

## ISOBARIC VAPOUR-LIQUID EQUILIBRIUM DATA OF THE 1,2-DICHLOROETHANE-WATER SYSTEM AT 101.3 kPa

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Isobaric vapour-liquid equilibrium data for the 1,2-dichloroethane-water system were calculated on the assumption of ideal behaviour of the vapour phase on using the van Laar equation for activity coefficients of the components in the liquid phase. The parameters of the van Laar equation were calculated from the solubility of 1,2-dichloroethane in water and of water in 1,2-dichloroethane determined experimentally in this work. On using the solubility data, the parameters of the heteroazeotropic point at the pressure of 101.3 kPa were also calculated.

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Water and 1,2-dichloroethane exhibit limited miscibility. Their mutual solubility is not large but it is significant. Riddick<sup>1</sup> reports that at the temperature of 20°C, the solubility of 1,2-dichloroethane in water is 0.81 mass % and that of water in 1,2-dichloroethane, 0.15 mass %. The complete isobaric equilibrium data for the 1,2-dichloroethane-water system have not hitherto been published. The parameters of the heteroazeotropic point taken from the literature are given in Table I. On comparing them, one can see that they are not consistent even though they are not substantially different. Only the composition of heteroazeotropic mixture given in refs<sup>2,3</sup> is considerably different from the data of the other authors. In this work, the parameters of the van Laar equation and the parameters of the heteroazeotropic point were determined on the basis of the mutual solubilities of 1,2-dichloroethane and water determined experimentally as a function of temperature.

### EXPERIMENTAL

#### Substances Used

1,2-Dichloroethane, supplied by Lachema, Brno and designated by "Import" was distilled at atmospheric pressure on a laboratory column of efficiency 20 theoretical plates. The chromatographic purity was better than 99.9 mass %. Refractive index  $n_D^{20} = 1.4448$  is identical with the data point of literature<sup>1</sup>. Water was a bidistillate.

## Determination of Solubility of Substances as a Function of Temperature

The samples of solutions of different composition were prepared by mixing the pure substances whose amount was determined by weighing. The samples of solutions in sealed glass ampoules were heated up to the temperature at which one homogeneous liquid phase was formed. By slow cooling, the temperature was found at which turbidity of solution appeared. This temperature determined with an accuracy of 0.1°C was considered to be the solution temperature of components of mixture of the given composition.

## CALCULATIONS

The solubility of 1,2-dichloroethane in water was expressed by the equation

$$\ln(100x_{12}) = 3.2774 - 1577.6/T. \quad (1)$$

Analogously, the solubility of water in 1,2-dichloroethane was expressed by the equation

$$\ln(100x_{21}) = 9.0913 - 2695.4/T. \quad (2)$$

The parameters of Eqs (1) and (2) were evaluated by processing the experimental data by the least-squares method. The experimental and calculated values of solubility in the range of temperatures of interest are given in Tables II and III. The mean and standard deviations of the measured and calculated values are as follows: for Eq. (1),  $d_x = 0.4 \cdot 10^{-4}$ ,  $\sigma_x = 0.62 \cdot 10^{-4}$ ; for Eq. (2),  $d_x = 0.165 \cdot 10^{-2}$ ,  $\sigma_x = 0.251 \cdot 10^{-2}$ .

The values of parameters of the van Laar equation

$$\log \gamma_1 = A_{12}x_2^2/(x_1A_{12}/A_{21} + x_2)^2, \quad (3)$$

$$\log \gamma_2 = A_{21}x_1^2/(x_1 + x_2A_{21}/A_{12})^2, \quad (4)$$

were calculated from the solubility data by the method described in monograph<sup>10</sup>. For the components of the conjugate equilibrium phases holds the equality of their activities in these phases. Thus, it is possible to write for 1,2-dichloroethane

$$\gamma_{12}x_{12} = \gamma_{11}x_{11}, \quad (5)$$

and for water

$$\gamma_{21}x_{21} = \gamma_{22}x_{22}. \quad (6)$$

Simultaneously, for the solubilities hold the constraints

$$x_{11} = 1 - x_{21}, \quad (7)$$

and

$$x_{22} = 1 - x_{12} . \quad (8)$$

If the activity coefficients are to be expressed in terms of the van Laar equation, then, by solving Eqs (5) and (6) in combination with these constraints, it is possible to calculate the values of binary parameters of the van Laar equation at those temperatures at which the values of solubilities of components in conjugate phases were determined.

