



SEPARATION OF AZEOTROPIC BINARY MIXTURES APPLYING DIFFERENTIAL DISTILLATION AND RECTIFICATION PROCESS

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ABSTRACT

A mathematical model, describing the dependence of the composition of the vapour resulting from the liquid composition for a positive azeotrope

$$\frac{x}{y} = \frac{1}{\alpha} + \left(1 - \frac{1}{\alpha}\right) \frac{x}{a_z} = ax + b \quad \text{and a negative azeotrope} \quad \frac{x-y}{x-1} = \frac{\left(1 - \frac{1}{\alpha}\right)(y-a_z)}{(1-a_z)} = cy + d$$

is discussed. These models were used for calculating the differential distillation process for the material balance of the composition $A \quad ydS = d(Sx)$ and $D = S_0 - S$:

$$\ln \frac{S}{S_0} = \int_{x_0}^x \frac{dx}{y-x} \quad \text{obtained of } D/S \text{ positive azeotrope} \quad \frac{D}{S} = 1 - \left(\frac{x}{x_0}\right)^{\frac{1}{\alpha-1}} \cdot \left(\frac{a_z - x_0}{a_z - x}\right)^{\frac{\alpha}{\alpha-1}} \quad \text{and}$$

$$\text{negative azeotrope} \quad \frac{D}{S} = 1 - \left(\frac{x-a_z}{x_0-a_z}\right)^{\frac{1}{\alpha-1}} \cdot \left(\frac{1-x_0}{1-x}\right)^{\frac{\alpha}{\alpha-1}}, \quad \text{where } a_z - \text{azeotropic concentra-}$$

tion, α – volatility coefficient. Results were obtained for 52 systems, and the values of α and a_z are given in Table 1. For the same concentration, adopted by the authors: $x_w = 0.02$, $x_s = 0.22$, $x_D = a_z - 0.02$, thermal state of feed $e = (c\Delta T + r)/r = 1.11$, obtained the dependence of the quantity of plates of the rectifying column as a function of relative volatility: $n = 23.3\alpha^{-0.64}$.

Keywords: mathematical models, azeotropic binary mixtures, rectification

INTRODUCTION

The mathematical model describing the dependences of the composition of steam (y) from the composition of liquid (x) for binary mixtures was formulated:

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

It can be shown by Trouton's rule ($\frac{L}{T_{boil}} = 85 \frac{J}{mol \cdot K}$) that relative volatility

$$\alpha = \frac{\gamma_A P_{A\infty}}{\gamma_B P_{B\infty}} \exp\left(\frac{85(T_B - T_A)}{RT}\right)$$
 depends on T temperature of distillation and rectification processes and, according to the authors [1, 2]

$$\frac{\gamma_A}{\gamma_B} = \exp\left(\frac{\left(\left(1 + Ax_A/x_B\right)^{-2} - A\left(1 + x_B/x_A\right)^{-2}\right)B}{T}\right)$$
 it depends on the composition

of the liquid ($x_A = x$ i $x_B = 1 - x$).

METHODS

The mathematical model describing the dependence of the composition of the vapour y resulting from the composition of the liquid x for the positive azeotrope (Eq. 1) (for example acetone-carbon disulphide) and the negative azeotrope (Eq. 2) (e.g., acetone chloroform) is as follows:

$$y = \frac{\alpha x}{1 + (\alpha - 1) \frac{x}{a_z}} \quad \text{for } x \in [0, a_z] \quad (1)$$

$$y = \frac{\alpha(x - a_z)}{1 + (\alpha - 1) \frac{x - a_z}{1 - a_z}} + a_z \quad \text{for } x \in [a_z, 1] \quad (2)$$

The volatility coefficient α and azeotrope concentration a_z were determined from (Eq. 1, 2) transforming into the linear forms (Eq. 3, 4):

$$\frac{x}{y} = \frac{1}{\alpha} + \left(1 - \frac{1}{\alpha}\right) \frac{x}{a_z} = ax + b \wedge x \in [0, a_z] \quad (3)$$

where: relative volatility $\alpha = 1/b$ and $a_z = (1 - b)/a$ for the positive azeotrope:

$$\frac{x - y}{x - 1} = \frac{\left(1 - \frac{1}{\alpha}\right)(y - a_z)}{(1 - a_z)} = cy + d \wedge x \in [a_z, 1] \quad (4)$$

where: for the negative azeotrope $a_z = -d/c$ and relative volatility $\alpha = 1/(1 - c - d)$.

