VAPOUR–LIQUID EQUILIBRIUM OF THE ETHANOL/DIOXANE SYSTEM

A NOVEL APPARATUS FOR MEASURING VAPOUR—LIQUID EQUILIBRIA UNDER PRESSURE

By

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I. Introduction

For the system ethanol/dioxane equilibrium data to be found in the literature refer to normal, or reduced, pressures [1, 2]. Various compositions of azeotropic mixtures calculable for atmospheric pressure contradict each other.

With the help of an apparatus designed by us, equilibria in the domain above normal pressure could be determined for $P = 190, 380, 760, 1140, 1520$ and 3040 torr. The data thus determined allowed the pressure to be found, above which this system does not form an azeotropic mixture.

II. Experimental

a) Substances used, analysis of mixtures

For the purpose of our experiments, analytical grade ethanol, and dioxane, were rectified on a column of 16 theoretical plates. The purity of the substances was checked by refraction and gas-chromatography.

Refractive indices, n_D^{20}, of the substances:

Ethanol, 1.3615 found, 1.36139 in the literature [3].
Dioxane, 1.4224 found, 1.42241 in the literature [3].

The composition of the samples was determined by refractometry, on the basis of the refraction vs. concentration function. Data for this calibration-diagram are listed in Table 1.

b) Description of the apparatus, and its checking

In a former communication [4] an apparatus suitable for the measurement of vapour—liquid equilibria under atmospheric, and reduced, pressures has been described. The operative principle of our novel apparatus is essentially that of the former, but stainless steel is its material of construction instead of glass, and this necessitated some changes in its design.

A drawing of the apparatus is shown in Fig. 1. For measurements, into liquid storage vessel *A* a mixture of arbitrary composition is filled through screw-port *M*. The mixture is heated electrically by wire S. Heating voltage is adjusted by a variable transformer. The

Table 1

Refractive index vs. concentration data for ethanol/dioxane mixtures at 20 °C

Ethanol, mole %	n_D^{20}
0.0	1.4224
6.8	1.4193
13.2	1.4165
23.7	1.4118
35.5	1.4057
38.3	1.4035
44.8	1.4008
47.6	1.3990
54.4	1.3949
63.0	1.3894
68.3	1.3860
69.1	1.3858
76.7	1.3801
81.3	1.3770
87.3	1.3720
92.2	1.3682
93.1	1.3672
100.0	1.3615

mixture of boiling liquid and vapour splashes, via Cotrell pump *C*, against thermometer-well *H*, and then separates in the equilibrium chamber *E*. The liquid runs into samplecollector K_1, to return through the overflow pipe into vessel *A*. Vapours are condensed in condenser L_1, the condensate runs into sample collector K_2, also to return by overflow into vessel *A*. Condensers L_2 and L_3 prevent vapour from entering the pressure regulator system. The apparatus is connected to the pressure regulation system through tubes P_1 and P_2.

Between vessel *A* and heating spiral *S* a throttle is *F* interposed, to prevent abrupt back-flow of the liquid.

Condensers L_2 and L_3 are yoked to sample collectors K_1 and K_2, respectively. The surfaces of the joints are ground, and carry a Teflon seal *T*.

The opening of vessel *A* is stopped by plug *D* being screwed in, here too Teflon serves as a seal.

Pressure in the apparatus is provided for by nitrogen gas from cylinders, regulated by pneumatic feed system, measured by mercury manometers. For measurements at pressure below normal the same regulator as formerly described [4] was applied.

After equilibrium is established, and this is shown by the constancy of temperature, heating is discontinued and pressure in the apparatus raised by about one half to one atmosphere in order instantaneously to stop boiling. The apparatus is then allowed to cool, and samples are drawn from collectors K_1 and K_2 for analyses.

First the equilibrium data of the ethanol/water system were measured at $P = 760$ torr, and compared with data determined in our glass apparatus [4], and with data in the literature [5]. Results are listed in Table 2, and shown in Fig. 2.

Fig. 2 shows a good agreement between data measured with the help of the metal apparatus, data in the literature, and data found with the glass apparatus.

