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# Thermodynamics of the Isopropanol/*n*-Hexane and Isopropanol/*n*-Heptane Systems. Part III. Gas/Liquid Equilibrium

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Vapour pressure measurements are carried out at different temperatures; the activity coefficients are calculated and compared with those devived from IR and NMR data (parts I and II).

*(Keywords: Activity coefficients, isopropanol/n-alkanes; Isopropanol/n-alkanes, thermodynamics; Vapour pressure, isopropanol/n-alkanes)*

*Zur Thermodynamik des Isopropanol/n-Hexan und Isopropanol/n-Heptan Systems, III. Gas-Flüssig-Gleichgewichte*

Es wurden Dampfdruckmessungen bei verschiedenen Temperaturen ausgeführt. Die daraus bestimmten Aktivitätskoeffizienten wurden mit den aus IR- und NMR-Daten berechneten (siehe Mitt. I und II) verglichen.

## Introduction

Following methods whose description have been given before[1–5] we measured the vapour-liquid equilibrium of the systems isopropanol/*n*-hexane and isopropanol/*n*-heptane.

## Experimental

The composition of both phases at equilibrium were known by density measurements.

Chemicals were purified by drying them with Sikkon Fluka and then distilling them twice; the main fraction was collected on calcinated potassium carbonate.

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*Table 1*

| $p$ (Torr) | $x_1'$ | $x_1''$ | $\log f_1$ | $\log f_2$ |
|---|---|---|---|---|
| *System Isopropanol (1)/n-Heptane (2)* | | | | |
| Isotherm 30 °C | | | | |
| 57.6 | 0.0000 | 0.0000 | | |
| 61.3 | 0.0135 | 0.0889 | 0.84322 | —0.00772 |
| 64.0 | 0.0201 | 0.1608 | 0.94636 | —0.00219 |
| 75.6 | 0.0394 | 0.2756 | 0.95995 | —0.00559 |
| 77.7 | 0.0549 | 0.3045 | 0.79833 | —0.00020 |
| 80.1 | 0.0755 | 0.3253 | 0.77445 | 0.00501 |
| 82.4 | 0.1102 | 0.3614 | 0.66813 | 0.00990 |
| 84.9 | 0.1457 | 0.3718 | 0.57204 | 0.03327 |
| 87.0 | 0.2704 | 0.4233 | 0.37038 | 0.07513 |
| 87.3 | 0.3450 | 0.4363 | 0.27919 | 0.11355 |
| 87.9 | 0.4321 | 0.4457 | 0.19363 | 0.17115 |
| 87.6 | 0.5092 | 0.4854 | 0.15791 | 0.20078 |
| 86.7 | 0.6035 | 0.4971 | 0.09001 | 0.27902 |
| 84.3 | 0.7614 | 0.5630 | 0.03126 | 0.42655 |
| 81.4 | 0.8436 | 0.6118 | 0.00753 | 0.54354 |
| 79.4 | 0.8865 | 0.6541 | 0.00429 | 0.62199 |
| 76.5 | 0.9152 | 0.6933 | —0.00318 | 0.68038 |
| 74.5 | 0.9403 | 0.7339 | 0.00122 | 0.75998 |
| 72.1 | 0.9702 | 0.7886 | 0.00471 | 0.96757 |
| 60.0 | 0.9971 | 0.9623 | —0.00004 | 1.14461 |
| 57.9 | 1.0000 | 1.0000 | | |
| Isotherm 40 °C | | | | |
| 94.2 | 0.0000 | 0.0000 | | |
| 132.0 | 0.0963 | 0.3521 | 0.65915 | —0.00011 |
| 136.6 | 0.1288 | 0.3589 | 0.55591 | 0.02583 |
| 144.3 | 0.2164 | 0.4209 | 0.42335 | 0.05107 |
| 145.0 | 0.3075 | 0.4670 | 0.32093 | 0.07371 |
| 145.6 | 0.3865 | 0.4758 | 0.22856 | 0.11791 |
| 148.0 | 0.5130 | 0.5136 | 0.14582 | 0.19266 |
| 145.2 | 0.6472 | 0.5481 | 0.06492 | 0.29257 |
| 141.9 | 0.7286 | 0.5831 | 0.03047 | 0.36409 |
| 141.0 | 0.7961 | 0.6448 | 0.03293 | 0.41360 |
| 130.5 | 0.8902 | 0.7332 | 0.00692 | 0.52511 |
| 105.6 | 1.0000 | 1.0000 | | |
| Isotherm 58 °C | | | | |
| 222.3 | 0.0000 | 0.0000 | | |
| 290.1 | 0.0620 | 0.2758 | 0.67555 | —0.00012 |
| 324.8 | 0.1711 | 0.3906 | 0.43400 | 0.01632 |
| 340.0 | 0.2504 | 0.4683 | 0.36687 | 0.03483 |
| 354.5 | 0.4195 | 0.4787 | 0.18785 | 0.13284 |
| 359.0 | 0.5581 | 0.5438 | 0.10683 | 0.21564 |

