

two wavelengths, at three angles or at different polarization of primary beam.

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Isobaric Binary Equilibrium Data for the System Water—Benzothiazole at 101.3 kPa

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A set of isobaric vapour-liquid equilibrium data for the water—benzothiazole system at 101.325 kPa is reported. These data were calculated on the assumption of ideal behaviour of the vapour phase and real behaviour of the liquid. In this work, activity coefficients were calculated using the van Laar equation the parameters of which were determined from experimental solubilities. On using the solubility data, both temperature and composition of the heteroazeotropic mixture at the pressure of 101.325 kPa were also obtained.

The binary system water(1)—benzothiazole(2) exhibits a limited miscibility; the solubility of components is low (the mass fraction has an order of magnitude 10^{-3}). Data on physical properties of benzothiazole are, as yet, not very plentiful in the literature [1, 2]. A survey of the literature indicates that up to the present practically no data have been reported for binary equilibrium for this system.

A detailed description of the method used for the determination of vapour-liquid (V-L) equilibrium is given in our previous work [3]. Solubilities were determined experimentally by the turbidity method. The saturated vapour pressure of benzothiazole was measured by the static method [4, 5]. The so obtained set of data enabled to calculate the composition of the heteroazeotropic mixture for the water—benzothiazole system and θ - x - y equilibrium data at 101.325 kPa.

EXPERIMENTAL

Material used was research grade 99.9 % benzothiazole supplied by VUCHT (Research Institute of Chemical Technology, Bratislava) with refractive index $n(D, 20\text{ }^{\circ}\text{C}) = 1.6425$ identical with the data point of literature [1], water was bidistilled.

Solubilities of the system water—benzothiazole were determined by the turbidity method. Heterogeneous binary samples of known composition were prepared. These samples in sealed glass ampoules were thoroughly stirred and heated in a water or glycerol bath up to the temperature at which one homogeneous liquid was formed. By cooling, the temperature was found at which heterogeneous phases appeared. The temperature of the water bath was determined with an accuracy of ± 0.1 K. The samples were weighed on an analytical balance with

an accuracy of $\pm 5 \times 10^{-4}$ g (which corresponds to $\pm 2 \times 10^{-4}$ mass fraction). Experimental solubilities of the system water—benzothiazole as a function of temperature are given in Tables 1 and 2.

Table 1. Solubility of Benzothiazole(2) in Water(1) as a Function of Temperature

$\theta/^\circ\text{C}$	$w_{21}/10^{-2}$	$x_{21}/10^{-3}$	$x_{21}(\text{calc.})/10^{-3}$
37.2	0.432	0.578	0.578
61.4	0.584	0.782	0.775
70.3	0.648	0.868	0.884
80.1	0.776	1.041	1.025
93.5	0.925	1.243	1.257
98.4	1.021	1.361	1.353

Coefficients in polynomial (1) for the 95 % interval of reliability: $B_0 = (0.5560 \pm 0.2370) \times 10^{-3}$, $B_1 = -(0.3950 \pm 0.7302) \times 10^{-5}$, $B_2 = (0.1225 \pm 0.0528) \times 10^{-6}$.

Table 2. Solubility of Water(1) in Benzothiazole(2) as a Function of Temperature

$\theta/^\circ\text{C}$	$w_{12}/10^{-2}$	x_{12}	$x_{12}(\text{calc.})$
55.9	3.029	0.1899	0.1900
65.7	3.257	0.2017	0.2019
74.3	3.451	0.2115	0.2124
83.0	3.726	0.2251	0.2230
90.2	3.854	0.2313	0.2318
95.6	3.989	0.2377	0.2383

Coefficients in polynomial (1) for the 95 % interval of reliability: $B_0 = 0.1218 \pm 0.7842 \times 10^{-2}$, $B_1 = 0.1219 \times 10^{-2} \pm 0.9969 \times 10^{-4}$.