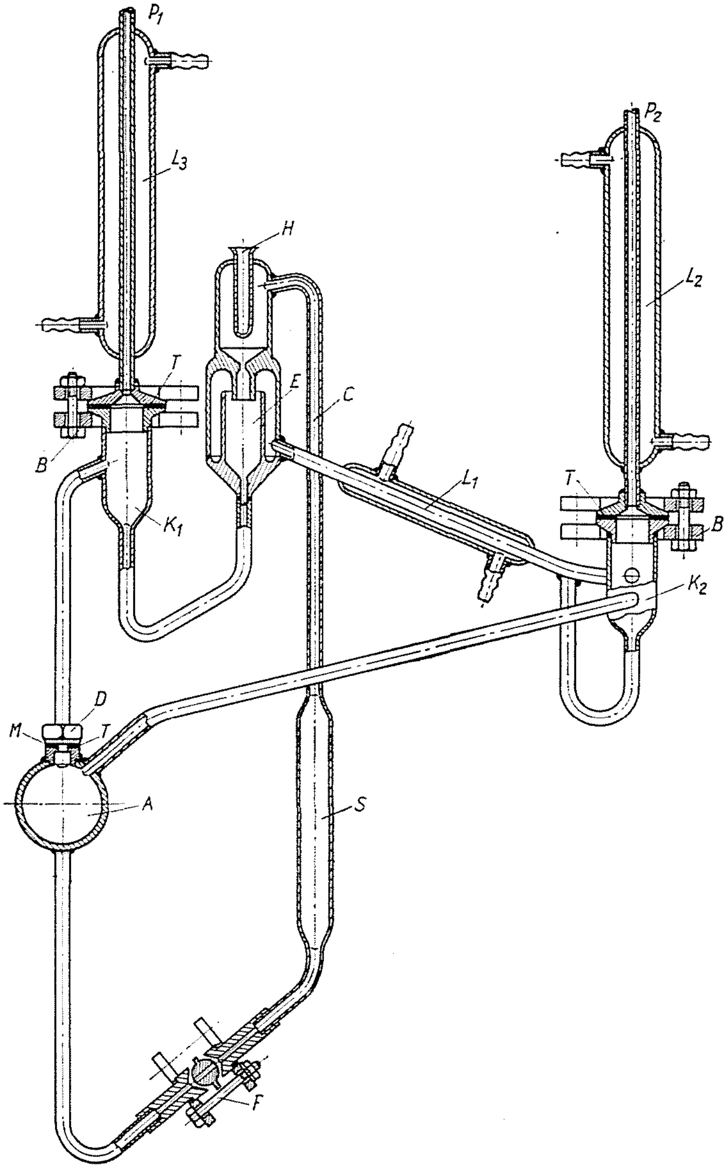

Fig. 1. Apparatus for the measurement of vapour—liquid equilibria

c) Equilibrium measurements

In further stages of our work, equilibrium data of the system ethanol/ dioxane at $P = 760$ were determined, in the glass as well as in the metal apparatus.

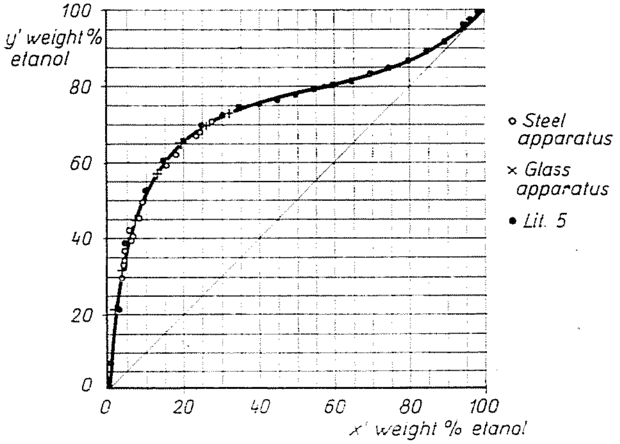

Fig. 2. Equilibrium diagram of the ethanol/water system at pressure $P = 760$ torr

Table 2

Equilibrium data of the ethanol/water system at pressure $P = 760$ torr

x' weight % ethanol	y' weight % ethanol
3.8	28.5
4.3	32.2
4.4	35.6
4.5	33.1
6.0	41.2
6.5	38.8
6.6	39.2
8.3	44.7
9.5	49.0
13.3	56.8
15.6	58.2
18.1	61.6
23.5	66.0
24.2	67.2
27.2	69.6
30.4	71.5

Results are presented in Tables 3 and 4, and in Figs 3 and 4, in comparison with data found in the literature [1, 2].

