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¹ Wydział Technologii i Inżynierii Chemicznej, Uniwersytet Technologiczno-Przyrodniczy, Bydgoszcz² Wojewódzka Stacja Sanitarno-Epidemiologiczna, Bydgoszcz**Mathematical model of batch distillation and rectification for positive and negative azeotropes****Introduction**

Azeotropes occur when a real solution reveals significant deviations from *Raoult's* law. There are two types of azeotropes: minimum boiling azeotrope and maximum boiling azeotrope. Each azeotrope has a characteristic boiling point. The boiling point of an azeotrope is either less than the boiling point temperatures of any of its constituents (a positive azeotrope), or greater than the boiling point of any of its constituents (a negative azeotrope). The first is encountered as a result of large positive deviation from *Raoult's* law when the total vapor pressure over a liquid mixture is higher than the vapor pressure of pure, more volatile component at a given temperature. Benzene-ethanol, water-ethanol or benzene-methanol are examples of positive azeotropes. Negative azeotropes will appear for reverse situation, i.e. when the total vapor pressure over a liquid mixture is lower than that for pure, less volatile component at a given temperature. Water-hydrochloric acid, water-nitric acid or acetone-chloroform systems can be classified as negative azeotropes. Interestingly, positive azeotrope happens more often than the negative one [Anderson and Doherty, 1984; Rousseau and Fair, 1987; Pigoń and Ruziewicz, 2013; Hasan et al., 2013; Billal et al., 2014].

In a process of azeotrope rectification separation agent (entrainer) affect the relative volatility of the azeotrope constituents of the mixture. More precisely, separation agent forms such an azeotrope with the component or components of the initial mixture that separation of components with boiling points close to each other or forming other azeotropes take place. If in the new formatted azeotrope systems a region of limited miscibility arises separation of components becomes much easier [Ciborowski, 1955; Ziółkowski, 1978; Bandrowski and Troniewski, 1980].

Sobczak and Korpala [2009], Sobczak et al. [2010], Sobczak and Ringel [2013] described distillation equilibria for both positive and negative azeotropes using the following linear relationships after determining the relative volatility (α) and concentrations of azeotropes (a_z) for $n = 152$ systems:

1. for $0 < x < a_z$, $y > x$ and $\alpha > 1$:

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

2. for $0 < x < a_z$, $y < x$ and $\alpha < 1$:

$$\frac{y}{x} = \alpha + (1 - \alpha) \frac{y}{a_z} \quad (2)$$

3. for $a_z < x < 1$, $y > x$ and $\alpha > 1$:

$$\frac{y-x}{1-x} = \left(\frac{1-\frac{1}{\alpha}}{1-a_z} \right) (y-a_z) \quad (3)$$

4. for $a_z < x < 1$, $y < x$ and $\alpha < 1$:

$$\frac{x-y}{1-y} = \left(\frac{1-\alpha}{1-a_z} \right) (x-a_z) \quad (4)$$

where: x, y are concentrations of the A - comp. in the liquid and vapour.**Derivation of mathematical model**

Differential balance for the A component stripped in a batch rectification process expressed as $d(Sx^*) = y_D dS$, after integration gives the following form:

$$\int_{S_0}^S \frac{dS}{S} = \int_{x_0}^{x_w} \frac{dx^*}{y_D - x^*} \quad (5)$$

For further calculations an operating line was drawn connecting points corresponding to composition of boiling liquid (x^*, y^*) on the equilib-

rium curve, and composition of the top product (x_D, y_D) located on diagonal $y = x$ ($x_D = y_D$)

$$y - y^* = \frac{R}{R+1} (x - x^*) \quad (6)$$

Making use of the condition that $x = y_D$ and $y = y_D$, Eq. (6) can be rearranged into a form enabling integral (5) to be solved:

$$y_D - x^* = (R+1)(y^* - x^*) \quad (7)$$

Substituting Eq. (7) into the integral (5) yields

$$\ln \frac{S}{S_0} = \frac{1}{R+1} \int_{x_0}^{x_w} \frac{dx^*}{y^* - x^*} \quad (8)$$