The models (Eq. 1, 2) were used for calculating the differential distillation process for the material balance of the composition $A y dS = d(Sx)$ and $D = S_0 - S$:

$$\ln \frac{S}{S_0} = \int_{x_0}^x \frac{dx}{y-x} \quad (5)$$

Substitution of y (Eq. 1, 2) into (5) of the following relationship derived for the solution of the azeotrope with the minimum boiling range:

$$\frac{D}{S} = 1 - \left(\frac{x}{x_0} \right)^{\frac{1}{\alpha-1}} \cdot \left(\frac{a_z - x_0}{a_z - x} \right)^{\frac{\alpha}{\alpha-1}} \wedge x \in [0, a_z] \quad (6)$$

and for the solution of the azeotrope with the maximum boiling range:

$$\frac{D}{S} = 1 - \left(\frac{x - a_z}{x_0 - a_z} \right)^{\frac{1}{\alpha-1}} \cdot \left(\frac{1 - x_0}{1 - x} \right)^{\frac{\alpha}{\alpha-1}} \wedge x \in [a_z, 1] \quad (7)$$

On the basis of available literature data [3, 4], including a binary equilibrium system positive azeotrope, the parameters of Equation 1, i.e., the coefficient of volatility α , and azeotrope concentration a_z were determined. The results of calculations are provided in Table 1. An example of linear dependence $x/y = ax + b$ of the system (benzene – n-heptane under pressure of $P = 760$ mm Hg) was presented in Fig. 1.

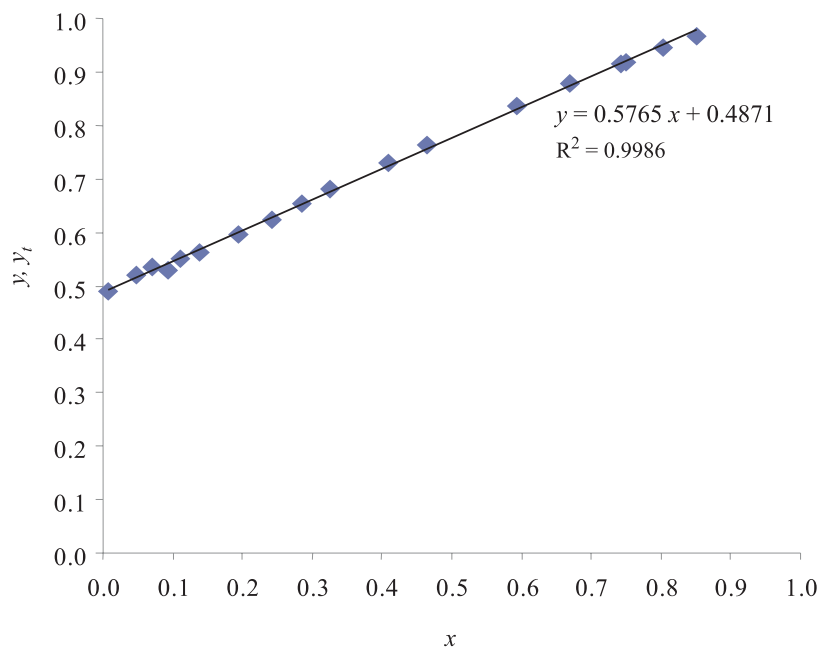


Fig. 1. Linear dependence of distillatory equilibrium $x/y = ax + b$ for benzene – n-heptane mixtures at a pressure $P = 760$ mm Hg.

The quantity of theoretical plates was shown in Fig. 2 and counted by the method reported in [5, 6] for equal compositions of the liquid, as received by the authors: $x_s = 0.22$, $x_w = 0.02$ and $x_D = a_z - 0.02$, thermal state of feed $e = (c\Delta T + r)/r = 1.11$ (the number e expresses the relationship of the quantity of heat necessary for the vaporization of 1 mole of feed S to the molar heat of the evaporation of feed S) as well as for the assumed optimal point of interception of operating lines: $x_z = (x_s + x_m)/2$ and $y_z = (ex_z - x_s)/(e - 1)$ calculated the value of the number of reflux ratio $R = (x_D - y_z)/(y_z - x_z)$ and $R_{min} = (x_D - y_m)/(y_m - x_m)$, where (x_m, y_m) is the point of interception of line e : $y = (ex - x_s)/(e - 1)$ with the equilibrium line: $y = x/(ax + b)$. The assumed coordinates (x_z, y_z) correspond to the values $R/R_{min} \in (3, 4)$ for a majority of equilibrium systems.