Tabe 3

Equilibrium data of the ethanol/dioxane system at pressure P=760 torr, measured in a glass apparatus

t °C	x m-% ethanol	y m-% ethanol	$\log \frac{\gamma_1}{\gamma_2}$
101.3	0.0	0.0	—
93.0	11.2	32.0	0.2145
90.0	16.4	38.9	0.1589
90.1	18.0	41.1	0.1493
88.9	20.5	43.8	0.1311
86.4	27.5	52.8	0.1208
84.8	32.3	56.3	0.0870
84.8	33.1	57.5	0.0925
84.0	35.2	59.3	0.0858
83.4	37.4	60.6	0.0688
82.3	44.1	64.4	0.0200
80.8	54.4	71.4	—0.0172
80.5	57.8	73.8	—0.0242
79.9	63.7	76.8	—0.0605
79.4	68.8	79.2	—0.0981
79.0	74.4	82.1	—0.1366
78.3	82.1	86.2	—0.2000
78.2	84.7	87.6	—0.2278
78.1	91.0	91.4	—0.3119
78.3	100.0	100.0	—

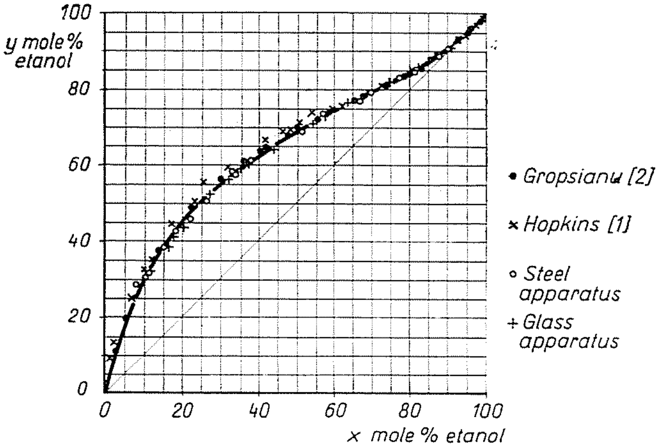

Fig. 3. Equilibrium diagram of the system ethanol/dioxane at pressure $P = 760$ torr

Table 4

Equilibrium data of the dioxane/ethanol system: atp=760 torr. measured in a metal apparatus

t °C	x m-% ethanol	y m-% ethanol	$\log \frac{\gamma_1}{\gamma_2}$
101.3	0.0	0.0	—
92.9	10.8	30.2	0.1958
92.6	11.6	31.4	0.1858
90.4	15.5	38.5	0.1796
89.5	18.2	42.7	0.1714
88.0	22.2	46.0	0.1254
86.8	26.8	50.8	0.1055
84.9	33.4	58.8	0.1101
84.5	34.0	57.4	0.0736
83.7	38.2	61.6	0.0716
81.1	51.3	69.2	—0.0093
80.4	57.6	74.0	—0.0163
79.4	66.7	77.1	—0.1098
79.7	69.5	79.6	—0.1022
78.8	77.2	83.6	—0.1664
78.4	81.4	85.0	—0.2279
78.0	87.5	89.1	—0.2661
77.8	90.0	91.2	—0.2712
78.3	100.0	100.0	—

Figs 3 and 4 show that values determined in a glass and in a metal apparatus, respectively, agree well, but concentrations in the vapour phase, to about 60 mole per cent ethanol, are lower than values mentioned in the literature, the deviation being from 2 to 4 mole per cent.

The explanation for this is likely to reside in the fact that the Othmer type still used by the authors cited allows partial condensation and this increases concentration in the vapour phase. This source of error is of significance if high relative fugacity is present. This view is supported by the fact that the nearer the azeotrope point, i.e. when relative fugacity decreases, the less vapour phase concentrations found in the literature and those measured by us differ.

The equilibrium data of the ethanol/dioxane system were determined, with our apparatus, at pressures $P = 190$, 380, 1440, 1520 and 3040 torr.