*Table 1 (continued)*

| $p$ (Torr) | $x_1'$ | $x_1''$ | $\log f_1$ | $\log f_2$ |
|---|---|---|---|---|
| 352.9 | 0.6254 | 0.5824 | 0.07988 | 0.24188 |
| 346.7 | 0.7051 | 0.6133 | 0.04270 | 0.20494 |
| 331.4 | 0.7881 | 0.6765 | 0.01776 | 0.35230 |
| 328.6 | 0.8512 | 0.7184 | 0.00648 | 0.44183 |
| 309.0 | 0.9218 | 0.8165 | 0.00173 | 0.50956 |
| 272.1 | 1.0000 | 1.0000 | | |
| *System Isopropanol (1)/n-Hexane (2)* | | | | |
| Isotherm 30 °C | | | | |
| 186.0 | 0.0000 | 0.0000 | | |
| 187.3 | 0.0213 | 0.0438 | 0.81890 | −0.00713 |
| 189.2 | 0.0224 | 0.0592 | 0.93243 | −0.00938 |
| 191.0 | 0.0408 | 0.0906 | 0.86088 | −0.01183 |
| 193.0 | 0.0648 | 0.1072 | 0.73750 | −0.00438 |
| 196.3 | 0.0874 | 0.1253 | 0.68259 | 0.00458 |
| 197.2 | 0.1051 | 0.1381 | 0.64670 | 0.00864 |
| 199.0 | 0.1590 | 0.1621 | 0.54039 | 0.02723 |
| 199.0 | 0.2526 | 0.1924 | 0.41377 | 0.06248 |
| 197.5 | 0.3197 | 0.1983 | 0.32134 | 0.09692 |
| 191.0 | 0.4852 | 0.2201 | 0.17112 | 0.19178 |
| 184.0 | 0.5805 | 0.2412 | 0.11698 | 0.22278 |
| 174.0 | 0.7025 | 0.2725 | 0.06316 | 0.36407 |
| 151.0 | 0.8125 | 0.3550 | 0.0484 | 0.44739 |
| 122.0 | 0.9137 | 0.4487 | 0.01294 | 0.62472 |
| 100.0 | 0.9435 | 0.5512 | 0.00264 | 0.63384 |
| 83.8 | 0.9651 | 0.6671 | −0.00058 | 0.70996 |
| 67.0 | 0.9875 | 0.8526 | −0.00066 | 0.63279 |
| 57.9 | 1.0000 | 1.0000 | | |
| Isotherm 40 °C | | | | |
| 257.7 | 0.0000 | 0.0000 | | |
| 282.0 | 0.0351 | 0.0813 | 0.78518 | −0.01172 |
| 291.0 | 0.0823 | 0.1486 | 0.69039 | −0.00963 |
| 300.5 | 0.1558 | 0.2021 | 0.56043 | 0.01203 |
| 302.5 | 0.1828 | 0.2138 | 0.51828 | 0.02254 |
| 299.0 | 0.3175 | 0.2417 | 0.32684 | 0.08015 |
| 297.0 | 0.3712 | 0.2478 | 0.26694 | 0.10939 |
| 293.2 | 0.4715 | 0.2641 | 0.18569 | 0.17032 |
| 269.8 | 0.6878 | 0.3072 | 0.05341 | 0.33887 |
| 259.0 | 0.7456 | 0.3375 | 0.03992 | 0.38912 |
| 244.1 | 0.8003 | 0.3768 | 0.03155 | 0.4423 |
| 166.0 | 0.9392 | 0.6147 | 0.00970 | 0.58545 |
| 105.8 | 1.0000 | 1.0000 | | |

