

## HEAT AND MASS TRANSFER IN RECTIFICATION OF BINARY MIXTURES AT TURBULENT VAPOUR FLOW

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Theoretical analysis of the heat and mass transfer mechanism in rectification of binary mixtures was made at the use of earlier obtained relations for the heat and mass transfer coefficients. Theoretical results were applied to the mixture methanol-water and have revealed that the effect of simultaneous heat transfer on mass transfer is insignificant and is little affected by both the reflux ratio and hydrodynamic conditions.

In recent twenty years a number of theoretical and experimental studies have been published regarding the mechanism of mass transfer in rectification of binary mixtures. The increased interest in this problem was due to published disagreement of results obtained by evaluation of experimental data with conclusions resulting from the present theoretical models<sup>1,2</sup>.

As a probable cause of the quoted discrepancies has been considered the fact that in rectification a mass transfer between the vapour and liquid phases takes place not only due to diffusion but also due to heat transfer which is the necessary consequence of temperature differences between both phases. This phenomenon is called in literature "thermal distillation". Already the first analysis of experimental results has pointed to the fact that the effect of thermal distillation cannot explain the mentioned discrepancies in the whole range and so the effect of surface tension has been considered<sup>3</sup> as another feasible reason which affects both the magnitude of interfacial area and mechanism of its renewal.

In theoretical analysis of this problem the authors started with material and heat balances which they arranged variously so as to obtain the dependence of efficiency on mixture composition. Conditions of total reflux are used advantageously especially in experimental studies which is considerably simplifying and making the experimental results more accurate as well as simplifies the corresponding balance relations. Another significant simplification is reached by the assumption that both phases during the flow through the unit are on the saturation point. This assumption as has been demonstrated by some experimental results<sup>4,13,14</sup>, holds with a high accuracy for the liquid phase.

Liang and Smith<sup>4</sup> started in the theoretical analysis from the overall material balance, balance of the lower boiling component and heat balance. The resulting relation is expressing the local ratio of total number of transfer units  $N_T$  to the number of transfer units reached by dif-

fusion  $N_D$  for a concrete mixture composition. The ratio is given in dependence on mixture composition for different values ( $\alpha/k$ ). It is interesting that for both studied mixtures (methanol-water and cyclohexane-toluene) the effect of thermal distillation in the region of lower ratios ( $\alpha/k < \text{about } 20$ ) is even negative. This region perhaps best corresponds to values of this ratio for a concrete mixture. Experimental results pointed to a significant effect of thermal distillation. For the methanol-water system the maximum value of ratio ( $N_T/N_D$ ) is equal to 3.6 and corresponds to the mixture composition  $y \approx 0.8$ . From theoretical relation of these authors results so high value after reaching the ratio ( $\alpha/k \approx 900$ ) which is an unrealistically high one.

Ruckenstein and Smigelski<sup>5</sup> have obtained the relation which also points to a significant effect of thermal distillation. They even state in another study<sup>6</sup> that they reached a good agreement of the theoretical and experimental results, when only the effect of thermal distillation was considered and this even in the case when a significant effect of Marangoni effect could be expected. In another study<sup>7</sup> the same authors state that experimental results are in a good agreement with both the classical diffusion and thermal theory and that their selection depends only on the position of maximum efficiency, which however, is not profound. Ruckenstein has analysed this problem by use of the penetration theory<sup>8</sup> and has proposed a model on how to know on basis of certain criteria which phenomenon is significant.

Moens<sup>9,10</sup> has reached on basis of own experiments the conclusion that the obtained number of transfer units is solely a function of surface tension (so-called stabilisation index) and that the effect of thermal distillation is negligible.

Maljusov and coworkers<sup>11</sup> have derived a formal relation, from which results that the ratio of mass transfer coefficient in rectification and absorption is identical in both phases and is equal to the ratio of total mass flux to the diffusion flux.