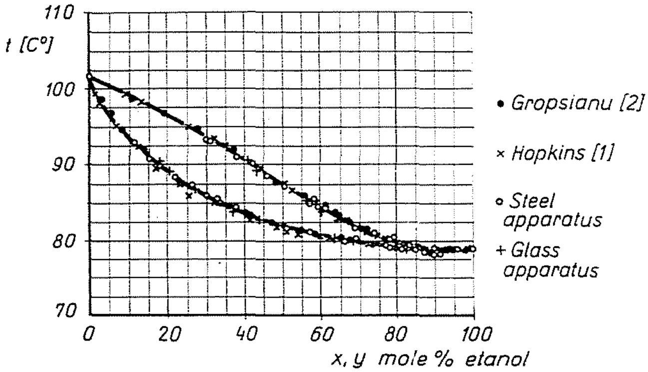

Fig. 4. Boiling point diagram of the ethanol/dioxane system at pressure $P = 760$ torr

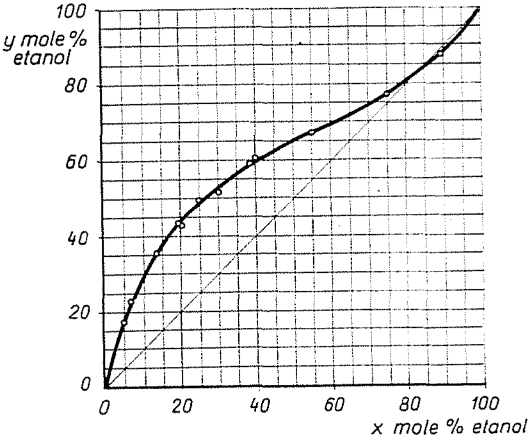

Fig. 5. Equilibrium diagram of the ethanol/dioxane system at pressure $P = 190$ torr

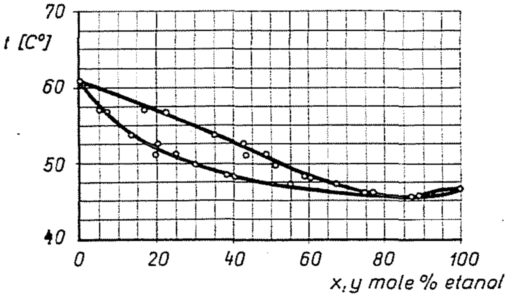

Fig. 6. Boiling point diagram of the ethanol/dioxane system at pressure $P = 190$ torr

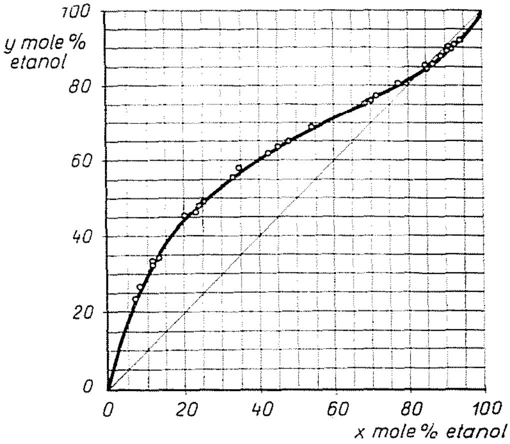

Fig. 7. Equilibrium diagram of the ethanol/dioxane system at pressure $P = 380$ torr

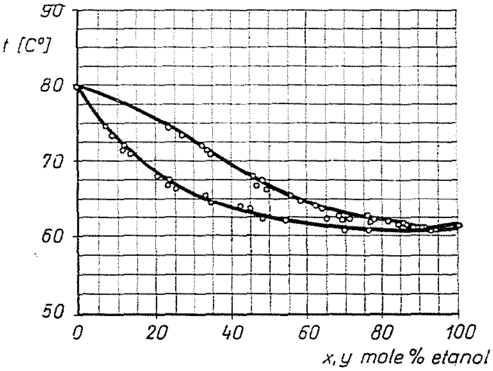

Fig. 8. Boiling point diagram of the ethanol/dioxane system at pressure $P = 380$ torr

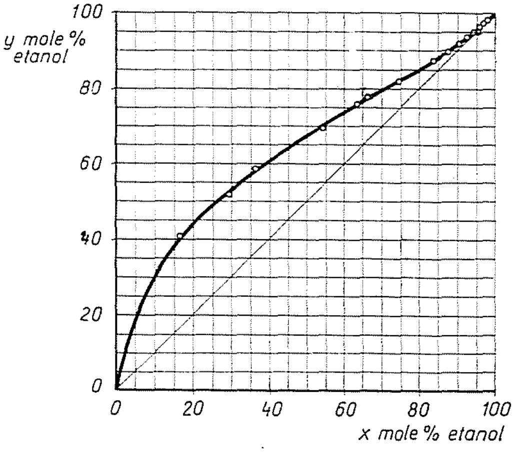

Fig. 9. Equilibrium diagram of the ethanol/dioxane system at pressure $P = 1140$ torr