For $y_A > x_A$; $x^* = x_A = x$; $y^* = y_A = y$; $dx^*/(y^* - x^*) = dx/(y-x)$ and for $y_A < x_A$; $x^* = x_B = 1-x$; $y^* = y_B = 1-y$; $dx^*/(y^* - x^*) = -dx/(x-y)$ the following integral is obtained

$$\ln \frac{S}{S_0} = \frac{1}{R+1} \int_{x_0}^{x_w} \frac{dx}{y-x} \quad (9)$$

and can be solved after substituting the equilibrium relationships $y = f(x)$ according to Eqs. (1) – (4) derived by the author of the present paper [Sobczak and Korpala, 2009; Sobczak et al., 2010; Sobczak and Ringel, 2013]. Integral (9) has been solved using the equilibrium relationships Eqs (1) – (4) to get the following model expressions for rectification process carried out at a constant reflux ration $R = L/D$, as well as for a batch process (at $R = 0$):

$$\text{for } x < a_z \text{ and } \alpha > 1 \quad \frac{S}{S_0} = \left(\frac{x}{x_0} \right)^{\frac{1}{(\alpha-1)(R+1)}} \left(\frac{a_z - x_0}{a_z - x} \right)^{\frac{\alpha}{(\alpha-1)(R+1)}} \quad (10)$$

$$x < a_z \text{ and } \alpha < 1 \quad \alpha_z = 1/\alpha \quad \frac{S}{S_0} = \left(\frac{x - a_z}{x_0 - a_z} \right)^{\frac{1}{(\alpha-1)(R+1)}} \left(\frac{x_0}{x} \right)^{\frac{\alpha_z}{(\alpha-1)(R+1)}} \quad (11)$$

$$\text{for } x > a_z \text{ and } \alpha > 1 \quad \frac{S}{S_0} = \left(\frac{x - a_z}{x_0 - a_z} \right)^{\frac{1}{(\alpha-1)(R+1)}} \left(\frac{1 - x_0}{1 - x} \right)^{\frac{\alpha}{(\alpha-1)(R+1)}} \quad (12)$$

$$x > a_z \text{ and } \alpha < 1 \quad \alpha_z = 1/\alpha \quad \frac{S}{S_0} = \left(\frac{x-1}{x_0-1} \right)^{\frac{1}{(\alpha-1)(R+1)}} \left(\frac{a_z - x_0}{a_z - x} \right)^{\frac{\alpha_z}{(\alpha-1)(R+1)}} \quad (13)$$

After substitution of parameters $t = f(x)$ and $k = f(x_0)$ which determine concentration of the boiling liquid [; Sobczak and Ringel, 2013] into Eqs (10) – (13) we get

$$\text{for } x < a_z \text{ and } \alpha > 1 \quad \frac{x}{x_0} = t \quad \frac{x_0}{a_z} = k \quad (14)$$

$$\text{for } x < a_z \text{ and } \alpha < 1 \quad \frac{x - a_z}{x_0 - a_z} = t \quad \frac{x_0}{a_z} = 1 - k \quad (15)$$

$$\text{for } x > a_z \text{ and } \alpha > 1 \quad \frac{x - a_z}{x_0 - a_z} = t \quad \frac{x_0 - a_z}{1 - a_z} = k \quad (16)$$

$$\text{for } x > a_z \text{ and } \alpha < 1 \quad \frac{x-1}{x_0-1} = t \quad \frac{x_0 - a_z}{1 - a_z} = 1 - k \quad (17)$$

The universal model of batch distillation and rectification processes of positive and negative azeotropes was obtained

$$\frac{S}{S_0} = t^{\frac{1}{(\alpha-1)(R+1)}} \left(\frac{1-k}{1-kt} \right)^{\frac{\alpha_z}{(\alpha-1)(R+1)}} \quad (18)$$

$$t = \frac{x - x_{\text{lim}}}{x_0 - x_{\text{lim}}} \quad (19)$$

where: $x_{lim} \rightarrow \{0, a_z, a_z^{-1}\}$ if $S/S_0 \rightarrow 0$ Eqs (10) – (13)

