

## LIQUID-VAPOUR AND LIQUID-LIQUID EQUILIBRIA IN THE TETRAHYDROFURAN(1)-n-HEXANE(2)-WATER(3) SYSTEM\*

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The object of this work is the isobaric vapour-liquid equilibrium (at 101.32 kPa) and the liquid-liquid equilibrium (at 30 and 50°C) in the ternary tetrahydrofuran-n-hexane-water system. Further, the isobaric vapour-liquid equilibrium (at 101.32 kPa) in the binary tetrahydrofuran-n-hexane and tetrahydrofuran-water systems has been established. The experimental data obtained have been fitted to the Redlich-Kister equation. The constants of the correlation relation determined from the data on the vapour-liquid equilibria have been proved to provide an adequate description of the liquid-liquid equilibrium.

This work continues our foregoing study of phase equilibria in aqueous solutions<sup>1,2</sup>. Experimental data on the vapour-liquid equilibrium (mostly isothermal) in the tetrahydrofuran (THF)-H<sub>2</sub>O system were published by a number of authors<sup>1-6</sup>. In the open literature there exist the only isobaric data (at 24.82 kPa) on the system THF-n-hexane (HX) published by Biroš and coworkers<sup>7</sup>. The binary system HX-H<sub>2</sub>O is noted for a very low mutual solubility of components and the available data on the liquid-liquid equilibrium show a considerable scattering<sup>8</sup>. For the ternary THF-HX-H<sub>2</sub>O system no experimental data have been found in the open literature.

### EXPERIMENTAL

*Pure substances.* Tetrahydrofuran (Laborchemie, Apolda) has been shaken with calcinated FeSO<sub>4</sub> and left at rest for 48 hours. Then it has been rectified with sodium on a packed column (40 theoretical plates). Before using it has always been dried up with LiAlH<sub>4</sub> and distilled over in vacuum. In such a way prepared THF has contained at most 0.01 mass % H<sub>2</sub>O and had the following physical constants:  $d$  (20°C) 0.88732 g/cm<sup>3</sup> (ref.<sup>4</sup> 0.8882),  $n_D^{25}$  1.4050 (ref.<sup>6</sup> 1.4048), n.b.p. 65.95°C (ref.<sup>9</sup> 65.965°C). The Antoine constants have been taken over from ref.<sup>1</sup> ( $A = 6.99589$ ,  $B = 1202.7$ ,  $C = 226.3$ ) and the critical constants from ref.<sup>10</sup>.

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n-Hexane has been synthesized by the reaction of n-propyl bromide with sodium. The product has been subjected to rectification on a packed column (40 theoretical plates). In this way prepared n-hexane has had the following physical constants:  $d$  (20°C) 0.6594 (ref.<sup>11</sup> 0.65945),  $n_D^{20}$  1.3749 (ref.<sup>12</sup> 1.3750), n.b.p. 68.68°C (ref.<sup>12</sup> 68.67). Its Antoine constants have been taken over from ref.<sup>13</sup> ( $A = 6.88555$ ,  $B = 1175.817$ ,  $C = 224.867$ ) and critical constants from ref.<sup>10</sup>.

Water used has been redistilled with specific conductivity  $5 \cdot 10^{-6} \Omega^{-1} \text{cm}^{-1}$ . Its Antoine constants have been taken over from ref.<sup>14</sup> ( $A = 7.96681$ ,  $B = 1668.2$ ,  $C = 228$ ) and critical constants from ref.<sup>10</sup>.

*Vapour-liquid equilibrium.* The measurement of vapour-liquid equilibrium has been carried out by a dynamic method at constant pressure similarly as it is described in detail in ref.<sup>1</sup>. The boiling temperature has been measured by a digital thermometer (Hewlett-Packard 2801 Quartz Thermometer) with an accuracy of  $\pm 0.05$  K. The constant pressure of 101.32 kPa has been maintained by letting in nitrogen from pressure cylinder *via* manostat and compensating reservoir (0.2 m<sup>3</sup>). The pressure has been checked by measuring boiling point of water in an ebulliometer connected parallel which has been separated from the system by a freezing trap.

*Liquid-liquid equilibrium.* The method of analyzing the conjugate phases has been used to determine the liquid-liquid phase equilibrium. First the heterogeneous mixture has been stirred for two hours in a thermostated cell (30 cm<sup>3</sup>) by a magnetic stirrer and then left 1–2 hours at rest. With respect to the fact that the region of limited miscibility extends on the hexane-rich side with decreasing temperature (*i.e.* the equilibrium phases existing at 30 and 50°C become turbid on cooling) we have proceeded in the following way: The equilibrium phase has been transferred by a heated syringe into a weighed flask and then weighed and homogenized by adding a known amount of THF. So obtained mixture has been analyzed and the composition of the sample taken has been determined from the result of the analysis.