The dependence of the pressure of saturated benzothiazole vapours on temperature was measured by a modified static apparatus [4]. A detailed description of this procedure is given in Ref. [4, 5]. The temperature of the water (or glycerol) was kept with an accuracy of ± 0.05 K. Pressure was measured with an U-tube manometer with an accuracy of ± 13 Pa. In order to trap residual moisture, both degassing of the sample and measurement of the benzothiazole vapour pressure was carried out in the presence of molecular sieves. Experimental data on saturated benzothiazole vapour pressure as a function of temperature are given in Table 3.

RESULTS AND DISCUSSION

Solubilities of the system water(1)—benzothiazole (2) determined by mole fraction x_{ij} as a function of temperature can be expressed by the following polynomial

$$x_{ij} = B_0 + B_1\theta + B_2\theta^2 \quad (1)$$

The parameters of this equation were evaluated by processing the experimental data by the least-

Table 3. Experimental and Calculated Vapour Pressures of Benzothiazole as a Function of Temperature

$\theta/^\circ\text{C}$	P_2^0/kPa	$P_2^0(\text{calc.})/\text{kPa}$
90	1.058	1.059
95	1.260	1.259
100	1.489	1.490

squares method. The calculated values of solubilities and parameters of the polynomials for the 95 % interval of reliability are listed in Tables 1 and 2. The standard deviations of correlations of the mole fractions x_{ij} are as follows: $s(x_{21}) = 0.16 \times 10^{-4}$; $s(x_{12}) = 0.12 \times 10^{-2}$.

The saturated vapour pressure of benzothiazole as a function of temperature, in the range from 90 to 100 °C was expressed by the relation

$$\log(P_2^0/\text{kPa}) = 5.5553 - (2008.36/T) \quad (2)$$

The values of parameters in this equation were evaluated from experimental data by the least-squares method. Calculated values of the vapour pressures are listed in Table 3. For solutions with a content of water lower than 15 mole % ($\theta > 110$ °C), the following relation was used for the calculation of the pressure P_2^0

$$\log(P_2^0/\text{kPa}) = 7.3646 - (2701.96/T) \quad (3)$$

Parameters of this relationship were determined on the basis of known vapour pressures at two temperatures: $\theta_1 = 110$ °C (calculated from eqn (2)) and $\theta_2 = 231$ °C (the boiling point of benzothiazole at $P = 101.325$ kPa).

For the equilibrium of two liquid phases holds the equality of activities of components of conjugated phases. Thus, it is possible to write for water

$$\gamma_{12}x_{12} = \gamma_{11}x_{11} \quad (4)$$

and for benzothiazole

$$\gamma_{21}x_{21} = \gamma_{22}x_{22} \quad (5)$$

Simultaneously, for the solubilities hold the constraints

$$x_{11} = 1 - x_{21} \quad (6a)$$

and

$$x_{22} = 1 - x_{12} \quad (6b)$$

If at a certain temperature, the composition of the equilibrium phases is known, then, by solving the set of nonlinear equations (4) and (5) in combination with these constraints (6), it is possible [6] to calculate the values of parameters of equations for the calculation of activity coefficients corresponding to the given temperature. For the chosen temperatures, over the range from 60 to 120 °C, the compositions of conjugated liquid phases were calculated by means of eqn (1). In addition to it, the cor-

Table 4. Values of Binary Parameters of the van Laar Equation

$\theta/^\circ\text{C}$	A_{12}	A_{21}
60	1.8488	7.0310
70	1.7956	6.8777
80	1.7457	6.7203
90	1.6990	6.5624
100	1.6550	6.4082
110	1.6136	6.2585
120	1.5743	6.1150

Coefficients in eqn (7) for the 95 % interval of reliability for A_{12} : $b_0 = 0.04982 \pm 0.01036$, $b_1 = 599.174 \pm 3.746$; for A_{21} : $b_0 = 1.01425 \pm 0.23236$, $b_1 = 2010.840 \pm 84.007$.

responding parameters of the van Laar equation were determined by the above-mentioned procedure. The results are summarized in Table 4. The dependence of parameters A_{12} and A_{21} on temperature can be given by

$$A_{ij} = b_0 + (b_1/T) \quad (7)$$

Coefficients in this equation were determined by the least-squares method. Standard deviations of correlations of parameters A_{ij} are: $s(A_{12}) = 5.88 \times 10^{-4}$ and $s(A_{21}) = 1.32 \times 10^{-2}$.

