

# Experimental Investigation of the Vapor-Liquid Equilibria of the Binary System Ethanol-Water at 26,7 kPa

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**Abstract** - Vapor-liquid equilibrium (VLE) data of binary system ethanol - water at low pressure (26,7 kPa) were measured using a modified Othmer equilibrium still. The experimental data of the studied system showed positive deviation from the ideal solution behavior. According to Herington's criterion a set of isobaric VLE data is thermodynamically consistent.

**Keywords** - Ethanol, Water, Mixtures, Vapor-liquid equilibrium, VLE low pressure.

## I. INTRODUCTION

Accurate vapor-liquid equilibrium data are important for the design of separation processes and in the testing of further development of thermodynamic models [11,12].

Because of its good solvency and relatively low boiling point ethanol is used widely as a recoverable reaction medium particularly for the preparation of pharmaceuticals. Water and other organic solvents are added to it according to the requirements of the technological process. As a result of this the mixtures consisting of them are obtained as a final waste products. At present they are thrown out in the rivers. Regeneration of the valuable components of these waste mixtures and their return back to the technological processes is required with a view to reach a definite economic and ecological effect.

One of these waste mixtures obtained in an industrial process is the system ethanol - water - formamid - dissolved involatile organic admixtures. Accurate VLE data of this system and of its subsystem ethanol - water at 26,7 kPa are necessary for the correct design of separation process of the mentioned above multi-component waste mixture [1].

In this study we report the results of our VLE measurements of the binary solution ethanol - water at 26,7 kPa. The experimental VLE data obtained in this work will serve as a supplement to the existing literature data regarding this system at condition that have not yet been covered.

## II. MATERIALS

Ethanol and distilled water were used in the experiments. Ethanol was purchased from *Merck* and was of the highest purity available, chromatography quality reagent with a stated purity of 99,9 %.

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Both reagents were further purified by removing the top and bottom 5 % cuts using a laboratory packed distillation column at atmospheric pressure and the intermediate fraction distilling at constant temperature was collected.

The purity of the products were checked by determining of two their parameters, measured at temperature 293,15 K - relative density and refractive index and by gas chromatography.

Relative density was measured picnometrically [10] and refractive index - with refractometer of Abbe [10] both with accuracy  $\pm 0,0001$ . Three to five parallel test samples were analyzed and their average value was accepted for valid. The relative measurement error was 0,02 %.

The gas chromatograph (Thermo Quest) used for analyzing of the test samples was with a flame ionization detector (FID) and a AT - 1701 column. The column parameters are: length - 30 m, diameter - 0,32 mm and film thickness - 0,25 nm. The column filling is 14 % cyanopropylphenyl and 86 % methylpolysiloxane.

Besides, water contents using Fisher's method was determined for the ethanol [6].

In Table I, the experimental data of the pure constituencies measured in this work are compared with those reported in the literature to check for their purity.

TABLE I.

Average values of experimental density, refractive index and water content measured in this work and corresponding literature values.

Components	Data	Relative density	Refractive index	Water contents
Ethanol	Experimental	0,7894	1,3613	0,08
	Literature	0,78945 [7] 0,78927 [7]	1,3613 [7] 1,3614 [2]	-
Water	Experimental	0,9983	1,3333	-
	Literature	0,99823 [7]	1,33297 [7] 1,3333 [2]	-

## III. EXPERIMENTAL METHOD

Isobaric vapor - liquid equilibrium of binary system ethanol - water at 26,7 kPa was measured using a modified Othmer's circulation still with a capacity of about 500 sm<sup>3</sup> of liquid phase. Detailed description of the apparatus is given elsewhere [3]. It was chosen on the base of our survey on the methods and apparatuses for the vapor - liquid equilibrium investigation [4,5,8,9].

For the experiments running at subatmospheric pressure the Othmer's apparatus was connected to a pressure regulation system. It is a sequence of a vacuum pump for creating of the

necessary vacuum, a manostat for holding of constant pressure and a double column mercury vacuumometer. The pressure was measured with an accuracy of  $\pm 133$  kPa.

The equilibrium boiling point temperatures were measured using a calibrated Pt-resistance thermometer (series TS of "COMECO" LTD - Plovdiv) with an accuracy of  $\pm 0,1$  K. The temperature sensor is Pt 100 with a range from 273 to 473 K.

The Othmer's apparatus was made entirely of glass and was tested through studying vapor - liquid phase equilibrium of the binary system ethanol - water at two constant pressure levels - 101,3 kPa and 25,33 kPa. The obtained results were compared with the correspondent literature data for the studied system. Measurement error was no more than  $\pm 0,2$  mol %.