*Table 1 (continued)*

| $p$ (Torr) | $x_1'$ | $x_1''$ | $\log f_1$ | $\log f_2$ |
|---|---|---|---|---|
| | | Isotherm 58 °C | | |
| 574.2 | 0.0000 | 0.0000 | | |
| 620.0 | 0.0572 | 0.1238 | 0.08288 | 0.00013 |
| 640.2 | 0.1812 | 0.2153 | 0.43563 | 0.02666 |
| 647.5 | 0.2251 | 0.2298 | 0.37459 | 0.05133 |
| 627.8 | 0.5385 | 0.3195 | 0.12772 | 0.20059 |
| 619.7 | 0.5882 | 0.3321 | 0.10082 | 0.24197 |
| 595.0 | 0.6948 | 0.3820 | 0.07205 | 0.32123 |
| 570.1 | 0.7597 | 0.4106 | 0.04663 | 0.38659 |
| 526.4 | 0.8263 | 0.4581 | 0.02394 | 0.46000 |
| 453.0 | 0.8955 | 0.5501 | 0.00550 | 0.53469 |
| 361.5 | 0.9561 | 0.7258 | 0.00184 | 0.60106 |
| 271.8 | 1.0000 | 1.0000 | | |

## Results

Table 1 shows the logarithm of the activity coefficients of the two systems at 30, 40 and 58 °C calculated by *Scatchard*'s equation[1]. The thermodynamic consistency of the experimental data were proved by *Herrington*'s method[6,7].

Molar volumes of pure components were calculated by densities. Virial coefficients of $n$-hexane and $n$-heptane were taken from *Schafer* and *Kunz*[8] and *McGlashan* and *Potter*[9], for isopropanol by extrapolation of data from *Moreland*, *McKetta* and *Silberberg*[10].

According to *Redlich* and *Kister*[11] it is possible to express the logarithms of the activity coefficients as a function of three constants as follows

$$\begin{aligned} \ln f_1 &= x_2^{2\prime}\,[B + C(3x_1' - x_2') + D(x_1' - x_2')(5x_1' - x_2') + \ldots\ldots\ldots\ldots] \\ \ln f_2 &= x_1^{2\prime}\,[B - C(3x_2' - x_1') + D(x_2' - x_1')(5x_2' - x_1') + \ldots\ldots\ldots\ldots] \end{aligned} \tag{1}$$

The constants and their temperature functions for the systems are shown in Table 2.

Fig. 1 shows the logarithms of the activity coefficients as function of the molar fraction at 40 and 58 °C; the 30° isotherm is shown in Part II of this work[15].

*Table 2*

| $t/°C$ | $B$ | $B_{AZ}$ | $B_{\text{for}\, x_1' \leftrightarrows 0}$ | $C$ | $C_{AZ}$ | $C_{\text{for}\, x_1' \leftrightarrows 0}$ | $D$ | $p_{AZ}$ Torr | $x_1'{}_{AZ}$ |
|---|---|---|---|---|---|---|---|---|---|
| | | | | System Isopropanol/*n*-Hexane | | | | | |
| 30 | 0.7508 | 0.768 | 0.769 | $-0.0820$ | $-0.075$ | $-0.092$ | 0.1713 | 199 | 0.1765 |
| 40 | 0.7215 | 0.738 | 0.723 | $-0.0732$ | $-0.067$ | $-0.071$ | 0.1636 | 303.5 | 0.2175 |
| 58 | 0.6695 | 0.691 | 0.680 | $-0.0587$ | $-0.050$ | $-0.054$ | 0.1509 | 649 | 0.2595 |
| | $B=\frac{284.5}{T}-0.1883$ | | | $C=-\frac{83.4}{T}+0.1934$ | | | $D=\frac{73}{T}-0.0698$ | | |
| | | | | System Isopropanol/*n*-Heptane | | | | | |
| 30 | 0.7266 | 0.729 | 0.7280 | $-0.1050$ | $-0.093$ | $-0.110$ | 0.1327 | 88 | 0.4700 |
| 40 | 0.6981 | 0.691 | 0.7015 | $-0.0972$ | $-0.085$ | $-0.089$ | 0.1256 | 145.5 | 0.5050 |
| 58 | 0.6471 | 0.656 | 0.6658 | $-0.0835$ | $-0.078$ | $-0.069$ | 0.1131 | 359.6 | 0.5375 |
| | $B=\frac{277.5}{T}-0.1893$ | | | $C=-\frac{75.5}{T}+0.1442$ | | | $D=\frac{68.7}{T}-0.0943$ | | |