$a_z = \alpha$ when $\alpha > 1$ and $a_z = 1/\alpha$ when $\alpha < 1$

$D/S_0 = 1 - S/S_0$ is degree of distillate removed from the feed, S_0

In order to perform a comparative analysis of rectification process for positive and negative azeotropes accomplished within the concentration ranges $0 < x < a_z$ and $a_z < x < 1$ a parameter related to feed concentration, $k = 0.5$ (Eqs (14) – (17)) was assumed. The reflux ratio, R , can be determined from the slope of the operating line (6):

$$\frac{R}{R+1} = \frac{y_D - y^*}{x_D - x^*} \quad (20)$$

for $0 < x < a_z$ and $\alpha > 1$; $y^* = y_A = y$, $x^* = x_A = x$, $x_D = y_D \rightarrow a_z$ when $R \rightarrow R_{lim}$ and limiting reflux ratio, R_{lim} , is taken from

$$\frac{R_{lim}}{R_{lim}+1} = \frac{a_z - y}{a_z - x} \quad (21)$$

Taking into account the phase equilibrium $y = f(x)$ (Eq. (1)), and $x = x_0$ we get

$$\frac{1}{R_{lim}} = (\alpha - 1) \left(\frac{x_0}{a_z} \right) = (\alpha - 1)k \quad (22)$$

where $k = \frac{x_0}{a_z}$ (Eq. (14)).

for $0 < x < a_z$ and $\alpha < 1$ ($y^* = y_B$) ($x^* = x_B$) ($1 - a_z < x_B < 1$) we have: $(x_D)_B = (y_D)_B \rightarrow 1$ when $R \rightarrow R_{lim}$ and Eq. (20) assumes the following form:

$$\frac{R_{lim}}{R_{lim}+1} = \frac{1 - y_B}{1 - x_B} = \frac{y}{x} \quad (23)$$

Taking into account the phase equilibrium $y = f(x)$, Eq. (2), in Eq. (23) and $x = x_0$ we get a minimum value of the reflux ratio, R_{lim} .

$$\frac{1}{R_{lim}} = \left(\frac{1}{\alpha} - 1 \right) \left(1 - \frac{x_0}{a_z} \right) = (\alpha_z - 1)k \quad (24)$$

where: $\alpha_z = \frac{1}{\alpha}$, $k = 1 - \frac{x_0}{a_z}$ (Eq. (15)).

for $a_z < x < 1$ and $\alpha > 1$ we have $y^* = y_A$, $x^* = x_A$ and $x_D = y_D \rightarrow 1$, when $R \rightarrow R_{lim}$ Eq. (20) assumes the following form:

$$\frac{R_{lim}}{R_{lim}+1} = \frac{1 - y}{1 - x} \quad (25)$$

and the minimum reflux ratio for $y = f(x)$, Eq. (3) and $x = x_0$ equals

$$\frac{1}{R_{lim}} = (\alpha - 1) \left(\frac{x_0 - a_z}{1 - a_z} \right) = (\alpha - 1)k \quad (26)$$

where: $k = \frac{x_0 - a_z}{1 - a_z}$ (Eq. (16)).

for $a_z < x < 1$ and $\alpha < 1$ we have: $(y^* = y_B) > (x^* = x_B)$ $0 < x_B < 1 - a_z$ $(x_D)_B = (y_D)_B \rightarrow 1 - a_z$ when $R \rightarrow R_{lim}$ and Eq. (20) assumes the following form:

$$\frac{R_{lim}}{R_{lim}+1} = \frac{1 - a_z - y_B}{1 - a_z - x_B} = \frac{y - a_z}{x - a_z} \quad (27)$$

The minimum value R_{lim} for $y = f(x)$ (Eq. (4)) and $x = x_0$ yields:

$$\frac{1}{R_{lim}} = \left(\frac{1}{\alpha} - 1 \right) \left(1 - \frac{x_0 - a_z}{1 - a_z} \right) = (\alpha_z - 1)k \quad (28)$$

where: $\alpha_z = \frac{1}{\alpha}$, $k = 1 - \frac{x_0 - a_z}{1 - a_z}$ (Eq. (17)).