The initial mixtures were charged into experimental still distillator and heated through a inside electrical heater. The heater power was controlled using a laboratory autotransformer. The vapor space of the Othmer's still was thermally insulated with aim to prevent the partial vapor condensation on its inside walls.

For the aim of the investigation binary solutions of all concentration range (from 0 to 100 mol %) and volume of about 300 sm<sup>3</sup> were prepared and charged into the experimental still. Then the necessary vacuum was created and the electrical heater was switch on. In the beginning of solution boiling the experimental still was degassed and the still condenser was fed with cooling water. The steady boiling process was maintained through the heater power regulation and the equilibrium temperature was controlled.

About after an hour at keeping the constant equilibrium temperature it was considered that the phase equilibrium was reached. Then the electric heater was switch off and the vacuum was break up. Samples of liquid and vapor (condense) phases were withdrawn.

Liquid and vapor phase compositions were analyzed through determining of refractive index with refractometer of Abbe at temperature 293 K with accuracy  $\pm 0,0001$ . Three parallel test samples were analyzed and their average values was accepted for valid. The relative measurement error was 0,02 %.

To confirm the obtained results some of the samples were analyzed and by gas chromatography.

#### IV. EXPERIMENTAL RESULTS AND DATA ANALYSIS

The experimental isobaric vapor - liquid equilibrium data of binary system at 26,7 kPa studied in this work are given in Table II. To display the behavior of the investigated solutions, the activity coefficients of both components  $\gamma_1$  and  $\gamma_2$  were calculated on the base of experimental data from the Eqs. (1) and (2):

$$\gamma_1 = \frac{y_1 P}{x_1 P_1^0} \quad (1)$$

$$\gamma_2 = \frac{y_2 P}{x_2 P_2^0} \quad (2)$$

TABLE II.

Experimental vapor - liquid equilibrium data of ethanol - water binary system at 26,7 kPa

Liquid x	Vapor y	t	P <sub>1</sub> <sup>0</sup>	P <sub>2</sub> <sup>0</sup>	γ <sub>1</sub>	γ <sub>2</sub>
mol %	mol %	<sup>0</sup> C	kPa	kPa	-	-
1	2	3	4	5	6	7
0,1	0,6	66,3	61,63	26,41	2,5952	1,0043
3,29	23,55	61,6	50,21	21,36	3,7970	0,9864
7,03	38,0	57,7	42,14	17,82	3,4194	0,9974
11,31	47,01	55,1	37,39	15,75	2,9632	1,0112
16,32	52,3	53,2	34,22	14,37	2,4967	1,0574
22,35	55,67	52,0	32,33	13,55	2,0534	1,1229
29,82	58,85	51,0	30,83	12,90	1,7068	1,2114
39,33	62,47	50,3	29,81	12,46	1,4204	1,3231
51,98	67,43	49,6	28,82	12,04	1,1998	1,5021
70,01	76,47	48,85	27,79	11,59	1,0476	1,8040
90,0	90,49	48,25	27,0	11,25	0,9929	2,2535

where y is the vapor phase mole fraction, x is the liquid phase mole fraction, P is the constant pressure of investigation (26,7 kPa), P<sup>0</sup> is the saturation pressure and subscript i denotes component i. The saturation pressures of ethanol and water, presented in the columns 4 and 5 of Table II were calculated using Antoine coefficients [7]. It is made assumption that the vapor phase behaves nearly as an ideal gas, which is truth for the pressures lower than the atmospheric.

The equilibrium phase diagram t-x-y of the ethanol - water binary system at 26,7 kPa in all the composition range is shown in Fig. 1.

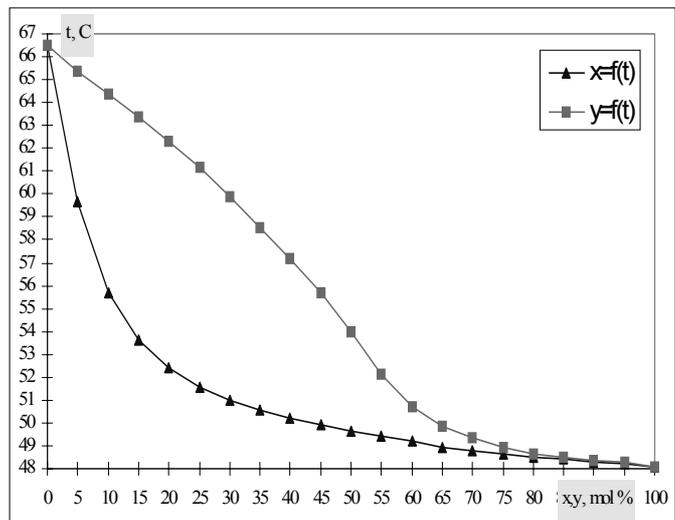


Fig.1. Saturation temperature as a function of the liquid - x<sub>1</sub>, and vapor composition - y<sub>1</sub>, of ethanol for the ethanol - water binary system at 26,7 kPa

The vapor composition - y<sub>1</sub> as a function of the liquid composition - x<sub>1</sub> of ethanol for the ethanol - water binary system at 26,7 kPa in all the composition range is shown in Fig. 2.