When calculating the values of binary parameters of the van Laar equation  $A_{12}$  and  $A_{21}$ , the solubilities of components in conjugate phases were expressed by

TABLE I

Parameters of the heteroazeotropic point in the 1,2-dichloroethane(1)–water(2) system taken from the literature

$t, ^\circ\text{C}$	$w_1 \cdot 10^3$	$w_2 \cdot 10^2$	$x_1 \cdot 10^2$	$x_2 \cdot 10^2$	Ref.
72	80.5	19.5	42.89	57.11	2, 3
72.28	90.8	9.2	64.22	35.78	4, 9
71.6	91.8	8.2	67.07	32.93	5, 9
75.5	91.5	8.5	66.19	33.81	6, 9
72	92.1	7.9	67.95	32.05	7, 8, 9

TABLE II

Experimental and calculated data on the solubility of water(2) in 1,2-dichloroethane(1) as a function of temperature

$T, \text{K}$	Experimental		Calculated
	$w_{21} \cdot 10^2$	$x_{21} \cdot 10^2$	$x_{21} \cdot 10^2$
305.7	0.25	1.36	1.32
315.7	0.30	1.63	1.74
329.2	0.47	2.53	2.47
335.2	0.55	2.95	2.86
347.7	0.73	3.88	3.82
365.2	1.08	4.89	5.53
371.7	1.24	6.45	6.29
380.7	1.54	7.91	7.47

means of Eqs (1) and (2). The values of parameters  $A_{12}$  and  $A_{21}$  at certain temperatures in the temperature range of interest are given in Table IV. On the basis of these data, the temperature dependence of parameters  $A_{12}$  and  $A_{21}$  was expressed by the equations

$$A_{12} = 0.56027 + 694.120/T, \quad (9)$$

and

$$A_{21} = -1.568333 + 1\,060.970/T. \quad (10)$$

TABLE III

Experimental and calculated data on the solubility of 1,2-dichloroethane(1) in water(2) as a function of temperature

<i>T</i> , K	Experimental		Calculated $x_{12} \cdot 10^2$
	$w_{12} \cdot 10^2$	$x_{12} \cdot 10^2$	
321.7	1.09	0.200	0.197
328.2	1.18	0.217	0.217
339.2	1.37	0.252	0.253
344.4	1.46	0.269	0.272
351.2	1.56	0.288	0.297
354.5	1.69	0.312	0.310
363.4	1.85	0.342	0.345
371.7	2.11	0.391	0.380

TABLE IV

Values of binary parameters of the van Laar equation

<i>T</i> , K	$A_{12}$	$A_{12,calc.}$	$A_{21}$	$A_{21,calc.}$
345.15	2.571	2.571	1.506	1.506
348.15	2.554	2.554	1.479	1.479
353.15	2.526	2.526	1.436	1.436
358.15	2.499	2.498	1.394	1.394
363.15	2.473	2.472	1.353	1.353
368.15	2.441	2.446	1.314	1.314
370.15	2.437	2.435	1.298	1.298
373.15	2.422	2.420	1.275	1.275

The mean and standard deviations of values of parameters  $A_{12}$  and  $A_{21}$  calculated on the basis of Eqs (9) and (10) from their values determined by the solution of Eqs (5) and (6) are as follows: for Eq. (9),  $d_{A_{12}} = 1.35 \cdot 10^{-3}$ ,  $\sigma_{A_{12}} = 2.30 \cdot 10^{-3}$ , and for Eq. (10),  $d_{A_{21}} = 0.20 \cdot 10^{-3}$ ,  $\sigma_{A_{21}} = 0.26 \cdot 10^{-3}$ .

## RESULTS AND DISCUSSION

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

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

and

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

By solving Eq. (11) or (12) at a chosen total pressure, the boiling point of the heteroazeotropic mixture is determined.

To calculate the values of saturated vapour pressures of pure components as a function of temperature, the Antoine equation was used. For 1,2-dichloroethane, this dependence takes the form<sup>11</sup>

$$\log(P_1^0/\text{kPa}) = 6.07712 - 1247.8/(t + 223.0), \quad (13)$$

and for water<sup>12</sup>

$$\log(P_2^0/\text{kPa}) = 7.19624 - 1730.63/(t + 233.426). \quad (14)$$

The results achieved by solving Eq. (11) or (12) need not be always mutually identical. The agreement of the calculated temperatures is influenced by the flexibility and goodness of fit of correlations (9) and (10) used. The temperature obtained by the solution of Eq. (11) does not differ from the results obtained by the solution of Eq. (12) more than corresponds to the accuracy with which the mutual solubility of 1,2-dichloroethane and water was determined. Nevertheless, we determined the probable boiling point of the azeotropic mixture as a temperature at which the sum of differences of the total pressure and the sum of partial pressures calculated from the relation

$$M_P = \sum_{j=1}^2 (P - \sum_{i=1}^2 \gamma_{ij}x_{ij}P_i^0)^2 \quad (15)$$

takes its minimum.

The value of boiling point of the heteroazeotropic mixture determined in this way is 71.87°C. Function  $M_P$  at this temperature has the value of  $3.63 \cdot 10^{-3} \text{ kPa}^2$ . At the total pressure of 101.3 kPa and at the temperature of 71.87°C, the expression on the left-hand side of Eq. (11) or (12) has the value 0.0259 kPa or  $-0.0544 \text{ kPa}$ ,

TABLE V

Calculated isobaric vapour-liquid equilibrium data in the 1,2-dichloroethane(1)-water(2) system at 101.3 kPa (\* limits of mutual solubility)