For modelling batch rectification process a constant value of the reflux ratio equal to $R = 0.9R_{lim}$ was assumed.

Making use of four similar values of the relative volatilities for the positive as well as negative azeotropes (2.17 $< \alpha_z < 2.27$) listed in Tab. 1 and the reflux ratio $R = 0.9R_{lim}$, values of $(S/S_0)_{rek}$ from Eq. (18) have been calculated for $0.04 \leq t \leq 0.96$ and the results compared with S/S_0 estimated from Eq. (18) assuming batch distillation process ($R = 0$), cf. Fig. 1. Then, based on four different values of the equivalent volatility (1.754 $< \alpha_z < 2.28$) listed in Tab. 2 for positive and negative azeotropes as well as the reflux ratio $R = 0.9R_{lim}$ and again using parameter t (0.04 $\leq t \leq 0.96$) values of $(S/S_0)_{rek}$ for rectification process and S/S_0 for batch distillation process ($R = 0$) from Eq. (18) have been calculated.

Tab. 1. Parameters of batch rectification process of azeotropes with similar values of α_z ($\alpha_z = 1/\alpha$ for $\alpha < 1$ and $\alpha_z = \alpha$ for $\alpha > 1$) and $k = 1/2$

x_0	R_{lim}	R	α	a_z	α_z	P [kPa]
x_0 (Eq.14) = 0.48 $0 < x_1 < a_z$	1.639	1.475	2.22	0.96	2.22	101.32 (1) acetone-ethyl acetate
x_0 (15) = 0.375 $0 < x_2 < a_z$	1.704	1.533	0.46	0.75	2.174	101.32 (2) methanol-dietyloamine
x_0 (16) = 0.79 $a_z < x_3 < 1$	1.613	1.452	2.24	0.58	2.24	9.33 (3) water-formic acid
x_0 (17) = 0.915 $a_z < x_4 < 1$	1.571	1.414	0.44	0.83	2.273	79.99 (4) NN-dimethylformamide-1 chloro-2-ethylhexane

Tab. 2. Parameters of batch rectification process of azeotropes with different values of α_z ($\alpha_z = 1/\alpha$ for $\alpha < 1$ and $\alpha_z = \alpha$ for $\alpha > 1$) and $k = 1/2$

x_0	R_{lim}	R	α	a_z	α_z	P [kPa]
x_0 (Eq.14) = 0.48 $0 < x_1 < a_z$	2.5	2.25	1.8	0.96	1.8	101.32 water-acetic acid
x_0 (Eq.15) = 0.21 $0 < x_2 < a_z$	2.651	2.386	0.57	0.42	1.754	101.32 water-formic acid
x_0 (Eq.16) = 0.77 $a_z < x_3 < 1$	1.563	1.406	2.28	0.54	2.28	26.66 water-formic acid
x_0 (Eq.17) = 0.83 $a_z < x_4 < 1$	1.774	1.596	0.47	0.66	2.128	101.32 methyl acetate-methanol

The obtained results are presented in Fig. 2 and used in determining the dependences between the concentration of the boiling liquid $x_1 \div x_4$ and that of distillate $x_{D1} \div x_{D4}$ or $x_{Drek1} \div x_{Drek4}$ on t as follows:

$$1) \text{ for } x < a_z \text{ and } \alpha > 1 \quad x_1 = t x_0$$

$$x_{Drek1} = \frac{x_0 - x_1(S/S_0)_{rek1}}{1 - (S/S_0)_{rek1}} \quad x_{D1} = \frac{x_0 - x_1(S/S_0)_1}{1 - (S/S_0)_1} \quad (29)$$

$$2) \text{ for } x < a_z \text{ and } \alpha < 1 \quad x_2 = t(x_0 - a_z) + a_z$$

$$x_{Drek2} = \frac{x_0 - x_2(S/S_0)_{rek2}}{1 - (S/S_0)_{rek2}} \quad x_{D2} = \frac{x_0 - x_2(S/S_0)_2}{1 - (S/S_0)_2} \quad (30)$$

$$3) \text{ for } x > a_z \text{ and } \alpha > 1 \quad x_3 = t(x_0 - a_z) + a_z$$