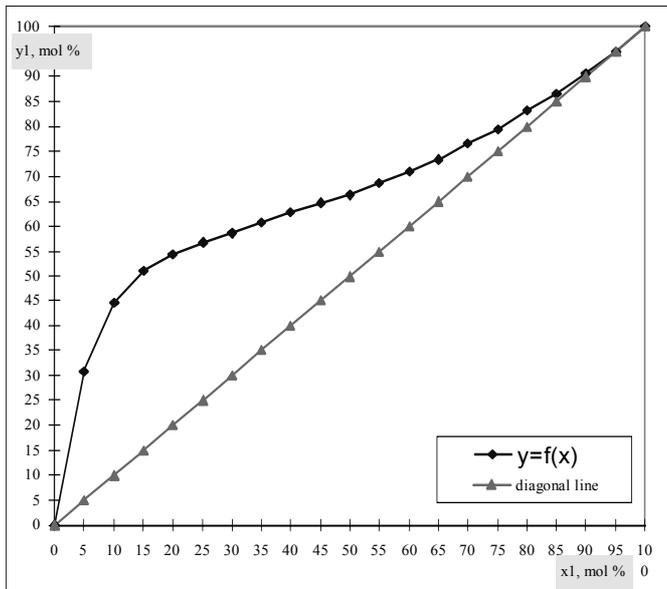


Fig. 2. The equilibrium phase diagram  $x$ - $y$  of the ethanol - water binary system at 26,7 kPa.

The dimensionless molar excess Gibbs free energy ( $G^E/RT$ ) and the dimensionless molar Gibbs free energy of mixing ( $G^M/RT$ ) were calculated as follows (Eqs. 3 and 4) [13]. The obtained values are given in Table III.

$$G^E/RT = x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (3)$$

$$G^M/RT = G^E/RT + x_1 \ln \gamma_1 + x_2 \ln \gamma_2 \quad (4)$$

TABLE III.

The dimensionless molar excess Gibbs free energy ( $G^E/RT$ ) and the dimensionless molar Gibbs free energy of mixing ( $G^M/RT$ ) calculated from the experimental vapor - liquid equilibrium data of ethanol - water binary system at 26,7 kPa

Liquid $x_1$	$\gamma_1$	$\gamma_2$	$\ln \gamma_1/\gamma_2$	$G^E/RT$	$G^M/RT$
mol %	-	-	-	-	-
1	3	4	5	6	7
0,1	2,5952	1,0043	0,412	0,0052	-0,003
3,29	3,7970	0,9864	0,585	0,0307	-0,114
7,03	3,4194	0,9974	0,535	0,084	-0,170
11,31	2,9632	1,0112	0,467	0,1327	-0,220
16,32	2,4967	1,0574	0,373	0,1961	-0,249
22,35	2,0534	1,1229	0,262	0,2509	-0,280
29,82	1,7068	1,2114	0,149	0,2940	-0,315
39,33	1,4204	1,3231	0,031	0,3079	-0,362
51,98	1,1998	1,5021	0,098	0,2901	-0,402
70,01	1,0476	1,8040	0,236	0,2095	-0,401
90,0	0,9929	2,2535	0,356	0,0748	-0,250

The ethanol - water binary system, as can be seen in Fig. 3 shows a positive deviation from the ideal solution. Values of  $G^M/RT$  for the studied system are also shown in Fig. 3. A complete miscibility over the whole composition range is observed.

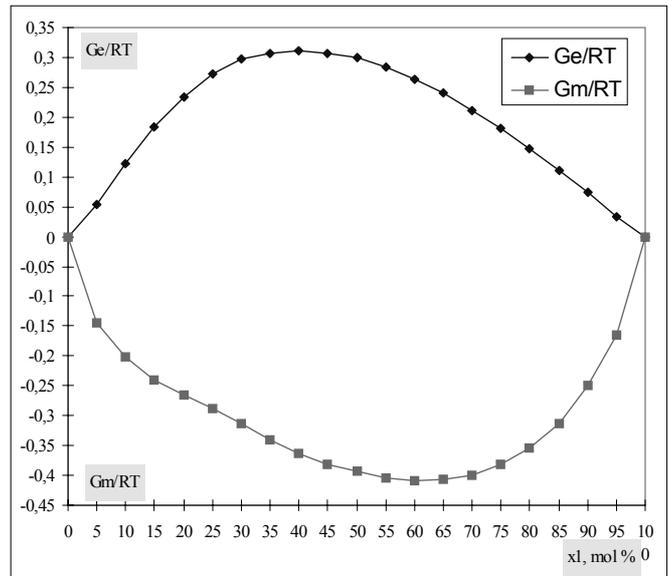


Fig. 3. Normalized excess and mixing energies (at 26,7 kPa) of ethanol - water binary system.

