



APPLICATION OF THE MATHEMATICAL MODELS OF DISTILLATION EQUILIBRIA FOR DESIGNING THE DIFFERENTIAL DISTILLATION PROCESS

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ABSTRACT

This paper presents the development of mathematical models for positive and negative azeotropes in the range of the more volatile concentrations component: $x \in [0; a_z] \vee [a_z; 1]$. The coefficients of these models, which, on their basis, were determined the relative volatility of α and the azeotrope concentration a_z , defined with the high accuracy ($R^2 \in [0,926; 0,999]$) and presented them to the table for all subjects of distillation systems. Based on these relationships, the integration of the mass balance equations of the distillation differential process $d(Sx) = ydS$ was carried out and determined the dependence of the distillate obtained from 1 mole of pig iron D/S_0 from the α , a_z coefficients and x_w , x_s concentrations. Based on these dependencies, charts D/S_0 were prepared from predefined by the authors parameter $t = [0,05; 0,25; 0,5; 0,75]$ which is the change in the concentration of pig iron in the process of concentration. Dependencies, presented for distillation balances of positive and negative azeotrope, in the tested ranges, for similar values of α , have the same mileage. The calculations were made for the 126 distillation systems.

Keywords: colorants, asymmetric metal complexes, heteroleptic complexes, resistance to UV radiation, acetylacetone

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INTRODUCTION

Two-component distillation balances can be divided into “perfect” ones, which can be described by the mole fraction dependence of component A in pair (y_A) on the mole fraction of that component in the liquid (x_A):

$$y_A = \frac{\alpha x_A}{1 + (\alpha - 1)x_A} \quad (1)$$

and “imperfect” ones, having either a positive azeotrope (minimum boiling point) or a negative azeotrope (maximum boiling point). Relative volatility α depends on the activity coefficients (γ_A , γ_B) and the partial pressure of components A and B (P_A , P_B):

$$\alpha = \frac{\gamma_A P_A}{\gamma_B P_B} \quad (2)$$

where activity coefficients are dependent on the temperature (T) of distillation processes and the composition of the liquid, according to the authors Serwiński (1982), Ciborowski (1976) and Troniewski (2006) due to:

$$\frac{\gamma_A}{\gamma_B} = \exp\left(\frac{\left(\left(1 + \frac{Ax_A}{x_B}\right)^{-2} - A\left(1 + \frac{x_B}{x_A}\right)^{-2}\right)B}{T}\right) \quad (3)$$

For distillation systems with the positive azeotrope, a linear relationship of the vapor composition was developed from the boiling liquid composition (Sobczak, 2010). According to Yu and Coull (Bandrowski J. T., 1980) for the positive and negative azeotropes, distillation equilibrium can be described by the formula:

$$\frac{y_A}{1 - y_A} = a \left(\frac{x_A}{1 - x_A}\right)^b \quad (4)$$

where: a and b are constants for certain distillation equilibria. However, the equation does not satisfy the azeotropes boundary conditions: $y_A = x_A = a_z$. These conditions did not meet the model developed for the positive azeotropes (Anderson and Doherty, 1984):

$$y' = \frac{\alpha x'}{1 + (\alpha - 1)x'} \quad (5)$$

where

$$y' = y_A/a_z \text{ i } x' = x_A/a_z$$

Also, the coefficient of determination α is analytically impossible to determine the condition of minimizing the error σ_y^2 :

$$\sigma_y^2 = \sum_{i=1}^n \left(y' - \frac{\alpha x'}{1 + (\alpha - 1)x'}\right)^2 \quad (6)$$

$$\frac{d\sigma_y^2}{d\alpha} = 2 \sum_{i=1}^n \left(\frac{x' y' (1 - x')}{(1 + (\alpha - 1)x')^2} - \frac{\alpha x'^2 (1 - x')}{(1 + (\alpha - 1)x')^3}\right) = 0 \quad (7)$$

Furthermore Anderson and Doherty (1984) did not use the selection of optimal concentrations of the azeotrope (a_z) for minimizing the error R (6), which made their method unsuitable for determination of the dependencies of “deformed” equilibria (such as ethanol-water).