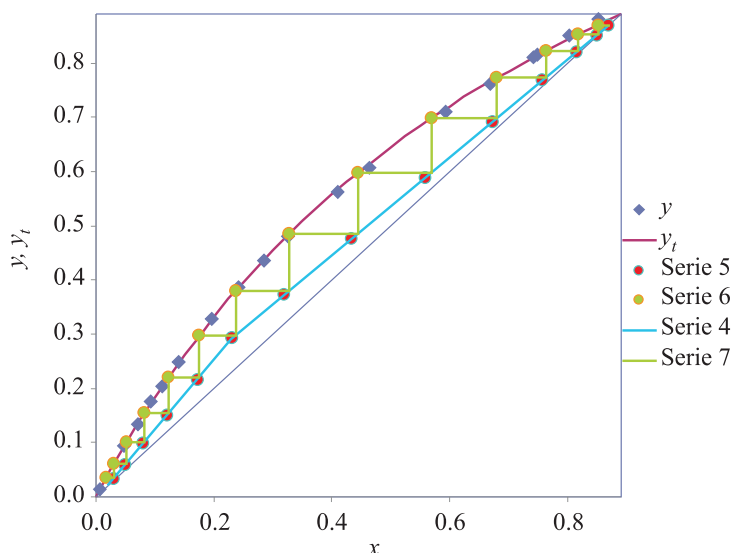


Fig. 2. Dependence of liquid composition from composition of steam $y = x/(ax + b)$ for benzene – n-heptane mixtures at a pressure $P = 760$ mm Hg with determined operating lines and plates of rectification column.

The example of distillation of mixtures (benzene – n-heptane at a pressure of $P = 760$ mm Hg) with triangles inscribed among the line of distillation equilibrium and the operating lines (Fig. 2), defining the equilibrium capacities for the respective plates of the distillation column. The following vertexes of triangles located on the line of equilibrium as well as on the operating lines were determined by means of a computerized method, after preparing the table of coordinates: (x_0, y_1) , (x_1, y_1) , (x_1, y_2) , (x_2, y_2) , (x_2, y_3) until (x_n, y_n) , where $x_n < x_w$. On the equilibrium line, the co-ordinates were calculated from the equation $x_n = b/(1/y_n - a)$. However, lying on the operating lines from the equations of these lines determined by the points (x_w, y_w) , (x_z, y_z) , as well as the point (x_D, y_D) ,

where $y_w = x_w$, $y_D = x_D$. The obtained results of calculation for 52 distillatory mixtures were collected in Table 1 and then shown in Fig. 3:

$$n = 23.3 \alpha^{-0.64} \tag{8}$$

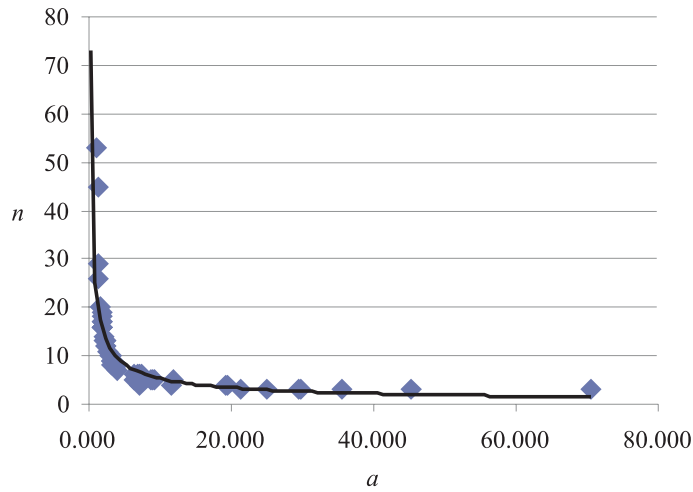


Fig. 3. Dependence of quantity of plates on relative volatility as received for concentrations: $x_w = 0.02$, $x_s = 0.22$ and $x_D = a_z - 0.02$ and for co-ordinates of a point of interception of operating lines $x_z = (x_s + x_m)/2$ and $y_z = (ex_z - x_s)/(e - 1)$, where: $n = 23.29\alpha^{-0.64}$, $R^2 = 0.862$, $a = \alpha$.

