

THERMODYNAMIC MIXING FUNCTIONS OF THE SYSTEM  
TETRAHYDROFURAN (1)-METHANOL (2)

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Isobaric vapour-liquid equilibria at pressures 235.5 and 384.5 Torr, enthalpy of mixing at temperatures 25.0 and 34.0°C and density at 25°C have been measured, depending on the composition of the mixtures tetrahydrofuran-methanol. From these data, the excess thermodynamic functions of mixing  $\Delta G^E$ ,  $\Delta TS^E$ ,  $\Delta C_p^E$  and  $\Delta V^E$  for 25°C have been determined. Correlation of the experimental data yielded the Redlich-Kister constants for  $\Delta G^E$  and  $\Delta H^E$  as functions of concentration, as well as constants of the equation representing the temperature dependence of the excess functions.

Thermodynamic description of the ternary system tetrahydrofuran-methanol-poly(vinyl chloride)<sup>1</sup> requires the knowledge of the behaviour of the system tetrahydrofuran-methanol. The data obtained in the measurements were also used to illustrate the efficiency of the calculating procedure<sup>2</sup> allowing to transform the isobaric data of the liquid-vapour equilibrium and the enthalpies of mixing to isothermal conditions and to calculate both the concentration and temperature dependences of the excess thermodynamic functions.

## EXPERIMENTAL

*Materials.* Tetrahydrofuran (Carlo Erba, Milan) was dried with sodium and rectified on a packed column (~40 TP) in nitrogen; every time it was freshly redistilled *in vacuo* with lithium aluminium hydride added before use. The physical constants determined here were in accordance with those in the literature: b.p. 65.95°C, (in ref.<sup>4</sup> 65.70°C, in ref.<sup>5</sup> 65.965°C),  $d_4^{20}$  0.88205 (in ref.<sup>6</sup> 0.8821, in ref.<sup>7</sup> 0.8826) and  $n_D^{25}$  1.4051 (in ref.<sup>6</sup> 1.4048). Methanol *purissimum* (Lachema, Brno) was dried with sodium and distilled on a packed column (~40 TP); b.p. 64.55 (in ref.<sup>8</sup> 64.51°C),  $d_4^{25}$  0.78667 (in ref.<sup>9,10</sup> 0.78675) and  $n_D^{25}$  1.32661 (in ref.<sup>10</sup> 1.32663).

*Working procedures.* The mixture densities were determined in 50 ml two-capillary pycnometers in a water thermostat at 25.00 ± 0.01°C with an accuracy of ± 1.10<sup>-5</sup> g cm<sup>-3</sup>. The enthalpies of mixing were measured in Calvet's calorimeter in stainless mixing cells, 2 × 3 ml in volume, with a nickel membrane<sup>11</sup>. Corrections for the vapour phase volume were negligible.

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The vapour-liquid equilibrium was measured isobarically in a modified Gillespie's circulation apparatus<sup>12</sup> (without stopcocks and with stirring of the condensed vapour phase). The pressure was kept constant to  $\pm 0.2$  Torr by means of a manostat<sup>13</sup>. The temperature was measured with a calibrated bead thermistor 12 NR 15 (Powder Metallurgy Works, Šumperk) with an accuracy of  $\pm 0.02^\circ\text{C}$ . The thermistor was calibrated at four temperatures using a Pt-normal and Mueller's bridge, model G 2, produced by L & N (Philadelphia, USA); the manostat was calibrated by measuring the boiling point of redistilled water<sup>14</sup> in a Swietoslawski ebullimeter. The concentrations of the equilibrium phases were measured with an accuracy of  $\pm 0.001$  by means of the refractive index, using an immersion refractometer produced by Zeiss, Jena. A calibration curve  $x = x(n_D)$  was determined prior to measurements, represented by a polynomial of the 4th degree with a standard error  $\sigma_x = 8 \cdot 10^{-4}$ . With respect to the instability of tetrahydrofuran the measurements were carried out in nitrogen and each concentration was prepared from pure components. The vapour pressures of pure components were taken from the literature<sup>8,9</sup> and smoothed by Antoine's equation. The boiling points measured here at two pressures fitted the literature data.

TABLE I

Excess Volumes  $\Delta V^E$  and Enthalpies  $\Delta H^E$

Constants of Eq. (1): for  $\Delta V^E$  at  $25^\circ\text{C}$   $C_0 = -0.6007$ ,  $C_1 = 0.1583$ ,  $C_2 = -0.0023$ ,  $C_3 = -0.0405$ ,  $\sigma_V = 0.0079$ ; for  $\Delta H^E$  at  $25^\circ\text{C}$  ( $34^\circ\text{C}$ )  $C_0 = 1\ 116.6$  ( $2\ 219.1$ ),  $C_1 = 944.9$  ( $997.3$ ),  $\sigma_H = 39.4$  ( $37.8$ ).