DETERMINATION OF MATHEMATICAL MODELS

For the distillation system with the positive azeotrope denoting the composition of the vapor and liquid $x_A = x$ and $y_A = y$ (for $y > x \wedge x \in [0; a_z]$) the authors have developed a linear composition of the vapor from the boiling liquid composition:

$$\frac{x}{y} = \frac{1}{\alpha} + \left(1 - \frac{1}{\alpha}\right) \frac{x}{a_z} = ax + b \quad (8)$$

where:

$$\alpha = \frac{1}{b} \quad (9)$$

$$a_z = \frac{1-b}{a} \quad (10)$$

whereas for distillation systems with the negative azeotrope ($y < x \wedge x \in [0; a_z]$):

$$\frac{y}{x} = \frac{1}{\alpha'} + \left(1 - \frac{1}{\alpha'}\right) \frac{y}{a_z} = ay + b \quad (11)$$

where:

$$\alpha' = \frac{1}{b} = \frac{1}{\alpha} \quad (12)$$

$$a_z = \frac{1-b}{a} \quad (13)$$

For distillation systems with the positive azeotrope ($y < x \wedge x \in [a_z; 1]$), the authors have developed a linear composition of the vapor from the boiling liquid composition:

$$\frac{x-y}{1-y} = \frac{1-\frac{1}{\alpha'}}{1-a_z} (x - a_z) = ax + b \quad (14)$$

where:

$$a_z = -\frac{b}{a} \quad (15)$$

$$\alpha' = \frac{1}{1-a-b} = \frac{1}{\alpha} \quad (16)$$

whereas for distillation systems with the negative azeotrope ($y > x \wedge x \in [a_z; 1]$):

$$\frac{y-x}{1-x} = \frac{1-\frac{1}{\alpha}}{1-a_z} (y - a_z) = ay + b \quad (17)$$

where:

$$a_z = -\frac{b}{a} \quad (18)$$

$$\alpha = \frac{1}{1-a-b} \quad (19)$$

The results of calculations α and α' and a_z are shown in Tables 1-4 and in the article (Sobczak et al., 2010) whereas accuracy is denoted by the coefficient R^2 :

$$R^2 = 1 - \frac{\sum_{i=1}^n (y_i - \hat{y})^2}{\sum_{i=1}^n (y_i - \bar{y})^2}$$

where: \hat{y} – is linear

$$\bar{y} \text{ – is the mean value: } \bar{y} = \frac{\sum_{i=1}^n y_i}{n}$$

Table 1. List of parameters α and a_z for the positive azeotropes for $y > x \wedge x \in [0; a_z]$

No.	System	Press. [kPa]	R^2	a_z	α
1.	Acetone – Carbon tetrachloride	40.00	0.9998	0.74	3.99
2.	Acetone – Methanol	101.32	0.9870	0.72	2.29
3.	Acetone – Carbon tetrachloride	101.32	0.9990	0.75	3.82
4.	Acetone – Ethanol	101.32	0.9997	0.82	3.28
5.	Acetone – Benzene	101.32	0.9990	0.81	3.09
6.	Acetone – Water	101.32	0.9893	0.88	29.56
7.	Ethanol – Water	12.67	0.9982	0.72	7.47
8.	Ethanol – Water	50.66	0.9968	0.72	8.99
9.	Ethanol – Water	101.32	0.9979	0.68	9.30
10.	Carbon disulphide – Carbon tetrachloride	101.32	0.9941	0.96	2.91
11.	Chloroform - Methanol	100.92	0.9983	0.65	3.22
12.	Methanol – Toluene	101.32	0.9417	0.85	25.13
13.	Carbon tetrachloride - Ethanol	99.32	0.9782	0.61	6.30
14.	Water – n-Butanol	102.26	0.9884	0.81	7.35
15.	Cyclohexane – Toluene	101.32	0.9261	0.95	3.11
16.	Cyclohexane – Aniline	101.32	0.9968	1.00	70.40
17.	n-Hexane – n-Heptane	101.32	0.9989	1.00	2.33
18.	n-Hexane – Benzene	97.99	0.9988	0.82	2.19
19.	Methanol – Water	101.32	0.9978	0.94	6.38
20.	Ethanol - Benzene	99.99	0.9952	0.44	7.12
21.	Carbon tetrachloride – Toluene	101.59	0.9985	1.00	2.37
22.	Carbon tetrachloride – Cyclohexane	101.32	0.9993	0.90	1.17
23.	Carbon tetrachloride – Benzene	101.32	0.9992	0.73	1.20
24.	Benzene – Acetic acid	101.32	0.9995	0.87	7.08
25.	Benzene – n-Heptane	101.32	0.9995	0.89	2.05
26.	Benzene – Toluene	101.32	0.9992	1.00	2.38
27.	Benzene – Cyclohexane	101.19	0.9989	0.50	1.33
28.	Ethanol – Amyl alcohol	101.32	0.9975	1.00	8.69
29.	Ethanol – n-Butanol	101.32	0.9921	1.00	3.95