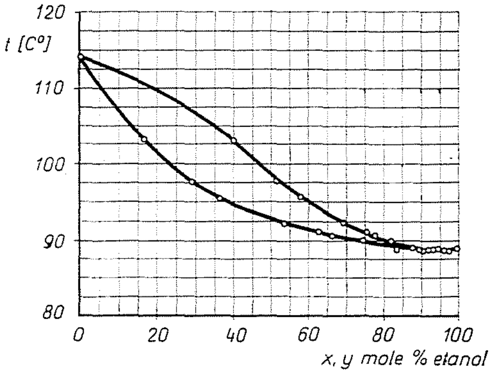

Fig 10. Boiling point diagram of the ethanol/dioxane system at pressure $P = 1140$ torr

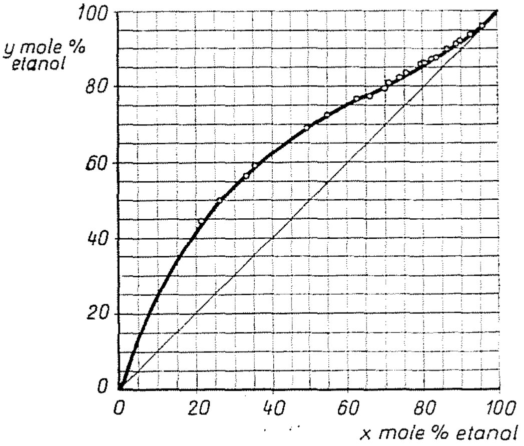

Fig. 11. Equilibrium diagram of the ethanol/dioxane system at pressure $P = 1520$ torr

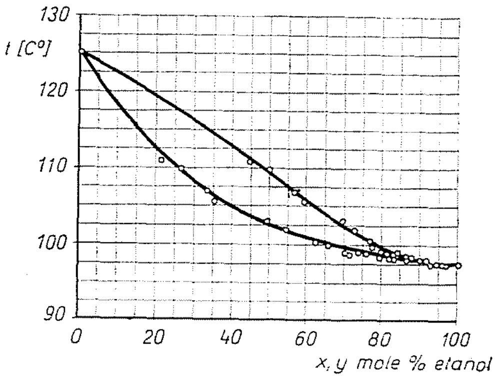

Fig. 12. Boiling point diagram of the ethanol/dioxane system at pressure $P = 1520$ torr

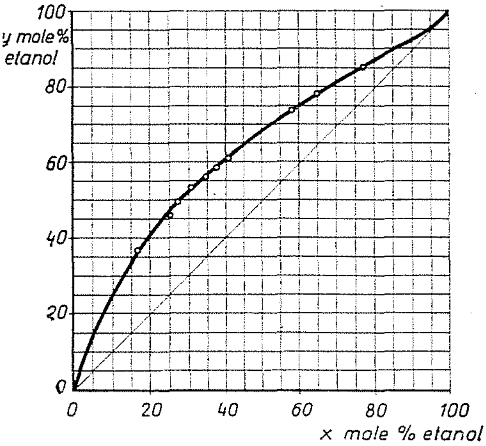

Fig. 13. Equilibrium diagram of the ethanol/dioxane system at pressure $P = 3040$ torr

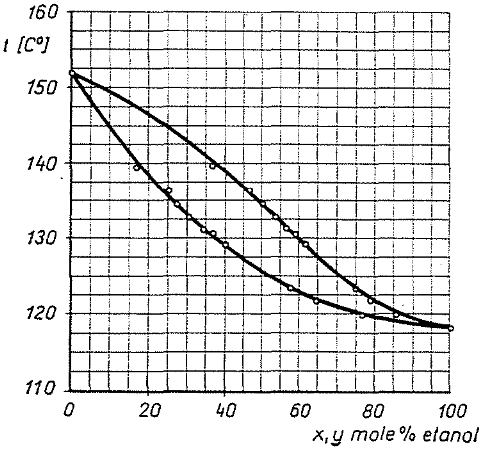

Fig. 14. Boiling point diagram of the ethanol/dioxane system at pressure $P = 3040$ torr

Results are listed in Table 5; equilibrium, and boiling point curves pertaining to each pressure are shown in Figs. 5 to 14.

d) Checking of data, evaluation

In order to check our data, activity coefficients were considered.