*Analysis of equilibrium phases.* The concentration of components in equilibrium phases of binary systems has been determined by means of density which has been determined at 20°C in 10 cm<sup>3</sup> pycnometers. Weighing has been carried out by an analytical balance WA 31 with an accuracy of  $\pm 1 \cdot 10^{-4}$  g. The concentration dependence of density has been expressed in terms of the Redlich-Kister expansion  $d = wd_1^0 + (1-w)d_2^0 + w(1-w)[A + B(2w-1)]$ , where  $w$  is the mass fraction of component 1,  $d_i^0$  the density of pure  $i$ -th component and  $A$  and  $B$  are the parameters evaluated by the least-squares method. The THF(1)-HX(2) system:  $A_{12} = -7.2122 \cdot 10^{-2}$ ,  $B_{12} = -4.924 \cdot 10^{-3}$ ; the THF(1)-H<sub>2</sub>O(3) system:  $A_{13} = 8.3758 \cdot 10^{-2}$ ,  $B_{13} = -6.675 \cdot 10^{-3}$ . To determine the concentration of components in the ternary system the density and the determination of water content by the Fischer method (with an automatic titrator DST1) have been used. The calculation of composition in the ternary system has been carried out numerically by the Newton method, the determined water content and density being utilized. To express the concentration dependence of density on composition in the ternary mixture we have used the relation

$$d = \sum_{i=1}^3 w_i d_i^0 + \sum_{i=1}^3 \sum_{j>i}^3 w_i w_j [A_{ij} + B_{ij}(w_i - w_j)] + w_1 w_2 w_3 (E_0 + E_1 w_1).$$

On the basis of the density data in the ternary mixture, the parameters  $A_{23} = -0.30426$ ,  $B_{23} = 0.0170$ ,  $E_0 = -0.1064$ ,  $E_1 = 0.2752$  have been evaluated. The remaining parameters have been taken over from the concentration dependence in the binary systems.

## RESULTS

The results of the experimental determination of isobaric vapour-liquid equilibrium (at 101.32 kPa) in the binary systems are given in Table I (THF-HX and THF-H<sub>2</sub>O). The experimental data on equilibrium in the ternary THF-HX-H<sub>2</sub>O system are presented in Table II (vapour-liquid equilibrium) and in Table III (liquid-liquid equilibrium at 30 and 50°C).

*Correlation of Equilibrium Data*

The phase vapour-liquid equilibrium have been described in terms of the concentration dependence of activity coefficients calculated from the relation

$$\gamma_i = y_i P \Theta_i / (x_i P_i^0), \quad (1)$$

where  $\Theta_i$  is the correction for the real behaviour of the vapour phase. To represent the concentration dependence of activity coefficients, the Redlich-Kister equation<sup>16</sup> for the dimensionless excess Gibbs energy ( $Q = G^E/RT$ ) has been applied in the form

$$Q = (1/2) \sum_{i=1}^3 \sum_{j=1}^3 x_i x_j [b_{ij} + c_{ij}(x_i - x_j) + d_{ij}(x_i - x_j)^2 + e_{ij}(x_i - x_j)^3 + \dots] + A_{123}, \quad (2)$$

where it holds

$$b_{ij} = b_{ji}, \quad d_{ij} = d_{ji}, \dots, \quad c_{ij} = -c_{ji}, \quad e_{ij} = -e_{ji}, \dots, \quad b_{ii} = b_{jj} = 0, \\ c_{ii} = c_{jj} = 0, \dots \quad (3)$$

The ternary term has been considered only in the form

$$A_{123} = x_1 x_2 x_3 C. \quad (4)$$

(This relation is identical with the traditionally used rule - see *e.g.* ref.<sup>16,19</sup>.)