Table 1 continued

30.	Methanol – Benzene	101.32	0.9999	0.61	21.44
31.	Methanol – Ethanol	101.32	0.9966	0.97	1.74
32.	Cyclohexane – n-Heptane	101.32	0.9986	0.99	1.92
33.	Benzene – Aniline	101.32	0.9981	1.00	19.56
34.	n-Heptane – Toluene	101.32	0.9980	0.74	1.77
35.	Water – Acetic acid	101.32	0.9984	0.96	1.80
36.	Acetone – Methanol	13.33	0.9377	0.84	2.59
37.	Acetone – Water	26.66	0.9916	0.90	45.18
38.	Acetone – Water	46.66	0.9941	0.92	35.51
39.	Methanol – n-butanol	101.32	0.9996	0.99	11.72
40.	Methanol – Amyl alcohol	101.32	0.9909	1.00	19.31
41.	Methanol – Water	26.66	0.9980	0.95	7.69
42.	Methanol – Water	46.66	0.9974	0.94	7.30
43.	Methanol – Water	66.66	0.9961	0.93	6.96
44.	Ethanol – Water	6.67	0.9991	0.76	7.53
45.	Ethanol – Water	25.33	0.9990	0.65	11.48
46.	Benzene – Aniline	46.66	0.9823	1.00	29.62
47.	Water – Acetic acid	13.33	0.9618	1.00	1.39
48.	Water – Acetic acid	16.67	0.9998	0.90	1.82
49.	Water – Acetic acid	26.66	0.9993	0.99	1.60
50.	Water – Acetic acid	33.33	0.9997	0.93	1.84
51.	Water – Acetic acid	46.66	0.9967	1.00	1.72
52.	Water – Acetic acid	66.66	0.9996	0.98	1.88
53.	Methanol – Benzene	101.32	0.9975	0.60	25.51
54.	Methyl palmitate – Ethyl stearate	0.53	0.9998	1.00	2.37
55.	Lauric acid – Myristic acid	0.53	0.9995	0.96	1.69
56.	Methyl laurate – Lauric acid	0.53	0.9983	1.00	9.44
57.	TAME – tert-amyl-ether – 1-Butanol	101.32	0.9997	0.96	3.89
58.	Acetone – Ethyl acetate	101.32	0.9869	0.96	2.22
59.	Acetone – Hexane	101.32	0.9998	0.63	7.25
60.	Hexane – Ethyl acetate	101.32	0.9870	0.63	3.04
61.	Diethyl ketone – 3-Pentanol	101.30	0.9990	0.97	1.65
62.	2-Pentanone – 3-Pentanol	101.30	0.9997	0.97	1.66
63.	Acetone – Dimethyl carbonate	101.30	0.9990	1.00	3.15
64.	Dimethyl carbonate – 2-Pentanone	101.30	0.9893	0.87	1.84
65.	2-Butanone - Dimethyl carbonate	101.30	0.9982	0.87	1.66
66.	Acetone – Methanol	100.00	0.9968	0.72	2.20
67.	Dibutyl ether – o-Xylene	50.60	0.9979	0.66	1.14
68.	Ethanol – EMC	101.30	0.9941	0.86	6.52
69.	DMC – EMC	101.30	0.9983	0.98	1.78
70.	EMC – DEC	101.30	0.9417	1.00	1.66
71.	Methanol – EMC	101.30	0.9782	0.93	9.21
72.	Methyl acetate – Methanol	101.30	0.9884	0.62	3.42
73.	n-Heptane – n-Butyl alcohol	192.65	0.9261	0.71	6.28
74.	n-Heptane – n-Butyl alcohol	293.97	0.9968	0.64	4.80