The values of activity coefficients listed in Tables 3, 4 and 5 were calculated according to the formula

$$\gamma_i = \frac{z_i y_i P}{x_i p_i^0}$$

Table 5

Equilibrium data of the ethanol/dioxane system at various pressures

P torr	t °C	x mole-% ethanol	y mole-% ethanol	$\log \frac{\gamma_1}{\gamma_2}$
190	62.1	0	0	—
	57.0	5.1	17.0	0.2846
	56.7	7.4	22.8	0.2713
	53.6	13.8	35.3	0.2419
	51.2	20.0	43.8	0.2081
	52.7	20.3	43.0	0.1837
	51.2	25.5	49.3	0.1677
	49.7	30.6	51.7	0.1058
	48.3	38.9	59.1	0.0759
	48.1	40.3	60.4	0.0744
	47.4	55.1	67.3	—0.0541
	46.1	75.0	77.0	—0.2284
	45.8	89.2	87.7	—0.3300
	47.1	100.0	100.0	—
380	80.2	0.0	0.0	—
	74.6	7.4	23.8	0.2644
	73.5	8.8	27.1	0.2600
	71.6	12.0	33.9	0.2532
	72.2	12.1	32.8	0.2265
	71.0	13.8	35.0	0.2057
	68.1	20.7	45.9	0.1958
	67.0	23.4	47.0	0.1483
	67.6	24.2	48.5	0.1541
	66.5	25.4	49.3	0.1421
	65.6	33.4	56.0	0.0925
	64.8	35.0	58.6	0.1092
	64.1	42.8	62.3	0.0346
	63.7	45.2	64.2	0.0263
	62.5	48.4	65.3	—0.0043
	62.3	54.4	69.4	—0.0269
	62.9	68.2	76.0	—0.1376
	60.9	70.0	76.4	—0.1614
	62.3	71.7	77.9	—0.1629

Table 5 (cont.)

P torr	t °C	x mole-% ethanol	y mole-% ethanol	log $\frac{\gamma_1}{\gamma_2}$
	62.0	77.2	81.1	—0.2028
	61.6	84.4	86.0	—0.2497
	61.7	84.8	85.2	—0.2917
	61.5	86.2	86.5	—0.2927
	61.4	88.8	88.6	—0.3134
	61.4	90.4	90.1	—0.3194
	61.3	90.5	90.2	—0.3193
	61.5	91.2	90.5	—0.3423
	61.3	92.2	91.4	—0.3510
	61.0	93.7	92.8	—0.3663
	61.1	94.1	93.4	—0.3863
	61.9	100.0	100.0	—
1140	114.0	0	0	—
	103.0	16.9	40.2	+0.1626
	97.5	29.2	51.8	+0.0684
	95.4	36.8	58.3	+0.0371
	92.0	54.3	69.2	—0.0640
	90.7	63.2	76.0	—0.0723
	90.4	66.3	77.6	—0.0931
	89.7	74.3	81.8	—0.1450
	88.6	83.6	87.3	—0.2039
	88.5	87.6	89.9	—0.2333
	88.5	90.4	92.0	—0.2471
	88.5	92.5	93.4	—0.2735
	88.6	94.3	94.8	—0.2921
	88.4	94.8	95.1	—0.3229
	88.4	96.0	96.1	—0.3228
	88.4	97.0	97.1	—0.3120
	88.3	97.7	97.6	—0.3522
	88.4	100.0	100.0	—
1520	125.0	0	0	—
	110.8	21.1	44.5	0.1008
	109.6	26.4	50.0	0.0829

Table 5 (cont.)

P torr	t °C	x mole-% ethanol	y mole-% ethanol	$\log \frac{\gamma_1}{\gamma_2}$
	106.7	33.1	56.5	0.0603
	105.5	35.4	59.1	0.0654
	103.0	49.0	69.4	0.0183
	101.9	54.4	72.8	—0.0008
	100.4	62.3	76.9	—0.0460
	99.6	65.8	77.6	—0.0940
	99.0	70.0	79.8	—0.1305
	98.9	71.0	81.1	—0.1052
	98.8	73.8	82.6	—0.1214
	98.7	75.5	83.9	—0.1184
	98.4	79.5	86.1	—0.1436
	98.5	79.7	86.2	—0.1555
	98.2	82.0	87.5	—0.1608
	98.1	83.2	87.9	—0.1810
	97.9	86.2	90.0	—0.1878
	97.8	88.7	91.7	—0.1980
	97.7	89.6	92.2	—0.2091
	97.4	92.3	94.0	—0.2285
	97.3	95.5	96.4	—0.2455
	97.2	100.0	100.0	—
3040	152.5	0	0	—
	139.6	17.0	37.0	0.0874
	136.5	25.4	46.6	0.0241
	134.8	27.6	50.0	0.0382
	133.0	31.0	53.6	0.0279
	131.4	35.0	56.6	0.0060
	130.8	37.8	59.0	—0.0033
	129.4	40.8	61.4	—0.0140
	123.5	57.6	74.6	—0.0352
	122.0	64.5	78.6	—0.0599
	120.1	76.3	85.2	—0.1099
	118.5	100.0	100.0	—