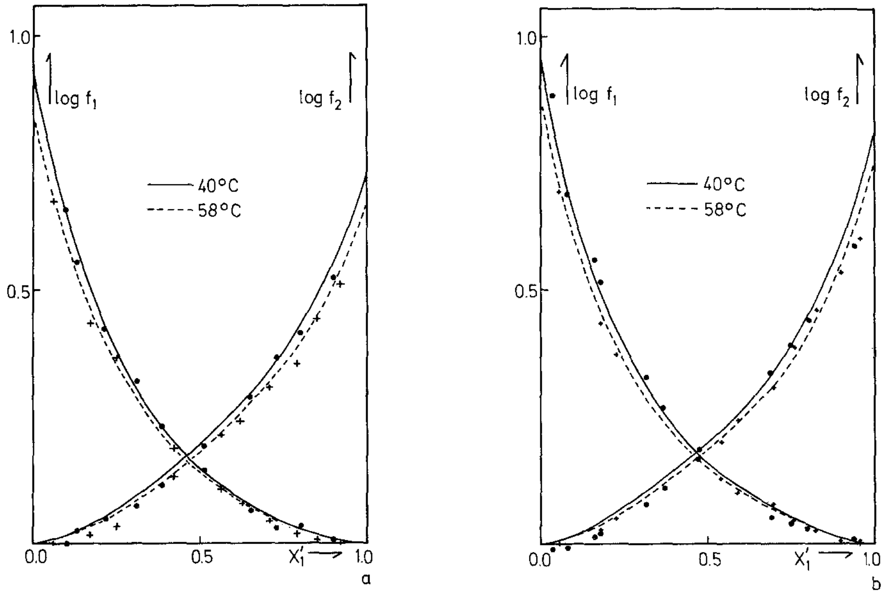

Fig. 1. Logarithms of activity coefficients as function of the mole fraction; *a* system isopropanol (1)/*n*-heptane (2); *b* system isopropanol (1)/*n*-hexane (2)

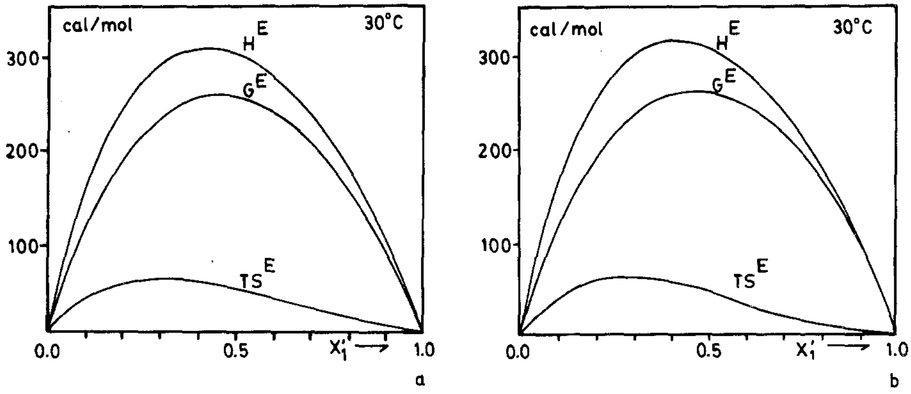

Fig. 2. The $G^E$, $H^E$ and $TS^E$ functions as functions of the mole fraction; *a* system isopropanol (1)/*n*-heptane (2); *b* system isopropanol (1)/*n*-hexane (2)

The thermodynamic excess functions are calculated from the activity coefficients by

$$\begin{aligned} G^E &= \text{molar excess free enthalpy} = RT(x_1'\ln f_1 + x_2'\ln f_2) = \\ &= 2{,}3\,RTx_1'(1-x_1')\,|B_{(T)} + C_{(T)}(2x_1'-1) + D_{(T)}(2x_1'-1)^2 + \ldots\ldots| \end{aligned}$$

$$\begin{aligned} H^E = \text{molar excess enthalpy} &= -RT^2\left[x_1'\frac{\mathrm{d}\ln f_1}{\mathrm{d}T} + x_2'\frac{\mathrm{d}\ln f_2}{\mathrm{d}T}\right] = \\ &= -T^2\frac{\mathrm{d}\dfrac{G^E}{T}}{\mathrm{d}T} \end{aligned}$$

$$S^E = \text{molar excess entropy} = \frac{H^E - G^E}{T}$$

These results are shown in Fig. 2 for the 30 °C isotherm. *Raoult*'s Law states $\dfrac{x_i''P}{p_{0i}} = x_i'$ and this law is expected to be valid for $x_i' \leftrightarrows 0$ if vapours are supposed to behave as ideal gases[12, 13].