Table 1 continued

75.	n-Heptane – n-Butyl alcohol	395.29	0.9989	0.60	4.42
76.	n-Heptane – n-Butyl alcohol	496.62	0.9988	0.56	4.47
77.	Ether – n-Heptane	101.32	0.9978	1.00	2.42
78.	Ether – n-Heptane	202.65	0.9952	1.00	2.35
79.	Ether – n-Heptane	303.97	0.9985	0.74	4.00
80.	Benzene – 2,2,2-Trifluoroethanol	102.00	0.9993	0.47	5.56
81.	Toluene – 2,2,2-Trifluoroethanol	102.00	0.9992	0.21	3.38
82.	Acetone – Isopropenyl acetate	101.30	0.9995	1.00	3.47
83.	2-Butanone – Isopropenyl acetate	101.30	0.9995	1.00	1.62
84.	Isopropenyl acetate – Acetylacetone	101.30	0.9992	0.97	4.16
85.	Tetrahydrofuran – (1-Methylethyl) benzene	97.99	0.9989	1.00	8.29
86.	Tetrahydropyran – (1-Methylethyl) benzene	97.99	0.9975	1.00	4.87
87.	N, N-dimethylformamide – 1-Chloro-2-ethylhexane	79.99	0.9921	0.74	2.85
88.	N, N-dimethylformamide - 2-Ethyl-1-ol	79.99	0.9999	1.00	1.86
89.	Toluene – 1-Chloro-2-ethylhexane	79.99	0.9966	1.00	5.11
90.	Toluene – 2-Ethyl-1-ol	79.99	0.9986	1.00	8.35
91.	Cumene – N-ethylacetamide	97.30	0.9981	0.86	22.37
92.	Cumene – N, N-dimethylacetamide	97.30	0.9980	0.71	4.30
93.	MTBE – 1-Propanol	101.32	0.9984	0.98	6.04
94.	DIPE – 1-Propanol	101.32	0.9377	0.90	5.17
95.	TAME – 1-Propanol	101.32	0.9916	0.72	2.92
96.	Acrylonitrile – Hexane	30.04	0.9941	0.39	11.74
97.	Acrylonitrile – Cyclohexane	30.03	0.9996	0.49	20.33
98.	Acrylonitrile – Toluene	26.94	0.9909	0.94	4.86
99.	Acrylonitrile – Benzene	30.03	0.9980	0.50	1.91
100.	Tetrachloroethylene – 1-Pentanol	20.00	0.9974	0.88	7.43
101.	Tetrachloroethylene – 3-Methyl-1-butanol	20.00	0.9961	0.84	6.42
102.	Tetrachloroethylene – 2-Methyl-1-butanol	20.00	0.9991	0.82	5.82
103.	Tetrachloroethylene – 2-Methyl-1-butanol	100.00	0.9990	0.67	3.49
104.	IBA – Isooctane	101.30	0.9823	0.32	4.68
105.	IBA – Toluene	101.30	0.9618	0.47	3.53
106.	IBA – Methylcyclohexane	101.30	0.9998	0.33	5.51
107.	1-Propanol – Water	100.00	0.9993	0.42	34.25
108.	2-METHF – Cumene	97.30	0.9997	1.00	6.81
109.	Acetate - Isopropylbenzene	97.30	0.9967	1.00	16.23
110.	HFC-4310mee – 2-Methylfuran	35.00	0.9996	0.52	5.63

Table 2. List of parameters $\alpha=1/\alpha'$ and a_z for the negative azeotropes for $y < x \wedge x \in [0; a_z]$

No.	System	Press. [kPa]	R ²	a _z	α
1.	Acetone – Chloroform	101.32	0.9961	0.38	0.66
2.	Methanol – Diethylamine	101.30	0.9853	0.75	0.46
3.	2-methylfuran – THF	35.00	0.9819	0.29	0.87
4.	Acetone – Chloroform	101.30	0.9922	0.35	0.62
5.	Water – Formic acid	101.32	0.9958	0.42	0.57
6.	Water – Formic acid	26.66	0.9984	0.45	0.39
7.	Water – Formic acid	9.33	0.9902	0.50	0.31