where γ_i = activity coefficient of the ith component
y_i = mole fraction of the ith component in the vapour phase
x_i = mole fraction of the ith component in the liquid phase
p_i° = tension of the ith pure component at the temperature of the system
P = overall pressure of the system
z_i = correction factor for a real gas, for the ith component.

In the calculation of activity coefficients for $P \leqq 760$ torr, $z_i = 1$ was used, values of z_i for $P > 760$ torr were determined on the basis of the nomogram constructed by Scheibel [6].

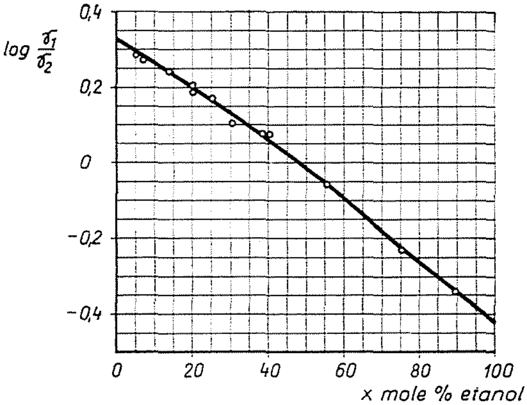

Fig. 15. $\frac{\gamma_1}{\gamma_2}$ vs. diagram, for pressure $P = 190$ torr

Tensions of the pure components were calculated according to Antoine equations

$$\text{ethanol} \quad [3], \log p_1^\circ = 8.24169 - \frac{1652.6}{230 + t}$$

$$\text{dioxane} \quad [3], \log p_2^\circ = 7.25111 - \frac{1406.8}{220.8 + t}$$

For a thermodynamical check of our measurements the method described by HERINGTON [7] was applied. The $\log \frac{\gamma_1}{\gamma_2}$ vs. x curves are presented in Figs 15 through 20. The diagrams show that our data are thermodynamically sound.

In order to determine the composition of azeotropic mixtures, we plotted the $(y - x)$ values of our measurements as a function of x and from this curve