| 25°C   |  |        |                                 | 34°C   |                                 |
|--------|--|--------|---------------------------------|--------|---------------------------------|
| $x_1$  | $\Delta V^E/(x_1 x_2)$<br>cm <sup>3</sup> /mol | $x_1$  | $\Delta H^E/(x_1 x_2)$<br>J/mol | $x_1$  | $\Delta H^E/(x_1 x_2)$<br>J/mol |
| 0.0494 | -0.7204  | 0.1403 | 1 403                           | 0.1035 | 1 384                           |
| 0.0928 | -0.7090  | 0.1897 | 1 526                           | 0.1803 | 1 591                           |
| 0.1539 | -0.6882  | 0.2021 | 1 577                           | 0.1836 | 1 626                           |
| 0.2044 | -0.6844  | 0.2466 | 1 692                           | 0.2474 | 1 742                           |
| 0.2462 | -0.6795  | 0.3327 | 1 814                           | 0.3428 | 1 924                           |
| 0.2987 | -0.6678  | 0.4224 | 1 983                           | 0.4658 | 2 169                           |
| 0.4004 | -0.6265  | 0.4864 | 2 111                           | 0.5086 | 2 257                           |
| 0.4490 | -0.6257  | 0.5443 | 2 183                           | 0.5557 | 2 266                           |
| 0.4969 | -0.6000  | 0.5910 | 2 232                           | 0.6516 | 2 520                           |
| 0.5988 | -0.5719  | 0.6027 | 2 253                           | 0.6582 | 2 472                           |
| 0.6457 | -0.5547  | 0.6861 | 2 435                           | 0.7750 | 2 754                           |
| 0.7006 | -0.5311  | 0.7657 | 2 583                           | 0.8464 | 2 958                           |
| 0.7475 | -0.5309  | 0.8600 | 2 802                           | 0.8917 | 3 009                           |
| 0.8040 | -0.5092  | 0.8603 | 2 858                           |        |                                 |
| 0.8480 | -0.5223  | 0.9169 | 2 959                           |        |                                 |
| 0.8910 | -0.4899  | 0.9687 | 3 024                           |        |                                 |

## RESULTS AND DISCUSSION

The measured dependence of density upon the mixture composition was used to calculate the excess volumes of mixing  $\Delta V^E$ . The volumes and enthalpies of mixing were correlated using the Redlich-Kister equation

$$\Delta Z^E/(x_1 x_2) = \sum_{i=0}^n C_i (2x_1 - 1)^i, \quad (1)$$

with statistical weights corresponding to the constant relative experimental error of the excess function  $\Delta Z^E$  (cf. list of symbols at the end of the paper). The corresponding optimum degrees of the polynomial were chosen on the basis of Fischer's test<sup>15</sup> at a 5% significance level (Table I). Since liquid-vapour equilibrium data (Table II) are nonisothermal, they were not treated independently as above. Their consistency was confirmed by the Redlich-Kister test<sup>16,17</sup>. The corresponding values of  $\ln(\gamma_1/\gamma_2)$  were calculated on the assumption of an ideal behaviour of the vapour phase<sup>12</sup>. The isobaric activity and enthalpy data were treated together by specializing a general procedure suggested by us<sup>2</sup> which allows to obtain the temperature dependence of the constants of Eq. (1) for  $\Delta Z^E \equiv \Delta G^E/RT$  in the form

$$C_i^G = C_{i0} + C_{i1}/T - C_{i2} \ln T, \quad i = 0, 1, \dots, n. \quad (2a)$$

TABLE II

Vapour-Liquid Equilibrium in the System Tetrahydrofuran (1)-Methanol (2)

| $p = 235.5$ Torr |        |                     | $p = 384.5$ Torr |        |                     |
|------------------|--------|---------------------|------------------|--------|---------------------|
| $x_1$            | $y_1$  | $T, ^\circ\text{C}$ | $x_1$            | $y_1$  | $T, ^\circ\text{C}$ |
| 0.0195           | 0.0480 | 36.80               | 0.0380           | 0.0800 | 47.05               |
| 0.0395           | 0.0890 | 36.20               | 0.0580           | 0.1090 | 46.70               |
| 0.0560           | 0.1220 | 35.85               | 0.1080           | 0.1950 | 45.65               |
| 0.0950           | 0.1910 | 34.90               | 0.1260           | 0.2210 | 45.25               |
| 0.2430           | 0.3700 | 32.55               | 0.1610           | 0.2640 | 44.70               |
| 0.3510           | 0.4550 | 31.60               | 0.2270           | 0.3290 | 43.95               |
| 0.3940           | 0.4880 | 31.50               | 0.2990           | 0.3880 | 43.25               |
| 0.5450           | 0.5750 | 31.00               | 0.3240           | 0.4090 | 43.05               |
| 0.7260           | 0.6880 | 30.85               | 0.4300           | 0.4870 | 42.45               |
| 0.8360           | 0.7720 | 31.30               | 0.6570           | 0.6250 | 42.25               |
| 0.8680           | 0.8030 | 31.55               | 0.8290           | 0.7500 | 43.10               |
| 0.9050           | 0.8460 | 32.00               | 0.9400           | 0.8910 | 44.75               |
| 0.9330           | 0.8870 | 32.40               | 0.9580           | 0.9210 | 45.20               |
| 0.9590           | 0.9280 | 32.95               |                  |        |                     |