Table 3. List of parameters $\hat{\alpha}=1/\hat{\alpha}'$ and a_z for the positive azeotropes for $y < x \wedge x \in [a_z; 1]$

No.	System	Press. [kPa]	R ²	a _z	α
1.	Methanol – Benzene	101.32	0.9934	0.58	0.22
2.	Acetone – Hexane	101.32	0.9971	0.65	0.24
3.	Hexane – Ethyl acetate	101.32	0.9996	0.67	0.53
4.	Acetone – Methanol	100.00	0.9853	0.79	0.76
5.	Methyl acetate – Methanol	101.30	0.9977	0.66	0.47
6.	n-Heptane – n-Butyl alcohol	192.65	0.9999	0.70	0.26
7.	n-Heptane – n-Butyl alcohol	293.97	0.9933	0.62	0.23
8.	n-Heptane – n-Butyl alcohol	395.29	0.9998	0.60	0.19
9.	n-Heptane – n-Butyl alcohol	496.62	0.9996	0.57	0.18
10.	N, N-Dimethylformamide – 1-Chloro-2-ethylhexane	79.99	0.9956	0.83	0.44
11.	Cumene – N-Methylacetamide	97.30	0.9850	0.88	0.53
12.	Cumene – N, N-Dimethylacetamide	97.30	0.9922	0.74	0.16
13.	TAME – 1-Propanol	101.32	0.9991	0.77	0.65
14.	Acrylonitrile – Hexane	30.04	0.9994	0.36	0.08
15.	Acrylonitrile – Cyclohexane	30.03	0.9978	0.48	0.14
16.	Acrylonitrile – Benzene	30.03	0.9857	0.58	0.64
17.	Tetrachloroethylene – 1-Pentanol	20.00	0.9981	0.89	0.32
18.	Tetrachloroethylene – 3-Methyl-1-butanol	20.00	0.9929	0.84	0.24
19.	Tetrachloroethylene – 2-Methyl-1-butanol	20.00	0.9998	0.82	0.23
20.	Tetrachloroethylene – 2-Methyl-1-butanol	100.00	0.9991	0.69	0.29
21.	IBA – Isooctane	101.30	0.9997	0.33	0.19
22.	IBA – Toluene	101.30	0.9982	0.49	0.40
23.	IBA – Methylcyclohexane	101.30	0.9997	0.34	0.22
24.	HFC-4310mee - 2-Methylfuran	35.00	0.9854	0.56	0.57
25.	Ethanol – MTBE	50.00	0.9961	0.09	0.17
26.	Ethanol – MTBE	75.00	0.9941	0.10	0.19
27.	Ethanol – MTBE	94.00	0.9923	0.11	0.21

Table 4. List of parameters α and a_z for the negative azeotropes for $y > x \wedge x \in [a_z; 1]$

No.	System	Press. [kPa]	R ²	a_z	α
1.	Acetone – Chloroform	101.32	0.9892	0.43	1.84
2.	Methanol – Diethylamine	101.30	0.9910	0.77	1.97
3.	Acetone – Chloroform	101.30	0.9748	0.40	1.99
4.	Phenol – Benzyl alcohol	10.00	0.9707	0.08	5.87
5.	Cyclohexanol – Phenol	12.00	0.9738	0.34	4.49
6.	Water – Formic acid	101.32	0.9842	0.47	2.30
7.	Water – Formic acid	26.66	0.9952	0.54	2.28
8.	Water – Formic acid	9.33	0.9969	0.58	2.24