For the activity coefficient of the  $k$ -th component, it follows the relation

$$\ln \gamma_k = \sum_{i=1}^3 x_i \{ [b_{ki} + c_{ki}(2x_k - x_i) + d_{ki}(x_k - x_i)(3x_k - x_i) + \\ + e_{ki}(x_k - x_i)^2(4x_k - x_i)] + \dots \\ - (1/2) \sum_{j=1}^3 x_j [b_{ij} + c_{ij}(3x_i - x_j) + d_{ij}(x_i - x_j)(5x_i - x_j) + \\ + e_{ij}(x_i - x_j)^2(7x_i - x_j) + \dots] \} + (A \ln \gamma_k)_{123}, \quad (5)$$

TABLE I  
Vapour-Liquid Equilibrium at 101.32 kPa

$x_1$	$y_1$	$t, ^\circ\text{C}$	$\Delta y_1$	$\ln \gamma_1/\gamma_2$
Tetrahydrofuran(1)-n-hexane(2)				
$b_{12} = 0.500 \quad c_{12} = 0.107^a$				
0.073	0.108	67.21	-0.001	0.3522
0.094	0.135	66.84	-0.002	0.3350
0.119	0.172	66.37	0.001	0.3456
0.152	0.212	65.87	0.000	0.3264
0.173	0.236	65.57	0.001	0.3187
0.229	0.292	64.97	-0.005	0.2501
0.275	0.341	64.44	-0.001	0.2384
0.352	0.408	63.87	-0.005	0.1661
0.439	0.480	63.36	-0.004	0.0975
0.528	0.546	63.07	-0.005	0.0043
0.593	0.595	63.02	-0.004	-0.0631
0.731	0.700	63.24	0.000	-0.2197
0.782	0.734	63.49	0.000	-0.2821
0.842	0.798	63.87	-0.001	-0.3714
0.894	0.854	64.20	0.000	-0.4401
0.923	0.888	64.62	0.000	-0.4878
0.945	0.917	64.93	0.000	-0.5218
0.966	0.944	65.29	-0.001	-0.5753
Tetrahydrofuran(1)-water(3)				
$b_{13} = 2.1701 \quad c_{13} = -0.2524 \quad d_{13} = 0.3291 \quad e_{13} = -0.2145^a$				
0.327	0.768	64.41	0.009	0.5358
0.438	0.766	64.31	-0.005	0.0510
0.516	0.774	64.27	-0.009	-0.2193
0.730	0.792	63.69	-0.034	-1.0511
0.792	0.809	63.6	-0.030	-1.2873
0.845	0.832	63.62	-0.020	-1.4868
0.926	0.885	64.02	-0.005	-1.8699
0.968	0.946	64.84	-0.010	-1.9445

<sup>a</sup> Constants of the Redlich-Kister equation (2).

where

$$(\Delta \ln \gamma_k)_{123} = x_i x_j (1 - 2x_k) C, \quad i \neq j \neq k. \quad (6)$$

To represent the real behaviour of the vapour phase, the virial equation of state with the second virial coefficient has been used and  $\Theta_k$  takes in this case the form

$$\Theta_k = \exp \left\{ \left[ \left( 2 \sum_{j=1}^N y_k B_{kj} - B \right) P - B_{kk} P_k^0 \right] / RT \right\}, \quad (7)$$

where  $B_{kk}$  is the second virial coefficient of the pure  $k$ -th component,  $B_{kj}$  is the cross virial coefficient which is approximated by the relation  $B_{kj} = (B_{kk} + B_{jj})/2$  and  $B = \sum_{j=1}^3 \sum_{i=1}^3 y_i y_j B_{ij}$  is the virial coefficient of mixture. The second virial coefficient

TABLE II

Vapour-Liquid Equilibrium in the Tetrahydrofuran(1)-n-Hexane(2)-Water(3) System at 101.32 kPa

$t, ^\circ\text{C}$	$x_1$	$x_2$	$x_3$	$y_1$	$y_2$	$y_3$
62.25	0.8146	0.1579	0.0275	0.7278	0.2008	0.0714
62.96	0.8500	0.1394	0.0107	0.7687	0.1826	0.0488
63.09	0.8910	0.0563	0.0529	0.8106	0.0912	0.0982
62.79	0.8765	0.0455	0.0780	0.7918	0.0808	0.1274
62.02	0.8442	0.0827	0.0731	0.7437	0.1294	0.1269
62.54	0.8657	0.0822	0.0520	0.7717	0.1252	0.1031
62.04	0.7662	0.0362	0.1976	0.7190	0.0882	0.1928
61.8	0.8072	0.0609	0.1319	0.7247	0.1097	0.1655
62.02	0.6849	0.3054	0.0097	0.6345	0.3230	0.0425
62.44	0.5731	0.4234	0.0035	0.5624	0.4105	0.0271
62.18	0.6710	0.3214	0.0076	0.6302	0.3345	0.0353
62.5	0.5534	0.4436	0.0030	0.5536	0.4251	0.0213
62.79	0.4994	0.4988	0.0018	0.5174	0.4683	0.0143
63.13	0.4387	0.5595	0.0018	0.4713	0.5178	0.0109
62.23	0.6596	0.3323	0.0080	0.6164	0.3445	0.0394
62.06	0.8095	0.1595	0.0311	0.7173	0.2035	0.0792
62.07	0.7945	0.0388	0.1667	0.7258	0.0872	0.1870
62.7	0.8128	0.0205	0.1667	0.7629	0.0508	0.1863
61.51	0.7993	0.1537	0.0470	0.7044	0.2000	0.0956
62.3	0.5864	0.4084	0.0052	0.5679	0.3993	0.0329
62.88	0.4671	0.5307	0.0022	0.4931	0.4921	0.0148