Calculation of Isobaric Equilibrium Data

On the assumption that ideal gas equation of state can be applied to the vapour phase, for the heteroazeotropic point the following equations must be fulfilled

$$P - (\gamma_{11}x_{11}P_1^\circ + \gamma_{21}x_{21}P_2^\circ) = 0 \quad (8)$$

and simultaneously

$$P - (\gamma_{12}x_{12}P_1^\circ + \gamma_{22}x_{22}P_2^\circ) = 0 \quad (9)$$

in which γ_1 and γ_2 are calculated by the van Laar equation, A_{12} and A_{21} by eqn (7), P_2° saturated vapour pressure of benzothiazole given by eqns (2) or (3). To calculate the saturated vapour pressures of water, the Antoine equation [7]

$$\log(P_i^\circ/\text{kPa}) = 7.19624 - 1730.63/(\theta + 233.426) \quad (10)$$

was used. By solving eqns (8) and (9) for the given pressure P , the boiling point of the heteroazeotropic mixture is obtained. Since the results gained by solving eqns (8) and (9) need not be always mutually equal, the boiling point of the azeotropic mixture was obtained in the following way. We searched for the temperature at which the objective function

$$M_P = \sum_{j=1}^2 \left(P - \sum_{i=1}^2 \gamma_{ij}x_{ij}P_i^\circ \right)^2 \quad (11)$$

takes its minimum. The value of boiling point of the heteroazeotropic mixture determined in this way is 99.71°C . The function M_P has the value of 6.82×10^{-5} kPa. The composition of equilibrium liquid phases at this temperature is

$$\begin{aligned} x_{11} &= 0.99861 & x_{12} &= 0.24327 \\ x_{21} &= 0.00139 & x_{22} &= 0.75673 \end{aligned}$$

The composition of the heteroazeotropic mixture at the temperature of 99.71°C was calculated from the relation

$$y_{1j} = \gamma_{1j}x_{1j}P_1^\circ / \sum_{i=1}^2 \gamma_{ij}x_{ij}P_i^\circ \quad j = 1, 2 \quad (12)$$

For both coexisting phases the same results $y_{11} = y_{12} = 0.9886$ were obtained. It means that the heteroazeotropic mixture contains at $P = 101.325$ kPa in the vapour phase 98.86 mole % water and 1.14 mole % benzothiazole. The calculated isobaric equilibrium data for the water(1)—benzothiazole(2) system over the range of mutual miscibility at the total pressure of 101.325 kPa were obtained in the following way. The temperature was calculated by numerical solution of the equation

$$P - \gamma_1 P_1^\circ x_1 - \gamma_2 P_2^\circ x_2 = 0 \quad (13)$$

for a set of mole fractions taken from the interval $x_{11} \in <0.00; x_{12}>$ and $x_{11} \in <x_{11}; 1>$. The mole fraction of components in the vapour phase is given by the relation

$$y_i = \gamma_i P_i^\circ x_{ij} / (\gamma_1 P_1^\circ x_{11} + \gamma_2 P_2^\circ x_{22}) \quad (14)$$

The calculated isobaric equilibrium data for the water(1)—benzothiazole(2) system in the region of mutual miscibility at the pressure of 101.325 kPa

Table 5. Calculated Isobaric V-L Equilibrium Data for the System Water(1)—Benzothiazole(2) at 101.325 kPa