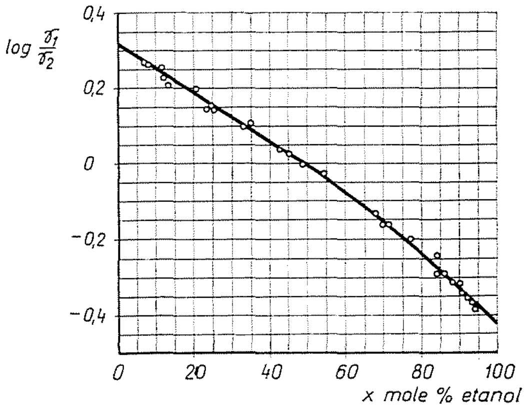

Fig. 16. $\frac{\gamma_1}{\gamma_2}$ vs. x diagram, for pressure $P = 380$ torr

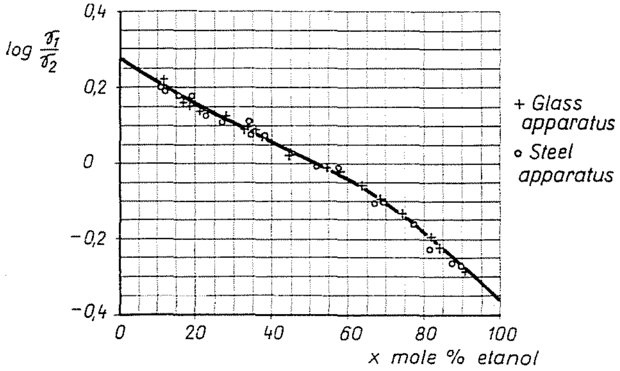

Fig. 17. $\frac{\gamma_1}{\gamma_2}$ vs. x diagram, for pressure $P = 760$ torr

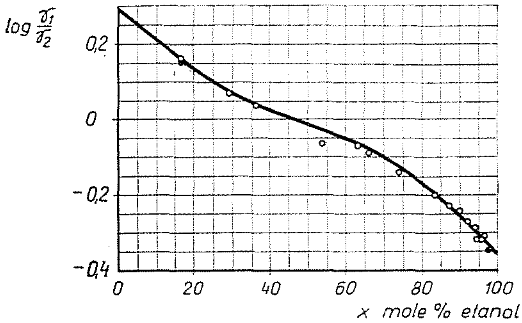

Fig. 18. $\frac{\gamma_1}{\gamma_2}$ vs. x diagram, for pressure $P = 1140$ torr

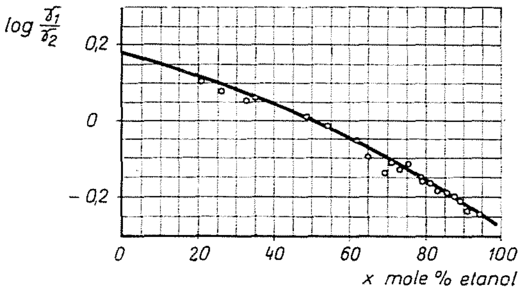

Fig. 19. $\frac{\gamma_1}{\gamma_2}$ vs. x diagram, for pressure $P = 1520$ torr

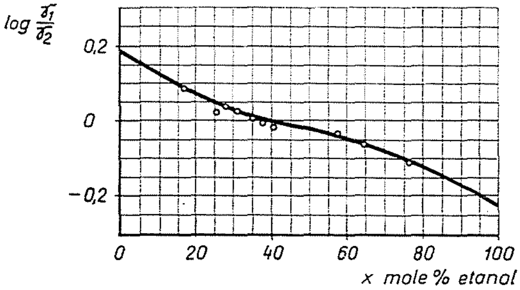

Fig. 20. $\frac{\gamma_1}{\gamma_2}$ vs. x diagram, for pressure $P = 3040$ torr

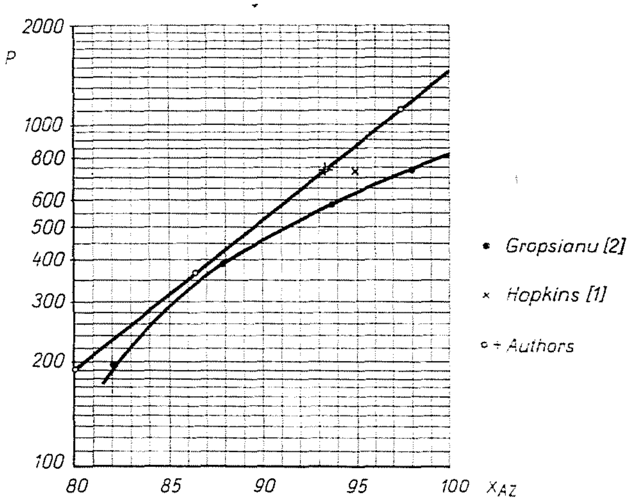

Fig. 21. Azeotropic composition as a function of pressure

we read off the compositions pertaining to the various pressures. Data thus collected are listed in Table 6.

Table 6

Data of azeotropic mixtures of ethanol and dioxane

P torr	t °C	x_1 mole-% ethanol
190	45.8	80.0
380	61.0	86.5
760	77.9	93.4
1140	88.2	97.5
1520	no azeotropic mixture	
3040	no azeotropic mixture	

Fig. 21 shows azeotropic composition as a logarithmic function of overall pressure, and indicates that azeotropy ceases at 1500 torr pressure.

This finding is supported by equilibrium data measured at $P = 1520$ torr pressure since according to these at this pressure this system does not form an azeotropic mixture.

Summary

An apparatus for the measurement of vapour-liquid equilibria has been constructed by which thermodynamically correct equilibrium data can be measured for pressures higher than atmospheric. With the help of this apparatus the equilibrium figures of the ethanol/dioxane system capable of forming binary azeotropic mixtures have been determined for pressures $P = 190$, 380, 760, 1140, 1520 and 3040 torr, and the composition of azeotropic mixtures at various pressures have been stated. Based upon the correlation elucidated between composition and pressure, it can be said that formation of an azeotropic mixture ceases at 1500 torr; this finding is supported by results of measurements carried out at pressures of 1520 and 3040 torr.

References

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