Moreover, for the process of differential distillation counted from the dependence (6) (D/S) for the concentration (as the process of rectification $x_w = 0.02$, $x_s = 0.22$) and put it in Table 1.

Table 1. Calculated values of mixtures.

#	Mixtures	Parametr									
		a_z	α	R_{min}	R	n	x_s	x_v	D/S		
1	Acetone-carbon tetrachloride (P = 300 mm Hg)	0.738	3.991	0.91	3.28	7	0.22	0.02	0.71		
2	Acetone-methanol (P = 760 mm Hg)	0.715	2.285	2.20	6.58	12	0.22	0.02	0.92		
3	Acetone-carbon tetrachloride (P = 760 mm Hg)	0.753	3.823	0.99	3.46	8	0.22	0.02	0.72		
4	Acetone-ethanol (P = 760 mm Hg)	0.817	3.280	1.36	4.29	9	0.22	0.02	0.77		
5	Acetone-benzene (P = 760 mm Hg)	0.813	3.092	1.48	4.60	9	0.22	0.02	0.79		
6	Acetone-water (P = 760 mm Hg)	0.883	29.556	0.07	1.35	3	0.22	0.02	0.30		
7	Ethanol-water (P = 95 mm Hg)	0.721	7.467	0.37	2.05	5	0.22	0.02	0.53		
8	Ethanol-water (P = 380 mm Hg)	0.724	8.993	0.29	1.86	5	0.22	0.02	0.49		
9	Ethanol-water (P = 760 mm Hg)	0.681	9.303	0.26	1.80	5	0.22	0.02	0.50		
10	Carbon disulfide-carbon tetrachloride (P = 760 mm Hg)	0.961	2.908	1.94	5.56	10	0.22	0.02	0.80		
11	Chloroform-methanol (P = 757 mm Hg)	0.652	3.221	1.10	3.85	8	0.22	0.02	0.80		
12	Methanol-toluene (P = 760 mm Hg)	0.849	25.129	0.09	1.38	3	0.22	0.02	0.32		
13	Carbon tetrachloride-ethanol (P = 745 mm Hg)	0.606	6.296	0.38	2.13	5	0.22	0.02	0.61		
14	Water - n-butanol (P = 767 mm Hg)	0.806	7.349	0.43	2.15	5	0.22	0.02	0.51		
15	Cyclohexane-toluene (P = 760 mm Hg)	0.955	3.112	1.73	5.06	10	0.22	0.02	0.77		
16	Cyclohexane-aniline (P = 760 mm Hg)	0.999	70.403	0.02	1.22	3	0.22	0.02	0.23		
17	n-Hexane - n-heptane (P = 760 mm Hg)	1.057	2.330	3.16	8.43	13	0.22	0.02	0.89		
18	n-Hexane-benzene (P = 735 mm Hg)	0.821	2.190	2.75	7.81	13	0.22	0.02	0.92		
19	Methanol-water (P = 760 mm Hg)	0.937	6.379	0.60	2.49	6	0.22	0.02	0.52		
20	Ethanol-benzene (P = 750 mm Hg)	0.436	7.124	0.17	1.83	4	0.22	0.02	0.68		
21	Carbon tetrachloride-toluene (P = 762 mm Hg)	1.005	2.370	2.91	7.88	12	0.22	0.02	0.88		
22	Carbon tetrachloride-cyclohexane (P = 760 mm Hg)	0.903	1.170	22.79	172.03	53	0.22	0.02	1.00		
23	Carbon tetrachloride-benzene (P = 760 mm Hg)	0.731	1.198	15.67	106.02	45	0.22	0.02	1.00		
24	Benzene-acetic acid (P = 760 mm Hg)	0.868	7.076	0.49	2.26	6	0.22	0.02	0.51		
25	Benzene - n-heptane (P = 760 mm Hg)	0.890	2.053	3.41	9.39	14	0.22	0.02	0.94		
26	Benzene-toluene (P = 760 mm Hg)	1.014	2.382	2.91	7.86	13	0.22	0.02	0.88		