In the limit $x_2' \leftrightarrows 0$, Equ. (1) becomes

$$\frac{1}{p_{01}}\left(\frac{\mathrm{d}p_1}{\mathrm{d}x_1'}\right)_{x_2'\leftrightarrows 0} - 1 + \frac{B_{11} - V_{01}}{RT}\left(\frac{\mathrm{d}p}{\mathrm{d}x_1'}\right)_{x_2'\leftrightarrows 0} = 0 \qquad (2)$$

since for

$$x_2' \leftrightarrows 0\,\frac{1}{p_{01}}\left(\frac{\mathrm{d}p_1}{\mathrm{d}x_1'}\right)_{x_2'\leftrightarrows 0} = \overset{\lim}{x_2' \leftrightarrows 0}\,\frac{p_{01} - p_1}{x_2'P}$$

and

$$\frac{1}{p_{01}}\left(\frac{\mathrm{d}p}{\mathrm{d}x_1'}\right)_{x_2'\leftrightarrows 0} = \overset{\lim}{x_2' \leftrightarrows 0}\,\frac{p - p_{01}}{x_2'p} = \overset{\lim}{x_2' \leftrightarrows 0}\,\frac{p - p_{01}}{x_1'p(x_1' - x_2')^2}.$$

To test the validity interval for *Raoult*'s law, i.e. Equ. (2), the differential coefficients are read graphically as shown in Fig. 3.

The substitution of these values for 30 °C in Equ. (2) leads to a deviation of 6,2% at $x_1' = 0.0848$ in the system isopropanol/*n*-heptane and 5.5% at $x_1' = 0.0863$ in the system isopropanol/*n*-hexane.

If Equ. (1) with two constants, $B$ and $C$, are considered in the limit of concentration a system might be formed which allows an independent calculation of these two constants since for

$$x_1' \leftrightarrows 0 \quad \log f_1 = B + C$$
$$x_1' \leftrightarrows 1 \quad \log f_2 = B - C$$

Values differ slightly and are given in Table 2. For the azeotropic point

$$\left(\frac{p}{p_0}\right)_{AZ} = (f_2)_{AZ}$$

and

$$\left(\frac{p_{01}}{p_{02}}\right)_{AZ} = \left(\frac{f_2}{f_1}\right)_{AZ} \tag{3}$$

Measured azeotropic points are given in Table 2.

Substitution of the values of Table 2 and 1 in Equ. (3) allow to know

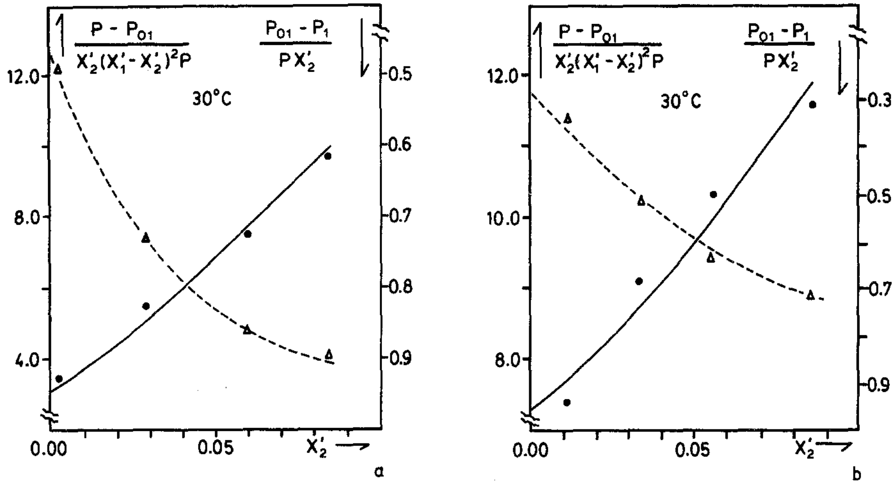

Fig. 3. Limit of $(p_{01}-p_1)/px_2'$ and $(p-p_{01})/|x_2'(x_1'-x_2')^2p|$ at low concentration of non polar component; *a* system isopropanol (1)/*n*-heptane (2); *b* system isopropanol (1)/*n*-hexane (2)

$(f_1)_{AZ}$; these values substituted on the left side of *Redlich* and *Kister*'s Equ. (1), with two constants, allow again to calculate $B$ and $C$; these values are also given in Table 2. These data demonstrate the coincidence of the interval where these systems behave ideally as was previously shown in Part I and II according to *Sarolea-Mathot*'s[14].

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