Kayihan and coworkers<sup>12,13</sup> have modelled simultaneous heat and mass transfer in rectification by use of three parameters (two mass transfer coefficients and ratio of interfacial area for mass and heat transfer), which must be determined experimentally. They have found experimentally that in a column with a wetted wall and with the system methanol-water the liquid phase is at the saturation limit during rectification, which means that the whole resistance to mass transfer is within the vapour phase. The effect of thermal distillation was not found. Similarly Honorat and Sandall<sup>14</sup> have found in rectification of the mixture toluene-trichlorethylene in packed column that the liquid phase is at the saturation limit during rectification and that the mass transfer coefficients are identical at physical absorption and rectification which basically corresponds to the statement by Maljusov and coworkers<sup>11</sup> in the case when thermal distillation is insignificant.

It is obvious from this survey that the problem of simultaneous heat and mass transfer is treated differently not only by different authors but also by the same authors in different studies. This study is devoted to the analysis of heat and mass transfer in rectification of binary mixtures at turbulent flow of vapour by use of the earlier derived relations<sup>15</sup> for the heat and mass transfer coefficients, whose validity has been already verified on a number of systems (cases).

## THEORETICAL

At countercurrent adiabatic rectification of two component mixtures the hotter vapour phase is in contact with the cooler liquid phase. With respect to this temperature gradient the heat transfer between both phases takes place which causes conden-

sation and cooling of the vapour phase and evaporation and heating of the liquid phase. Heat transfer thus induces secondarily, due to condensation and evaporation, also mass transfer between phases. Besides mass transfer takes place between phases by diffusion.

Let us consider the column which has only the enrichment section into which enter the vapour and liquid phases which are saturated. To preserve this state during rectification it is necessary that the changes in temperature and concentration are in a certain relation. If the pressure changes are neglected this relation is determined by the dependences of  $t(x)$  and  $t(y)$ , by physical properties of the system and by hydrodynamic conditions determining the coefficients  $\alpha$  and  $k$ .

Temperature and concentration conditions during rectification in vicinity of the phase boundary are schematically denoted in Fig. 1. In view of considerably better thermal conductivity of the liquid than of vapour we can assume that temperature on the phase interface is approximately equal to the temperature of liquid and so temperature of the vapour phase will change from the temperature  $t_v$  in the bulk of vapour phase to the temperature  $t_i \approx t_L$  on the phase boundary. Thus also composition of vapour phase will change so that it would correspond in each point to the saturated value. Concretely on the phase boundary  $y_i \approx y^*$ .

At turbulent flow of vapour phase the mentioned temperature and concentration changes take place in the laminar boundary layer which is adjacent to the interface. In the transition region which forms the transition between the laminar boundary layer and the region of fully developed turbulence temperature and composition will suddenly change to values corresponding to values in the region from which they come due to turbulent fluctuations incomming from the region of fully developed

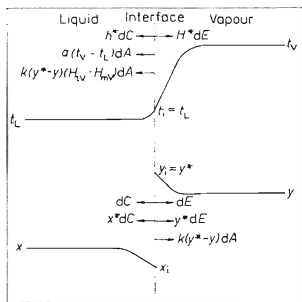


FIG. 1

Transport conditions in vicinity of interface at rectification of binary mixtures

turbulence which will result in condensation of vapours with composition  $y$  and temperature  $t_v$ . A condensate will thus form having the composition  $x^*$  and temperature  $t_v$ , which will be cooled at the passage through the laminar boundary layer down to the temperature  $t_L$  with which it passes into the liquid phase.

Simultaneously due to the equimolar diffusion the lower boiling component is transferred into the vapour and the higher boiling component into the liquid, while they carry a certain quantity of heat which is transferred at temperature of the interface  $t_L$ . The heat transferred from vapours into liquid per one mole of by diffusion transferred component is thus given by the difference of molar enthalpies of vapours of pure components of the mixture at temperature  $t_L$ . With regard to the fact that at the liquid interface the content of lower boiling component  $x_i$  is lower, evaporation of liquid will take place having the composition  $x$  in the bulk of liquid and vapour originated will have a composition  $y^*$ .