$\theta/^\circ\text{C}$	x_1	y_1	$\theta/^\circ\text{C}$	x_1	y_1
231.00	0.0000	0.0000	99.71	0.24327 ^a	0.9886
213.02	0.0050	0.3703	99.71	0.99861 ^b	0.9886
187.76	0.0150	0.6909	99.75	0.9988	0.9900
171.22	0.0250	0.8148	99.79	0.9990	0.9916
146.92	0.0500	0.9197	99.83	0.9992	0.9932
133.06	0.0750	0.9527	99.87	0.9994	0.9948
123.78	0.1000	0.9678	99.91	0.9996	0.9965
111.79	0.1500	0.9812	99.95	0.9998	0.9982
104.25	0.2000	0.9862	100.00	1.0000	1.0000

a) x_{12} ; b) x_{11} .

are given in Table 5. The y_1 — x_1 dependence is depicted in Fig. 1 and Fig. 2 shows the θ — x_1 — y_1 plot.

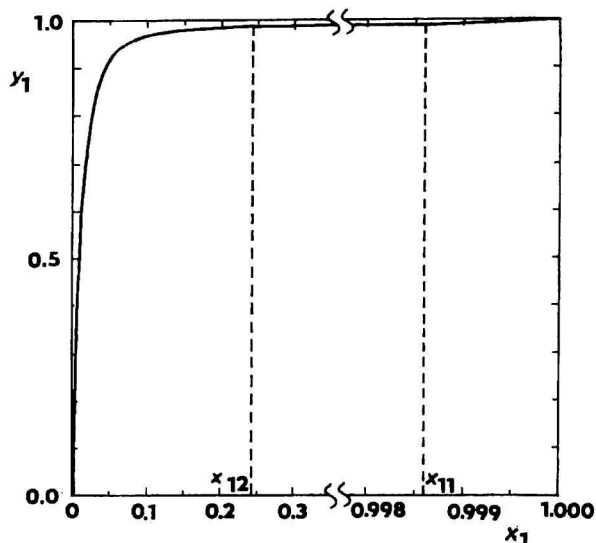


Fig. 1. y_1 - x_1 diagram for the water(1)-benzothiazole(2) system at 101.325 kPa; x_{ij} solubilities.

SYMBOLS

- A_{ij} binary parameters of the van Laar equation
 B, b parameters of eqns (1) and (7)
 M_P objective function
 P total pressure
 P_i° saturated vapour pressure of pure component i
 θ, T temperature, thermodynamic temperature
 x_i mole fraction of the component i in the liquid phase
 x_{ij} mole fraction of the component i in the phase j
 w_{ij} mass fraction of the component i in the phase j
 y_i mole fraction of the component i in the vapour phase
 γ_{ij} activity coefficient of the component i in the phase j
 s standard deviation

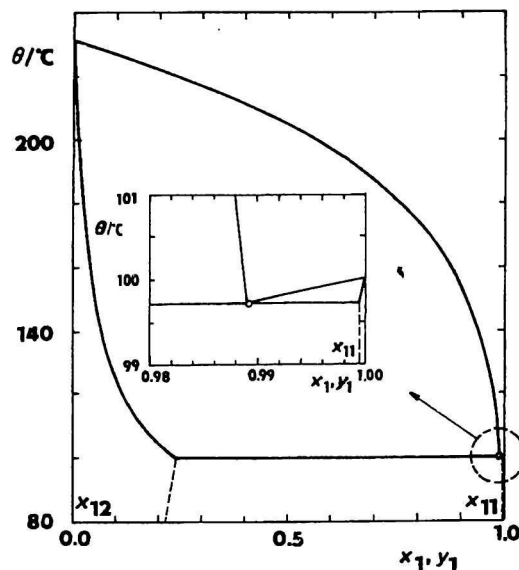


Fig. 2. θ - x_1 - y_1 diagram for the water(1)-benzothiazole(2) system at 101.325 kPa; x_{ij} solubilities.

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