$$x_{Drek3} = \frac{x_0 - x_3(S/S_0)_{rek3}}{1 - (S/S_0)_{rek3}} \quad x_{D3} = \frac{x_0 - x_3(S/S_0)_3}{1 - (S/S_0)_3} \quad (31)$$

$$4) \text{ for } x > a_z \text{ and } \alpha < 1 \quad x_4 = t(x_0 - 1) + 1$$

$$x_{Drek4} = \frac{x_0 - x_4(S/S_0)_{rek4}}{1 - (S/S_0)_{rek4}} \quad x_{D4} = \frac{x_0 - x_4(S/S_0)_4}{1 - (S/S_0)_4} \quad (32)$$

where: x_{Drek} and x_D are concentrations of distillate for the reflux ratio $R = L/D$ and $R = 0$

The results are compared on Figs (3) – (6)

Discussion

Mathematical models of batch distillation or rectification for positive and negative azeotropes are similar and have been derived based on considerations for vapour-liquid phase equilibria (1) - (4). Parameters k and t (Eqs (14) - (17)) that "steer" batch distillation process [Sobczak and Ringel, 2013] control also batch rectification process.

It is interesting that for all azeotropes four models of rectification and distillation processes (Eqs (10) - (13)) can be substituted by two models, 1) for $x < a_z$ (Eq. (10)) and 2) for $x > a_z$ (Eq. (12)) and after introducing reduced parameters $0 < k < 1$ and $0 < t < 1$ which determine the initial ($x_F = x_0$) and final concentrations ($x_w = x$) of azeotrope subjected to batch distillation or rectification processes and using the equivalent volatility $\alpha_z = \alpha$ when $\alpha > 1$ or $\alpha_z = 1/\alpha$ when $\alpha < 1$ one universal model can be obtained (Eqs. 18), which enables optimal design and control of the batch distillation and rectification processes.

Designated for rectification and distillation differential process dependencies of the concentration solution $x = f(t)$ and distillate $x_{Drek} = f(t)$, $x_D = f(t)$ of the t parameter are the growing functions of the S/S_0 for the relative volatility $\alpha > 1$, while for $\alpha < 1$ are the decreasing functions of the S/S_0 and satisfy the condition:

$$x_{Drek} > x_D > x \text{ for } \alpha > 1 \text{ and } x_{Drek} < x_D < x \text{ for } \alpha < 1$$

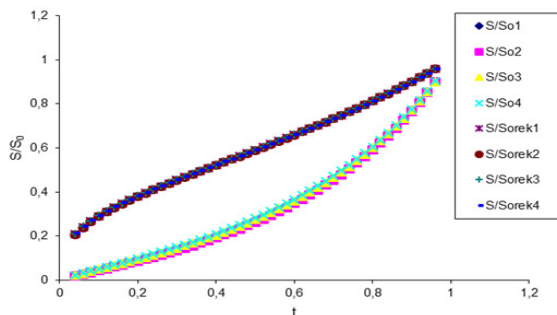


Fig. 1. Comparison of a dependence $(S/S_0)_{rect}$ on parameter $t = 0.04-0.96$ (Eq. 18) obtained for rectification process at constant reflux ratio $R = 0.9R_{lim}$ with a dependence of S/S_0 resulting for batch distillation process at $R = 0$ based on parameters listed in Table 1 featuring four types of azeotropes of similar equivalent volatility ($2.17 < \alpha_z < 2.27$) ($\alpha_z = \alpha$ for $\alpha > 1$ and $\alpha_z = 1/\alpha$ for $\alpha < 1$) for $x < \alpha_z$ and for $x > \alpha_z$