In accordance with the Gibbs-Helmholtz equation we then obtain for  $\Delta Z^E \equiv \Delta H^E$

$$C_i^H = R(C_{i1} + C_{i2}T), \quad i = 0, 1, \dots, n. \quad (2b)$$

It can be seen from Eqs (2a) and (2b) that we assumed  $\Delta C_p^E(T) = \text{const.}$

The comparison of the  $\Delta G^E$  values thus calculated for 25°C with the isothermal data by Arm and coworkers<sup>3</sup> confirmed the main conclusions of our preceding paper<sup>2</sup>: 1) The best estimates of the  $C_{ij}$  constants of Eqs (2a,b)

|           |        |         |       |       |         |       |
|-----------|--------|---------|-------|-------|---------|-------|
| $i, j:$   | 0, 0   | 0, 1    | 0, 2  | 1, 0  | 1, 1    | 1, 2  |
| $C_{ij}:$ | 14.137 | -375.65 | 2.110 | 6.086 | -172.42 | 0.960 |

and the  $C_i^G$  values calculated therefrom ( $C_0^G = 0.8556$ ,  $C_1^G = 0.0378$ ), and of  $C_i^H$  ( $C_0^H = 2107.2$ ,  $C_1^H = 946.43$ ) are obtained from a combination of all the above activity and enthalpy measurements. The dependences calculated using these constants are in agreement with those measured within the limits of experimental error. The  $\Delta G^E$  calculated for 25°C differed insignificantly from the curve of  $\Delta G^E$  at the same temperature calculated by Arm and coworkers (Table VIII in ref.<sup>3</sup>) from the isothermal dependence of the total vapour pressure on composition. 2) Constants  $C_i^G$  ( $C_0^G = 0.9097$ ,  $C_1^G = 0.0164$ ) calculated from the isobaric data alone (two isobars obtained in the present work and supplemented by an isobar at 600 Torr measured by Papoušek and Págo<sup>4</sup>) yield a curve for  $\Delta G^E$  identical with the data<sup>3</sup> within the limits of experimental error. However, the  $C_i^H$  thus obtained yield  $\Delta H^E$  considerably higher than experimental; the isobaric  $T$ - $x$  curves determined experimentally have rather a flat minimum, so that the experimental points are agglomerated within the narrow neighbourhoods of three temperatures. The numerical accuracy of the derivatives  $\partial(\Delta G/T)/\partial T$  is then bound to be very low.

The  $\Delta G^E$  and  $\Delta H^E$  values were also used to calculate  $T\Delta S^E$  whose concentration dependence was S-shaped. Fig. 1 shows our smoothed results compared with those obtained by Arm and coworkers<sup>3</sup>; a systematical difference between the measured  $\Delta H^E$  is easy to see. The calorimeter, the deflection method

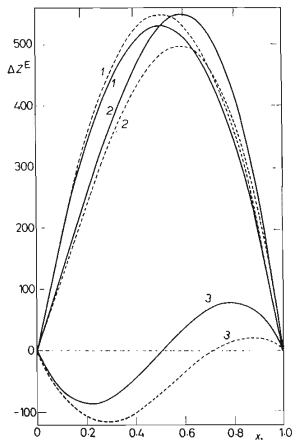


FIG. 1  
Comparison of Curves of the Excess Functions  $\Delta Z^E$   
(Joule/mol) at 25°C

1  $\Delta G^E$ , 2  $\Delta H^E$ , 3  $T\Delta S^E$ ; ——— our measurements treated after ref.<sup>2</sup>; - - - - data taken from ref.<sup>3</sup>.

of measurement and calibration by means of the heat of neutralization of acetic acid and sodium hydroxide described in paper<sup>6</sup> do not exclude a systematic error.

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#### LIST OF SYMBOLS

|                |  |
|----------------|--|
| $C_i$          | constants of the Redlich-Kister equation   |
| $C_i^G$        | constants $C_i$ in expansion (I) for the function $\Delta G^E/RT$  |
| $C_i^H$        | constants $C_i$ in expansion (I) for the function $\Delta H^E$   |
| $\Delta C_p^E$ | excess heat capacity of mixing   |
| $\Delta G^E$   | excess Gibbs energy of mixing  |
| $\Delta S^E$   | excess entropy of mixing   |
| $T$            | absolute temperature   |
| $\Delta V^E$   | excess volume of mixing  |
| $x_i$          | mole fraction of the $i$ -th component in the liquid phase   |
| $y_i$          | mole fraction of the $i$ -th component in the vapour phase   |
| $\Delta Z^E$   | general excess function  |
| $\gamma_i$     | activity coefficient of the $i$ -th component ( $i = 1, 2$ )   |
| $\sigma_z$     | standard deviation of the experimental value $Z$ (for $\Delta V^E$ and $\Delta H^E$ the deviations are given for tabulated functions $\Delta V^E/(x_1 x_2)$ and $\Delta H^E/(x_1 x_2)$ , respectively) |

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