To test the vapor - liquid equilibrium data of the investigated system for thermodynamic consistency, values of  $\ln(\gamma_1/\gamma_2)$  presented in Table III were plotted against liquid mole fraction of ethanol -  $x_1$ , as shown in Fig. 4 and the areas above and below the zero  $x_1$ -axis were calculated.

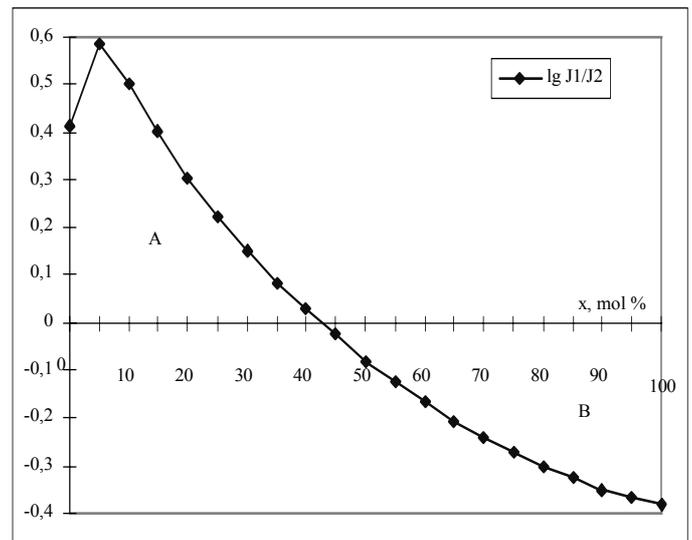


Fig. 4. Herington's consistency test for the ethanol - water binary system at 26,7 kPa.

In accordance with Herington [13], the percentage deviation of areas mentioned above,  $D$  was compared with the empirical quantity  $J$ , which is related to the boiling points of pure constituents  $T_1$  and  $T_2$  and the lowest boiling point observed in the entire composition range,  $T_{\min}$  (Eqs. 5 and 6):

$$D = 100 \cdot (A - B) / (A + B) \quad (5)$$

$$J=150*(T_2-T_1)/T_{\min}, \quad (6)$$

A and B represent the areas above and below the zero axis, respectively. According to Herington's criterion, a set of isobaric vapor - liquid equilibrium data is thermodynamically consistent if the following condition is satisfied (Eq. 7):

$$D < J \quad (7)$$

But if the VLE data satisfied the Eq. 8 they still may be considered for thermodynamically consistent:

$$D - J < 10 \quad (8)$$

In our case  $A=12,92$ ,  $B=13,073$ . Then  $D=0,59$ ,  $J=8,59$  and inequality  $D < J$  is satisfied. Therefore the experimental VLE data of ethanol - water at 26,7 kPa are thermodynamically consistent.

## V. CONCLUSIONS

1. Experimental vapor - liquid equilibrium data of ethanol - water binary system at 26,7 kPa was measured in this work. According to the Herington's criterion they are thermodynamically consistent. The studied system showed a positive deviation from an ideal solution.

2. The obtained VLE data are necessary for determining of the ternary system ethanol - water - formamid isobaric VLE data at 26,7 kPa and respectively for the correct design of separation process of the mentioned above ternary system.

3. Also this work contributes with an experimental investigation of the thermodynamic parameters of VLE at 26,7 kPa of the ethanol - water binary system.

## VI. LIST OF SYMBOLS

$x_i$  - liquid phase mole fraction of  $i$  - component

$y_i$  - vapor phase mole fraction of  $i$  - component

$\gamma_i$  - activity coefficient of  $i$  - component

$P_i^0$  - saturation pressure of  $i$  - component

$P$  - total pressure

$T_i$  - absolute temperature of  $i$  - component

$t$  - boiling temperature of studied solutions, °C

$G^E/RT$  - molar excess Gibbs free energy

$(G^E/RT)$  molar Gibbs free energy of mixing

### Subscripts:

1 - ethanol

2 - water

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