THE USE OF MATHEMATICAL MODELS TO CALCULATE THE DIFFERENTIAL DISTILLATION

To calculate a simple distillation process, integration of the mass balance equation was carried out $d(Sx) = ydS$ for $x \in [x_w; x_s]$:

$$\ln \frac{S}{S_0} = \int_{x_s}^{x_w} \frac{dx}{y-x} \quad (20)$$

Using Equations (8, 11, 14 and 17) to the integral (20), the amount of the distillate $D = S_0 - S$ in relation to the amount of the solution used S_0 was calculated. The following was obtained for the positive azeotrope for $y > x \wedge x \in [0; a_z]$:

$$\frac{D}{S_0} = 1 - \left(\frac{x_w}{x_s}\right)^{\frac{1}{\alpha-1}} \left(\frac{a_z - x_s}{a_z - x_w}\right)^{\frac{\alpha}{\alpha-1}} \quad (21)$$

For the negative azeotrope for $y < x \wedge x \in [0; a_z]$, the following was obtained:

$$\frac{D}{S_0} = 1 - \left(\frac{x_s}{x_w}\right)^{\frac{\alpha'}{\alpha'-1}} \left(\frac{a_z - x_w}{a_z - x_s}\right)^{\frac{1}{\alpha'-1}} \quad (22)$$

For the positive azeotrope for $y < x \wedge x \in [a_z; 1]$, the following was obtained:

$$\frac{D}{S_0} = 1 - \left(\frac{1-x_w}{1-x_s}\right)^{\frac{1}{\alpha'-1}} \left(\frac{x_s - a_z}{x_w - a_z}\right)^{\frac{\alpha'}{\alpha'-1}} \quad (23)$$

For the negative azeotrope for $y > x \wedge x \in [a_z; 1]$, the following was obtained:

$$\frac{D}{S_0} = 1 - \left(\frac{x_w - a_z}{x_s - a_z}\right)^{\frac{1}{\alpha-1}} \left(\frac{1-x_s}{1-x_w}\right)^{\frac{\alpha}{\alpha-1}} \quad (24)$$

The calculations were carried out for the following parameter distillation value $t = [0.05, 0.25, 0.5, 0.75]$, as proposed by the authors, which defines the driving force of the distillation process:

$$t = \frac{x_w - x_L}{x_s - x_L} \tag{25}$$

where: x_L is the boundary concentration level achieved by the liquid exhausted in the distillation process, where $D/S_0 \rightarrow 1$ to $x_w \rightarrow x_L$ ($x_w = x_L$) is the zero place in the dependence from (21) to (24). Moreover, the authors defined the distribution parameter $k \in [0; 1]$, defining the composition of the solution. For $x \in [0; a_z]$ the concentration of the solution x_s equals to:

$$x_s = ka_z \text{ dla } y > x \wedge x_L = 0 \tag{26}$$

$$x_s = (1 - k)a_z \text{ dla } y < x \wedge x_L = a_z \tag{27}$$

However, for $x \in [a_z; 1]$ the concentration of x_s equals to:

$$x_s = a_z + (1 - k)(1 - a_z) \text{ dla } y < x \wedge x_L = 1 \tag{28}$$

$$x_s = a_z + k(1 - a_z) \text{ dla } y > x \wedge x_L = a_z \tag{29}$$

After carrying out the calculation, the value D/S_0 for the adopted range $t \in [0.05, 0.25, 0.5, 0.75]$ and $k = 0.5$, obtained according to D/S_0 from the parameter t ; the results are shown in the graph of (1) to (5).

DISCUSSION OF THE RESULTS

Because the relationships D/S_0 from (21) to (24) for the approximated values α and α' are convergent (Fig. 5) the authors, using Equation (26), replaced x_w by t in Equations (21) to (24):

$$x_w = x_L + t(x_s - x_L) \tag{30}$$

and then, using the dependence from (26) to (29), expressed the concentration x_s by k . In effect, the following was obtained:

$$\frac{D}{S_0} = 1 - t \left(\frac{1}{\alpha_z - 1} \right) \left(\frac{1 - k}{1 - kt} \right) \left(\frac{\alpha_z}{\alpha_z - 1} \right) \tag{31}$$

for $y > x$ $\alpha_z = \alpha$, and for $y < x$ $\alpha_z = \alpha' = \alpha^{-1}$

The above dependences are presented for $k = 0.5$ shown in Figures 1, 2, 3 and 4. Convergence of the dependence, shown in Figure 5 and obtained for $k = 0.5$, has been proved by the authors (Equations (31) and (32)).