$t, ^\circ\text{C}$	$x_1$	$y_1$	$t, ^\circ\text{C}$	$x_1$	$y_1$
100.0	0.0000	0.0000	71.87	$x_{12}^* = 0.002739$	0.6685 <sup>a</sup>
98.82	0.0001	0.0416	71.87	$x_{11}^* = 0.96407$	0.6685 <sup>b</sup>
97.65	0.0002	0.0815	72.11	0.9650	0.6741
96.48	0.0003	0.1197	73.39	0.9700	0.7063
94.19	0.0005	0.1913	74.77	0.9750	0.7422
91.94	0.0007	0.2568	76.27	0.9800	0.7825
88.64	0.0010	0.3445	77.88	0.9850	0.8276
86.50	0.0012	0.3966	79.61	0.9900	0.8784
83.39	0.0015	0.4662	81.48	0.9950	0.9356
81.39	0.0017	0.5075	82.26	0.9970	0.9604
78.48	0.0020	0.5624	83.07	0.9990	0.9865
75.69	0.0023	0.6101	83.47	1.0000	1.0006
73.91	0.0025	0.6383			

<sup>a</sup>  $P = 101.38$  kPa; <sup>b</sup>  $P = 101.30$  kPa.

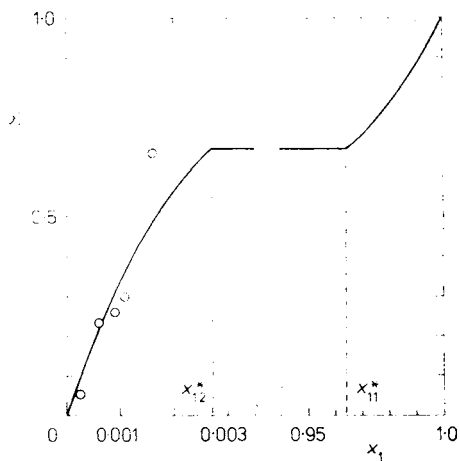


FIG. 1

$y$ - $x$  Isobaric equilibrium diagram of the 1,2-dichloroethane(1)-water(2) system at 101.3 kPa. — Calculated curve,  $\circ$  experimental data<sup>13</sup>

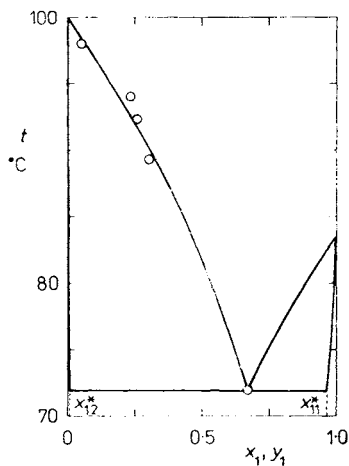


FIG. 2

$t$ - $x$ - $y$  Isobaric equilibrium diagram of the 1,2-dichloroethane(1)-water(2) system at 101.3 kPa. — Calculated curve,  $\circ$  experimental data<sup>13</sup>

respectively. The mole fractions of 1,2-dichloroethane in the equilibrium liquid phases at the temperature of 71.87°C have the values  $x_{12} = 0.002739$  and  $x_{11} = 0.96407$ .

The composition of the heteroazeotropic mixture at the temperature of 71.87°C was calculated from the relations

$$y_{1j} = \gamma_{1j} x_{1j} P_i^0 / \sum_{i=1}^2 \gamma_{ij} x_{ij} P_i^0, \quad j = 1, 2. \quad (16)$$

In both cases the same value  $y_{11} = y_{12} = 0.6685$  was obtained.

The calculated isobaric equilibrium data in the 1,2-dichloroethane(1)-water(2) system at the total pressure of 101.3 kPa are presented in Table V. The  $y_1-x_1$  dependence at the total pressure of 101.3 kPa is depicted in Fig. 1 and the  $t-x_1-y_1$  dependence in Fig. 2. The points corresponding to the experimentally determined values taken from ref.<sup>13</sup> are plotted in both figures, too.

The calculated values of the heteroazeotropic point exhibit comparatively good agreement with the data taken from the literature and given in Table I. The best agreement appears with the unpublished results of Union Carbide Chem. Co. (refs<sup>5,9</sup>).

#### SYMBOLS

$A_{ij}$	binary parameters of van Laar equation; $i \neq j$
$d$	mean deviation
$M_p$	sum of squares of differences of total pressure and sum of partial pressures of components
$P$	total pressure
$P_i^0$	saturated vapour pressure of pure component $i$
$t$	temperature (centigrade)
$T$	thermodynamic temperature
$w_i$	mass fraction of component $i$ in liquid at heteroazeotropic point
$w_{ij}$	mass fraction of component $i$ in phase rich in component $j$
$x_i$	mole fraction of component $i$ in liquid
$x_{ij}$	mole fraction of component $i$ in phase rich in component $j$
$y_i$	mole fraction of component $i$ in vapour
$\gamma_{ij}$	activity coefficient of component $i$ in phase rich in component $j$
$\sigma$	standard deviation

#### Superscripts

o	pure component
*	solubility limit

#### Subscripts

$i = 1, 2$	ordinal number of component; 1 1,2-dichloroethane, 2 water
$j = 1, 2$	ordinal number of phase rich in component $j$

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