When proceeding along the column in the direction of vapour flow it is possible to describe the corresponding changes, resulting from the diffusion and thermal processes by relations

$$V = L + D \quad (1)$$

$$dV = dE - dC \quad (2)$$

$$d(VH) = -[\alpha(t_v - t_L) + k(y^* - y)(H_{1v} - H_{mv})] dA - h^* dC + H^* dE \quad (3)$$

$$d(Vy) = y^* dE - x^* dC + k(y^* - y) dA \quad (4)$$

$$d(VH) = d(Lh). \quad (5)$$

From these relations, after elimination of quantities  $E$  and  $C$  and arrangement the relation is obtained

$$\eta(y) = \frac{(\alpha/k)(t_v - t_L)(y^* - y) + (H_{1v} - H_{mv}) + N}{[1 + (y^* - y)P]N - dH/dy + (H - H^*)P}, \quad (6)$$

where

$$\eta(y) = [dy/(y^* - y)] / [(k/V) dA], \quad (7)$$

$$N = (H^* - h^*)/(y^* - x^*) \quad (8)$$

and

$$P = [(dH/dy - (R/(R + L_2/L))(dh/dx)] / (H - h). \quad (9)$$

As both terms in the denominator in Eq. (6) including  $P$  are of little significance and the ratio  $(L_2/L)$  is close to one, Eq (9) can be arranged to the form

$$P = [(dH/dy - (R/(R + 1)) (dh/dx)]/(H - h) \quad (10)$$

which is more suitable for the analysis.

Eq (6), as is obvious from Eq. (7), represents ratio of the actual differential concentration change of the lower boiling component in the vapour to the change caused only by diffusion. As the coefficients of heat and mass transfer are functions of both physical properties and hydrodynamic conditions it would be possible after substitution into Eq. (6) to determine hydrodynamic conditions which would guarantee the assumed saturated state in each cross-section of the unit. For expressing  $\alpha$  and  $k$  relations are used, which were derived earlier<sup>15</sup> and which were verified on various systems in wide range of variables. As the two-phase flow is concerned, parameters defining the relative motion of both phases are used

$$Sh = Re_r(f/2)_r^{1/2} \cdot F(Sc)/[\delta_1^+ F(Sc) + \lambda_p^+ + (1/\sqrt{2}) [Re f/2]_r^{1/4} \cdot \Phi(Sc)] \quad (11)$$

and

$$Nu = Re_r(f/2)_r^{1/2} \cdot F(Pr)/[\delta_1^+ F(Pr) + \lambda_p^+ + (1/\sqrt{2}) [Re f/2]_r^{1/4} \cdot \Phi(Pr)], \quad (12)$$

where

$$\delta_1^+ = (\delta_1 u_r \sqrt{(f/2)_r})/\nu \quad (13)$$

$$\lambda_p^+ = (\lambda_p u_r \sqrt{(f/2)_r})/\nu \quad (14)$$

$$F(Sc) = 1 - \frac{1}{3} Sc - (2/\pi^2) Sc \sum_{n=1}^{\infty} (1/n^2) \exp(-n^2 \pi^2 / Sc) \quad (15a)$$

which converges well for small values of  $Sc$ , or

$$F(Sc) = (2/\sqrt{\pi}) (Sc)^{1/2} [1 + 2\sqrt{\pi} \sum_{n=1}^{\infty} \text{ierfc}(n Sc^{1/2})] \quad (15b)$$

which converges well for high values of  $Sc$

Moreover

$$\Phi(Sc) = 2F(Sc)/[Sc f(Sc)] - 1, \quad (16)$$

where

$$f(Sc) = 1 - (8/\pi^2) \sum_{n=1}^{\infty} (1/(2n + 1)^2) \exp[-(2n + 1)^2 \pi^2 / Sc]. \quad (17)$$

Similar relations are obtained for  $F(Pr)$ ,  $\Phi(Pr)$  and  $f(Pr)$ .