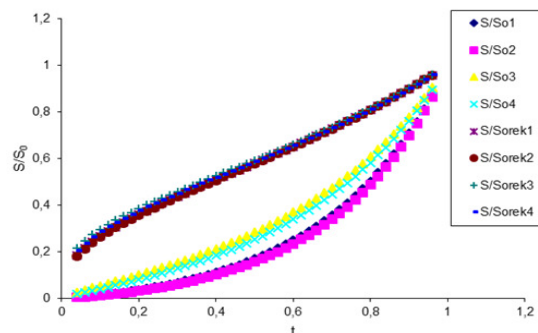


Fig. 2. Comparison of a dependence $(S/S_0)_{rect}$ on parameter $t = 0.04-0.96$ (Eq. 18) obtained for rectification process at constant reflux ratio $R = 0.9R_{lim}$ with a dependence of S/S_0 resulting for batch distillation process at $R = 0$ (determining concentration of boiling solution) based on parameters listed in Table 2 featuring four types of azeotropes of similar equivalent volatility ($1.754 < \alpha_z < 2.28$) ($\alpha_z = \alpha$ for $\alpha > 1$ and $\alpha_z = 1/\alpha$ for $\alpha < 1$) for $x < \alpha_z$ and for $x > \alpha_z$

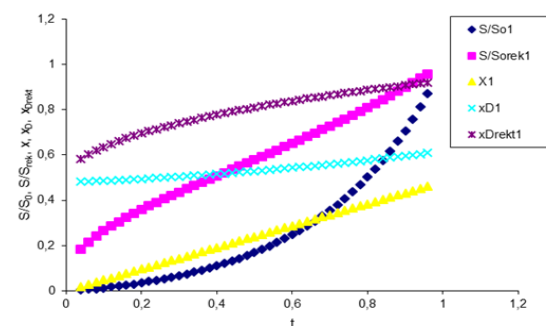


Fig. 3. Dependency statement of the parameter t : concentration $x_j = t \cdot x_0$ solution and distillate, x_{Drekt1} , x_{D1} (Eq. 29) and the relation $(S/S_0)_{rect1}$ and S/S_{0j} (Eq. 18) on the basis of the data contained in Table 2: water-acetic acid ($P = 101,32$ kPa, $x_0 = 0,48$, $\alpha_z = \alpha = 1,80$; $R = 0,90R_{lim} = 2,25$; $x_j < \alpha_z = 0,96$)

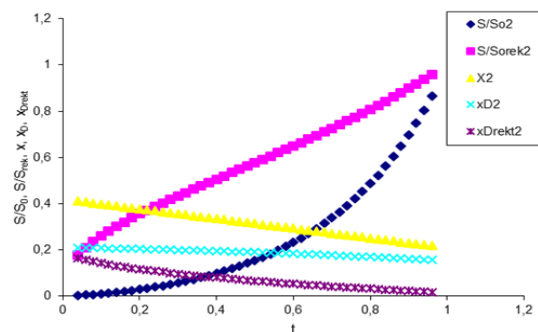


Fig. 4. The comparison of dependency to the parameter t : solution concentration $x_2 = t(x_0 \cdot \alpha_z) + \alpha_z = 0,42-0,21t$ and distillate x_{Drekt2} , x_{D2} (Eq. 30) and the relation $(S/S_0)_{rek2}$ and S/S_{02} (Eq. 18) on the basis of the data in Table 2 rectification parameters: water-formic acid ($P = 101,32$ kPa, $x_0 = 0,21$, $\alpha_z = 1/\alpha = 1,754$; $R = 0,90 R_{lim} = 2,386$; $x_2 < \alpha_z = 0,42$).

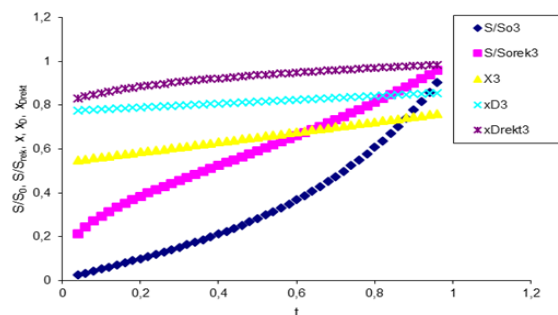


Fig. 5. Dependency statement of the parameter $t = 0,04-0,96$ concentration solution $x_3 = t(x_0 \cdot \alpha_z) + \alpha_z = 0,23+0,54$ and distillate, x_{Drekt3} , x_{D3} (Eq. 31) dependencies $(S/S_0)_{rek3}$ and S/S_{03} (Eq. 18); included in Table 2 rectification parameters of water-formic acid ($P = 26,66$ kPa, $x_0 = 0,77$, $\alpha_z = \alpha = 2,28$, $R = 0,90R_{lim} = 1,40625$; $x_3 > \alpha_z = 0,54$).