Table 1 continued

27	Benzene-cyclohexane (P = 759 mm Hg)	0.501	1.330	6.15	32.01	26	0.22	0.02	1.00
28	Ethanol-amy alcohol (P = 760 mm Hg)	0.996	8.686	0.43	2.10	5	0.22	0.02	0.44
29	Ethanol – n-butanol (P = 760 mm Hg)	1.057	3.952	1.32	4.06	8	0.22	0.02	0.67
30	Methanol-benzene (P = 760 mm Hg)	0.606	21.444	0.05	1.37	3	0.22	0.02	0.43
31	Methanol-ethanol (P = 760 mm Hg)	0.973	1.744	5.39	14.70	18	0.22	0.02	0.98
32	Cyclohexane – n-heptane (P = 760 mm Hg)	0.991	1.920	4.39	11.79	16	0.22	0.02	0.95
33	Benzene-aniline (P = 760 mm Hg)	1.032	19.564	0.16	1.51	4	0.22	0.02	0.30
34	n-Heptane-toluene (P = 760 mm Hg)	0.740	1.765	3.95	11.58	17	0.22	0.02	0.98
35	Water-acetic acid (P = 760 mm Hg)	0.955	1.805	4.87	13.27	17	0.22	0.02	0.97
36	Acetone-methanol (P = 100 mm Hg)	0.840	2.595	2.06	5.98	11	0.22	0.02	0.86
37	Acetone-water (P = 200 mm Hg)	0.903	45.177	0.04	1.27	3	0.22	0.02	0.27
38	Acetone-water (P = 350 mm Hg)	0.916	35.512	0.06	1.31	3	0.22	0.02	0.28
39	Methanol – n-butanol (P = 760 mm Hg)	0.992	11.715	0.29	1.80	5	0.22	0.02	0.38
40	Methanol-amy alcohol (P = 760 mm Hg)	1.002	19.311	0.16	1.51	4	0.22	0.02	0.31
41	Methanol-water (P = 200 mm Hg)	0.949	7.694	0.48	2.21	5	0.22	0.02	0.47
42	Methanol-water (P = 350 mm Hg)	0.937	7.297	0.50	2.28	6	0.22	0.02	0.49
43	Methanol-water (P = 500 mm Hg)	0.929	6.958	0.53	2.34	6	0.22	0.02	0.50
44	Ethanol-water (P = 50 mm Hg)	0.758	7.533	0.39	2.07	5	0.22	0.02	0.52
45	Ethanol-water (P = 190 mm Hg)	0.646	11.482	0.18	1.64	4	0.22	0.02	0.48
46	Benzene-aniline (P = 350 mm Hg)	1.036	29.624	0.09	1.37	3	0.22	0.02	0.27
47	Water-acetic acid (P = 100 mm Hg)	1.000	1.393	10.78	33.53	29	0.22	0.02	1.00
48	Water-acetic acid (P = 125 mm Hg)	0.896	1.817	4.49	12.41	16	0.22	0.02	0.97
49	Water-acetic acid (P = 200 mm Hg)	0.988	1.601	6.85	19.14	20	0.22	0.02	0.99
50	Water-acetic acid (P = 250 mm Hg)	0.933	1.836	4.57	12.48	16	0.22	0.02	0.97
51	Water-acetic acid (P = 350 mm Hg)	1.009	1.719	5.80	15.76	19	0.22	0.02	0.98
52	Water-acetic acid (P = 500 mm Hg)	0.980	1.881	4.54	12.25	16	0.22	0.02	0.96

RESULTS AND DISCUSSION

52 distillatory equilibria were calculated with the help of dependence (3) and the coefficients of correlation were obtained from $R^2 = 0,945$ (carbon tetrachloride – benzene, $P = 760$ mm Hg) to $R^2 = 0.999$ (methanol – amyl alcohol, $P = 760$ mm Hg). On this basis of the process distillation differential was calculated (D/S with dependence (6)). Moreover, dependence of the quantity of plates in a column was determined from the relative volatility of the respective distillatory rectification mixtures (dependence (8)) for the optimum position of the operating lines (in half of a section of line $y = (ex - x_s)/(e - 1)$) contained among the diagonal $y = x$ and the equilibrium line:

$$y = \frac{\alpha x}{1 + (\alpha - 1) \frac{x}{a_z}} \quad (9)$$

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