) System**

| press., mmHg | $x_1$ | *t*, °C | press., mmHg | $x_1$ | *t*, °C |
|---|---|---|---|---|---|
| 765.5 | 0.835 | 194.50 | 100.0 | 0.448 | 129.48 |
| 400.0 | 0.698 | 171.55 | 50.0 | 0.350 | 112.91 |
| 200.0 | 0.544 | 150.30 | | | |

**Table IV. Wilson Parameters for the 1-Octanol (1)-Tetralin (2) System**

| press., mmHg | $\lambda_{12}-\lambda_{11}$,[a] J/mol | $\lambda_{21}-\lambda_{22}$,[a] J/mol | $\lambda_{12}-\lambda_{11}$,[b] J/mol | $\lambda_{21}-\lambda_{22}$,[b] J/mol |
|---|---|---|---|---|
| 760 | −415.2 | 2476.0 | −2231.6 | 4975.7 |
| 400.0 | 457.2 | 1879.2 | 40.9 | 2311.1 |
| 200.0 | 1452.5 | 829.9 | 1703.4 | 581.0 |
| 100.0 | 2007.0 | 1112.1 | 2154.7 | 1245.6 |
| 50.0 | 1475.3 | 1223.4 | 1963.5 | 953.7 |

[a] Obtained from vapor-liquid equilibrium data. [b] Obtained from azeotrope data.

polymerized after the 3-h heating. The azeotropic point of the mixture of 1-octanol and Tetralin was determined by the wetted wall distillation column described above.

## Results

The vapor-liquid equilibrium data for the still and the azeotrope data for the wetted wall column are presented in Tables II and III, respectively. The liquid-phase activity coefficients were calculated with the expression $\gamma_i = y_iP/(x_ip_i)$, where the vapor pressures of the pure substances $p_i$ were obtained from the Antoine equation, the coefficients of which were given by

Table V. Average Deviations of Vapor-Phase Compositions and Temperatures

| | atmos press. | | 400.0 mmHg | | 200.0 mmHg | | 100.0 mmHg | | 50.0 mmHg | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta y_1{}^a$ | $\Delta t^b$ | $\Delta y_1{}^a$ | $\Delta t^b$ | $\Delta y_1{}^a$ | $\Delta t^b$ | $\Delta y_1{}^a$ | $\Delta t^b$ | $\Delta y_1{}^a$ | $\Delta t^b$ |
| $\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ obtained from equilibrium data | 0.023 | 0.31 | 0.017 | 0.41 | 0.021 | 0.23 | 0.014 | 0.41 | 0.012 | 0.12 |
| $\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ obtained from the azeotropic point at the respective pressures | 0.023 | 0.90 | 0.016 | 0.41 | 0.022 | 0.31 | 0.009 | 0.28 | 0.010 | 0.13 |
| $\lambda_{12}-\lambda_{11}$, $\lambda_{21}-\lambda_{22}$ obtained from the azeotropic point at 50 mmHg | 0.026 | 0.58 | 0.021 | 0.48 | 0.010 | 0.55 | 0.018 | 0.65 | | |

[a] $\Delta y_1 = \Sigma|y_{1,\text{exptl}} - y_{1,\text{calcd}}|/n$. [b] $\Delta t = \Sigma|t_{\text{exptl}} - t_{\text{calcd}}|/n$. $n$ = number of data.

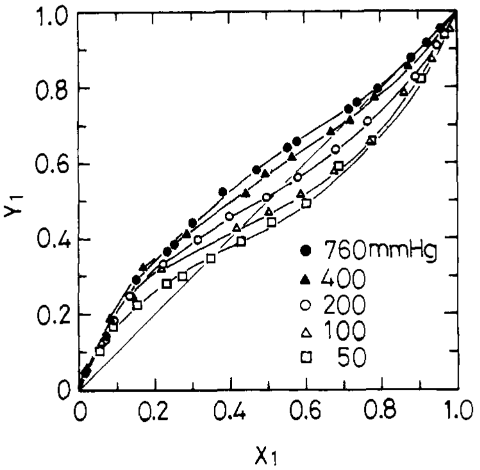

**Figure 1.** Relation between vapor and liquid composition for 1-octanol (1)–Tetralin (2) system at various pressures.

Boublik et al. (*3*). The vapor–liquid compositions are shown in Figure 1. The results for 50, 100, and 200 mmHg were thermodynamically consistent by the test of Herington (*7*); however, those for 400 and 760 mmHg were not consistent by the test.

## Discussion

The results are represented by the Wilson equation

$$\ln \gamma_i = -\ln (x_1\Lambda_{i1} + x_2\Lambda_{i2}) + 1 - \sum_{k=1}^{2} \frac{x_k\Lambda_{ki}}{x_1\Lambda_{k1} + x_2\Lambda_{k2}} \qquad (1)$$

where

$$\Lambda_{ij} = (v_j/v_i) \exp[-(\lambda_{ij} - \lambda_{ii})/RT] \qquad (2)$$

$$i \neq j \qquad i, j = 1 \text{ or } 2$$

$$\Lambda_{11} = \Lambda_{22} = 1.0$$

The Wilson parameters, $\lambda_{12} - \lambda_{11}$ and $\lambda_{21} - \lambda_{22}$, were determined from the vapor–liquid equilibrium data by means of a least-squares fit of the Q function ($g^E/RT$), and from the azeotrope data, which are given in Tables II and III, respectively. The parameters calculated by these two methods are listed in Table IV.

The Wilson parameters and the liquid compositions were used to calculate the bubble point, the temperature, and the vapor compositions at the given pressures. The average differences between the predicted and experimental values of the vapor compositions and the temperatures are shown in Table V. Since the predicted values at 50 mmHg pressure were the best, the Wilson parameters obtained from the azeotropic point at 50 mmHg were also used to make the bubble point calculations at other pressures. The differences are also listed in Table V. The differences, the values of $\Delta y_1$ and $\Delta t$ calculated by applying the Wilson parameters at 50 mmHg, were close to those which were calculated by using the Wilson parameters at other pressures. Therefore, the parameters at 50 mmHg were applicable to the other pressures up to 760 mmHg.

Checking the results of Herington's test and of the calculation of the bubble point using the Wilson parameters, we concluded that the experimental data at higher pressures were less accurate than the ones at 50 mmHg because of the thermal sensitivity of Tetralin.

## Glossary

| | |
|---|---|
| $g^E$ | molar excess Gibbs energy, J/mol |
| $n_D$ | refractive index |
| $P$ | total pressure, mmHg |
| $p_i$ | vapor pressure of pure substance $i$, mmHg |
| $Q$ | $Q$ function ($=g^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2$) |
| $R$ | gas constant, J/(mol K) |
| $T$, $t$ | temperature, K, °C |
| $v_i$ | molar liquid volume of pure $i$ at temperature $T$, cm$^3$/mol |
| $x_i$,$y_i$ | mole fraction composition of component $i$ in the liquid and vapor phases |

### *Greek Letters*

| | |
|---|---|
| $\gamma_i$ | $i$-component activity coefficient of liquid phase |
| $\Lambda_{12}$, $\Lambda_{21}$ | Wilson parameters defined by eq 2 |
| $\lambda_{ij} - \lambda_{ii}$ | Wilson parameters ($i \neq j$; $i$, $j$ = 1 or 2), J/mol |

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