The relationship D/S_0 depends only on the parameters α and t for the concentration of the solution x_s defined by the parameter distribution k , for $y > x$:

$$k = \frac{x_s}{a_z} \text{ dla } x < a_z \tag{32}$$

$$k = \frac{(x_s - a_z)}{(1 - a_z)} \text{ dla } x > a_z \tag{33}$$

whereas for $y < x$:

$$1 - k = \frac{x_s}{a_z} \quad \text{dla } x < a_z \quad (34)$$

$$1 - k = \frac{(x_s - a_z)}{(1 - a_z)} \quad \text{dla } x > a_z \quad (35)$$

Dependencies of the equilibria (14) and (17) using the selection of parameters α and a_z guarantee the highest precision of the relationships. In addition, the authors showed that using the Trouton's rule:

$$\frac{L}{T_{\text{boiling}}} = 85 \frac{\text{J}}{\text{mol} \cdot \text{K}} \quad (36)$$

relative volatility, α :

$$\alpha = \frac{\gamma_A P_{A\infty}}{\gamma_B P_{B\infty}} \exp\left(\frac{85(T_B - T_A)}{RT}\right) \quad (37)$$

decreases with increasing temperatures.

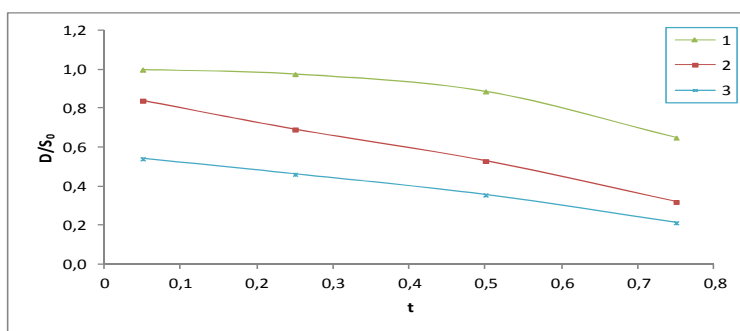


Fig. 1. The dependence D/S_0 on the parameter t for the positive azeotrope and $x \in [0; a_z]$, calculated from Equation (21): 1 – 2-butanone-Isopropenyl acetate ($\alpha = 1.62$), 2 – Isopropenyl acetate-acetylacetone ($\alpha = 4.16$), 3 – 1-Propanol-Water ($\alpha = 34.25$)

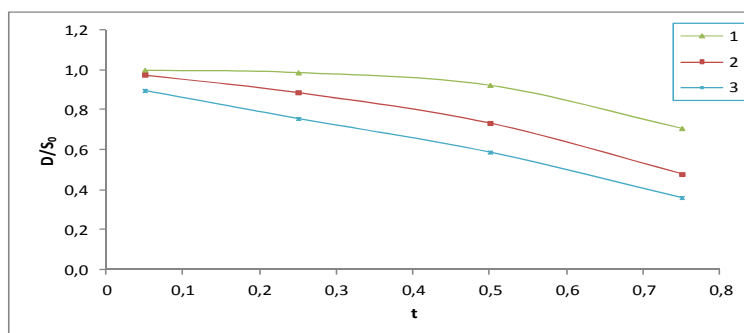


Fig. 2. The dependence D/S_0 on the parameter t for the negative azeotrope and $x \in [0; a_z]$, calculated from Equation (22): 1 – Acetone – Chloroform ($\alpha' = 1.51$), 2 – Methanol – Diethylamine ($\alpha' = 2.2$), 3 – Water – Formic acid ($\alpha' = 3.28$)