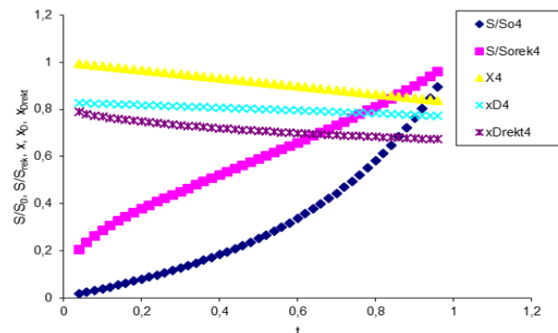


Fig. 6. Dependency statement of the concentration solution $x_4 = t(x_0 - 1) + 1 = 1 - 0,17t$ and the distillate x_{Drekt4} , x_{D4} (Eq. 32) and the relation $(S/S_0)_{rek4}$ and S/S_{04} (Eq. 18) from the parameter t (included in Table 2 the rectification parameters: methyl acetate-methanol ($P = 101,32$ kPa; $x_0 = 0,83$; $\alpha_z = 1/\alpha = 2,128$; $R = 0,90 R_{lim} = 1,596$ $x_4 > \alpha_z = 0,66$).

The limit value of the reflux R_{lim} determined for the four types of azeotropes (Eqs (22), (24), (26), (28)) replaced with one model (Eq. (33)) using the k parameter (Eqs (14) – (17)) and the volatility replacement α_z defined for the differential distillation model:

$$R_{lim} = \frac{1}{k(\alpha_z - 1)} \quad (33)$$

LITERATURE

- Anderson N.J., Doherty M.F., (1984). An approximate model for binary azeotropic distillation design. *Chem. Eng. Sci.*, 39, 11-19. DOI: 10.1016/0009-2509(84)80125-6
- Bandrowski J., Troniewski L., (1980). *Distillation and rectification* (in Polish). PWN, Warszawa
- Billal S.F., Elamin, I.H.M., Mustafa H.M., (2014). Separation of azeotropes by shifting the azeotropic composition. *J. Appl. Ind. Sci.*, 2(3), 110-115.
- Ciborowski J., (1955). *Chemical engineering* (in Polish). WNT, Warszawa, 704-708
- Hasan, S.U., Mahajani S., Malik R.K., (2013). *A conceptual design algorithm for single-feed hybrid reactive distillation column involving azeotropic systems*. [in:] Kraslawski A., Turunen I., (Editors). Proc. of the 23rd European Symposium on Computer Aided Process Engineering - ESCAPE 23, June 9-12, 2013, Lappeenranta, Finland, Elsevier, 313-318
- Misbah C., (1986). The Mullins-Sekerka instability in directional solidification of quasi-azeotropes. *J. Physique*, 47 (6), 1077-1090. DOI: 10.1051/jphys:019860047060107700
- Pigoń K., Ruziewicz Z., (2013). *Physical chemistry* (in Polish). PWN, Warszawa
- Rousseau R.W., Fair J.R., (1987). *Handbook of separation process technology*. Wiley-IEEE, 261-262
- Sobczak E., Korpala W., (2009). Separation of azeotropic binary mixtures applying differential distillation and rectification process. *Ars Separatoria Acta* 7, 61-68
- Sobczak E., Ringel T., Kasprzak J., (2010). Mathematical model of distillation equilibrium and its application in designing of distillation and rectification (in Polish). *Inż. Ap. Chem.* 49(1), 99-100
- Sobczak E., Ringel T., (2013). Elaboration of mathematical models of positive and negative azeotropic systems and their application in distillation process design (in Polish). *Inż. Ap. Chem.*, 52(1), 11-13
- Ziółkowski Z., (1978). *Distillation and rectification in chemical industry* (in Polish). WNT, Warszawa 1978