of pure components has been calculated in terms of the McGlashan-Potter relation<sup>18</sup>. For n-hexane, the value  $n = 6$ , for water  $n = 11.5$  (ref.<sup>15</sup>) and for tetrahydrofuran  $n = 5$  has been used. Since most experimental values lie in the temperature range of 60–67°C the temperature dependence of the second virial coefficients has not been considered but the values used correspond to 64°C ( $B_{11} = B_{\text{THF}} = -905 \text{ cm}^3/\text{mol}$ ,  $B_{22} = B_{\text{HX}} = -1346 \text{ cm}^3/\text{mol}$ ,  $B_{33} = B_{\text{H}_2\text{O}} = -629 \text{ cm}^3/\text{mol}$ ).

*Binary mixture THF(1)–HX(2)*. This system exhibits comparatively small positive deviations from the Raoult law and the computation of parameters of the Redlich–

TABLE III  
Liquid–Liquid Equilibrium in the Tetrahydrofuran(1)–n-Hexane(2)–Water(3) System at 30 and 50°C

$x_1$	$x_2$	$x_3$	$\bar{x}_1$	$\bar{x}_2^a$	$\bar{x}_3$
30°C					
0.5567	0.4090	0.0343	0.050	N	0.950
0.2913	0.6998	0.0088	0.032	N	0.968
0.7077	0.1084	0.1839	0.104	N	0.896
0.2798	0.7119	0.0082	0.029	N	0.971
0.5466	0.4074	0.0459	0.051	N	0.949
0.1350	0.8614	0.0035	0.021	N	0.978
0.6380	0.3035	0.0585 <sup>b</sup>	—	—	—
0.2775	0.7145	0.0080 <sup>b</sup>	—	—	—
0.4356	0.5456	0.0187 <sup>b</sup>	—	—	—
50°C					
0.5883	0.0338	0.3778	0.123	0.0025	0.874
0.6959	0.1843	0.1197	0.051	N	0.950
0.5845	0.3630	0.0524	0.039	N	0.961
0.2929	0.6891	0.0179	0.024	N	0.974
0.7070	0.1060	0.1869	0.068	N	0.931
0.1685	0.8247	0.0068	0.017	N	0.983
0.6862	0.938	0.2200	0.075	N	0.925
0.3739	0.6056	0.0204	0.030	N	0.970
0.4961	0.4631	0.0408 <sup>b</sup>	—	—	—
0.6432	0.2824	0.0744 <sup>b</sup>	—	—	—
0.4159	0.5620	0.0221 <sup>b</sup>	—	—	—

<sup>a</sup> N denotes  $\bar{x}_2 < 0.001$ , <sup>b</sup> denotes only the points of binodal curve.

-Kister equation has been carried out by the classical method, *i.e.* by minimizing the deviations in the logarithm of the activity coefficient ratio. The parameters obtained have had the values  $b_{12} = 0.50$ ,  $c_{12} = 0.107$ .

*Binary mixture* THF(1)-H<sub>2</sub>O(3). This system shows so high deviations from the Raoult law that the system is close to the lower critical solution temperature<sup>1</sup> (LCST = 71.8°C) at its normal boiling point. In this case we have utilized, when calculating the parameters of the correlation relation, the procedure<sup>17,1</sup> which ensures a physically correct description, *i.e.* the system homogeneity under the given conditions. The method consists in the following: According to Suška<sup>17</sup> on the basis of our and literature data<sup>2-5</sup>, we have evaluated the concentration dependence of  $G11 = \partial^2(G^M/RT)/\partial x_1^2$  and ascertained its minimum value  $(G11)_{x_0} \approx 0.01$  and the concentration coordinate  $x_0 = 0.24$  corresponding to it. When calculating the parameters, the restraining conditions have been respected

$$(G11)_{x_0, \text{exp}} = 0.01 = (G11)_{x_0, \text{calc}}$$

and

$$(G11)_{x_0, \text{exp}} = \partial(G11)/\partial x_1 = 0 = (G11)_{x_0, \text{calc}},$$