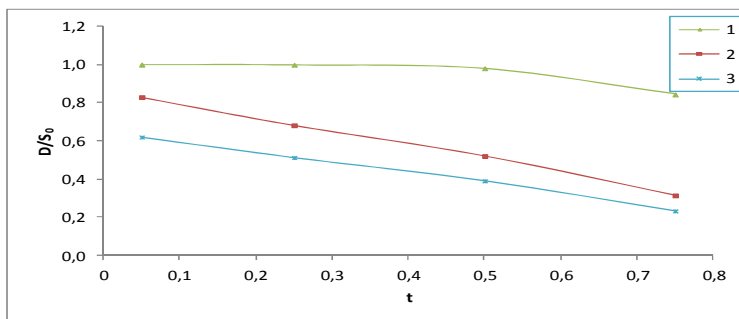


Fig. 3. The dependence D/S_0 on the parameter t for the positive azeotrope and $x \in [a_z; 1]$, calculated from Equation (23): 1 – Acetone – Methanol ($\alpha' = 1.31$), 2 – n-Heptane – n-butyl alcohol ($\alpha' = 4.33$), 3 – Acrylonitrile – Hexane ($\alpha' = 13.21$)

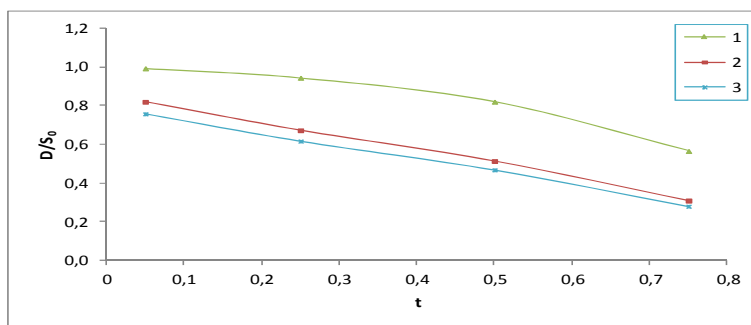


Fig. 4. The dependence D/S_0 on the parameter t for the negative azeotrope and $x \in [a_z; 1]$, calculated from Equation (24): 1 – Acetone – Chloroform ($\alpha = 1.84$), 2 – Cyclohexanol – Phenol ($\alpha = 4.49$), 3 – Phenol – Benzyl alcohol ($\alpha = 5.87$)

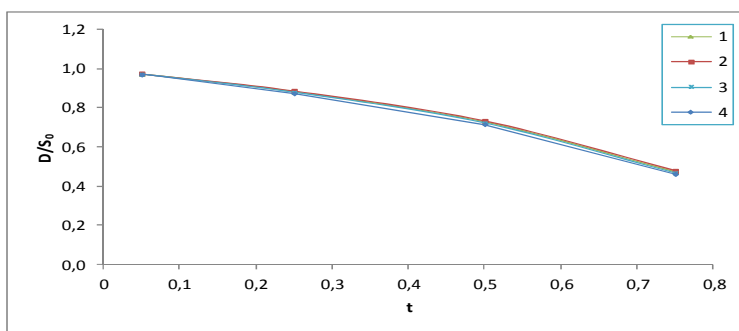


Fig. 5. The dependence D/S_0 on the differential distillation parameter t for the positive and negative azeotropes, and $x \in [0; a_z] \wedge [a_z; 1]$ and similar values: 1 – Acetone – Ethyl acetate $\alpha = 2.22$; calculated from the Equation (21), 2 – Methanol – Diethylamine $\alpha' = 2.2$; calculated according to (22), 3 – N, N-Dimethylformamide – 1-Chloro-2-ethylhexane $\alpha' = 2.25$; calculated from the formula (23), 4 – Water – Formic acid $\alpha = 2.281$; calculated from Equation (24)

CONCLUSION

Mathematical models, obtained for positive and negative azeotropes, were obtained with high accuracies $R^2 = 0.926 \div 0.999$.

Relative volatility α for $y > x$ and its inverse $\alpha' = 1/\alpha$ for $y < x$, which are present in these models, both for the positive and negative azeotropes, are consistent with experimental data, as evidenced by identical dependences D/S_0 on the parameters t defining the relative distillation driving force and, for a given k , defining the composition of the solution.

The dependences presented for the distillation balance with the positive and negative azeotrope in the ranges $x \in [0; a_z]$ and $x \in [a_z; 1]$ for the approximated values of α for $y > x$ and $\alpha' = 1/\alpha$ for $y < x$ are identical – Figure 5 and Equation (31) indicate that the coefficients α for $y > x$ and α' for $y < x$ are the corresponding parameters.

The authors showed that using the Trouton's rule, the relative volatility, α , decreases with increasing temperatures.

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