from which two parameters of the correlation relation have been evaluated and the remaining ones have been established by the least-squares method by optimizing the logarithm of the activity coefficient ratio<sup>17</sup>. Our equilibrium data (Table II) and all the data set of Sada and coworkers<sup>5</sup> have been employed for the computation. Altogether 3 sets of parameters of the Redlich-Kister equation ( $b, c, b; b, c, d, e; b, c, d, e, f$ ) have been computed. In further applications, four parameters proved to be sufficient and therefore we give here only this set:  $b_{13} = 2.1707$ ,  $c_{13} = -0.2524$ ,  $d_{13} = 0.3291$ ,  $e_{13} = -0.2145$ . The mean deviation in composition of the vapour phase has amounted to 0.0079 and the mean deviation in pressure 2 kPa. The consistence of the vapour-liquid equilibrium data in the binary systems has been checked by the Redlich-Kister test and it has been found that the data are thermodynamically consistent.

*Ternary system* THF(1)-HX(2)-H<sub>2</sub>O(3). The correlation of the vapour-liquid equilibrium data in the ternary system has been carried out by the classical way, *i.e.* by minimizing the logarithm of the activity coefficient ratio. A satisfactory fit has been obtained by using an only ternary parameter  $C = -2.8$ . Its value has been practically independent of the minimized quantity. The binary parameters of the correlation relation for the HX(2)-H<sub>2</sub>O(3) system could not be determined on the basis of the vapour-liquid equilibrium and therefore the data by Polák<sup>8</sup>, which have been extrapolated to the temperature of 64°C, have been used. The parameters  $b_{23} = 9.61$  and  $c_{23} = -2.67$  correspond to this temperature. With regard to the

fact that practically all the data occur on the side of n-hexane, an only parameter  $b_{23} = 7.0$  ( $\approx 9.61 - 2.67$ ) is sufficient to characterize this binary mixture. The mean deviations in single quantities have been as follows:  $\Delta\bar{y}_1 = 0.0011$ ,  $\Delta\bar{y}_2 = 0.0051$ ,  $\Delta\bar{y}_3 = 0.0083$ ,  $\Delta\bar{P} = 1.7$  kPa.

## DISCUSSION

The correlation parameters obtained from the isobaric vapour-liquid equilibrium have been used to calculate the liquid-liquid equilibrium. The computation of equilibrium compositions of liquid phases has been carried out by the method described in detail in ref.<sup>19</sup>. The values calculated, *i.e.* both the shape of binodal curves and the slope of tie-lines are in agreement with the experimental data (Fig. 1). The calculated binodal curve (corresponding to n.b.p., *i.e.*  $\approx 65^\circ\text{C}$ ) is also in agreement with the temperature trend. It provides a larger heterogeneous region than the  $50^\circ\text{C}$  isotherm, which is especially well evident on the side of the binary THF(1)-H<sub>2</sub>O(3) system.

Further, the existence of heterogeneous azeotrope has been tested in the ternary system. Here we have proceeded so that for the calculated points of the binodal curve, the boiling point has been evaluated, too. It has been found that the temperature changes monotonously along the binodal curve, which gives evidence that the system does not exhibit a ternary azeotrope. When computing the composition of coexisting phases, it has been found as well that the n-hexane content in the water-rich phase has usually been lower than 0.001 and we have failed to determine it quantitatively. Owing to the very low n-hexane content this phase can be considered as practically two-component one. The critical point could not be established by a direct computation<sup>19</sup> because of insufficient number of significant figures of the computer used. The last pair of coexisting phases (in the vicinity of critical point) has

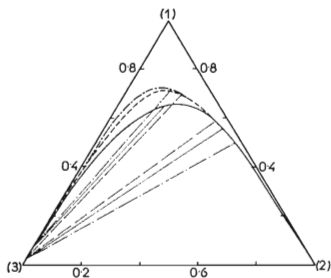


FIG. 1  
Liquid-Liquid Equilibrium in the Tetrahydrofuran(1)-n-Hexane(2)-Water(3) System  
— 30°C; --- 50°C; ·-·-· calculated for n.b.p. ( $\approx 65^\circ\text{C}$ ).



had the following compositions:  $x_1 = 0.8172$ ,  $x_2 = 0.1822$ ,  $x_3 = 0.00057$ ,  $\bar{x}_1 = 0.6549$ ,  $\bar{x}_2 = 0.3429$ ,  $\bar{x}_3 = 0.0022$ . Provided that we determined the critical point by linear interpolation from this pair it would have the composition  $x_{1c} = 0.736$ ,  $x_{2c} = 0.262$ ,  $x_{3c} = 0.0014$ .

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