The given relations can be considerably simplified in majority of cases. So *e.g.* for  $Sc \leq 1$  the third right hand side term in Eq. (15a) can be neglected. For  $Sc \geq 3$  the second term in brackets of the right hand side term of Eq. (15b) is negligible as compared to one and in the region  $1 \leq Sc \leq 3$  the relation can be used

$$F(Sc) = 1.32Sc^{0.358}. \quad (18)$$

For  $Sc \leq 1$  it is possible to use  $f(Sc) = 1$  and for  $Sc \geq 10$  to use  $\phi(Sc) = 0$ . Relation between the mass transfer coefficient  $k$  and  $K$  is given by

$$k = K\varrho/M. \quad (19)$$

The ratio  $(\alpha/k)$  in Eq. (6) can be expressed by relation

$$\begin{aligned} (\alpha/k) = (Sc/Pr) (F(Pr)/F(Sc)) \cdot C_p [\delta_1^+ F(Sc) + \lambda_p^+ + \\ + (1/\sqrt{2}) \Phi(Sc) \cdot (Re f/2)_i^{1/4}] / [\delta_1^+ F(Pr) + \\ + \lambda_p^+ + (1/\sqrt{2}) \Phi(Pr) \cdot (Re f/2)_i^{1/4}]. \end{aligned} \quad (20)$$

Number of transfer units reached by diffusion transfer is given by relation

$$N_D = \int_A (k/V) dA = \int_{y_1}^{y_2} [1/(\eta(y) \cdot (y^* - y))] dy \quad (21)$$

resulting from Eq. (7) and the total number reached *i.e.* incl. the effect of thermal distillation is

$$N_T = \int_{y_1}^{y_2} (1/y^* - y) dy \quad (22)$$

so that

$$(N_T/N_D) = \int_{y_1}^{y_2} (1/(y^* - y)) dy \Big/ \int_{y_1}^{y_2} [1/(\eta(y) (y^* - y))] dy. \quad (23)$$

TABLE I  
Calculated dependence of ratio  $\eta(y)$  (Eq. (7)) on  $y$

$y$	0.00	0.04	0.10	0.30	0.50	0.70	0.90	0.95	1.00
$\eta(y)$	1.0000	1.0009	1.0177	1.0644	1.0658	1.0410	1.0155	1.0084	1.0000

Eq. (23) is expressing the relative effect of thermal distillation at the change of composition of vapour phase from  $y_1$  to  $y_2$ .

### DISCUSSION

To be able to judge the accuracy of theoretical conclusions and to compare them with the results of other authors, the dependence of  $\eta(y)$  was calculated for one of the most suitable systems *i.e.* for methanol-water system at total reflux. For calculation of ratio  $(\alpha/k)$  from Eq. (20) the values were used  $\delta_1^+ = 1$  and  $\lambda_p^+ = 20$  which were found suitable at verification for the wetted wall and some particular packings. From the shape of dependence (20) and with regard to the fact that  $Sc$  and  $Pr$  are close one to the other and smaller than one it is obvious that the hydrodynamic conditions will not have a profound effect on the ratios  $(\alpha/k)$  and even less on  $\eta(y)$ . For calculation was chosen value  $Re_\tau = 10^4$ . In Table I are given data obtained for the dependence of ratio  $\eta(y)$ . It can be seen from this Table that the dependence has a maximum at mean concentrations, which is in agreement with conclusions of many authors. But the value of this maximum is relatively low and at its evaluation by Eq. (23), which is usual, the effect of thermal distillation will appear even smaller and correspond more to findings of those authors which state that the effect of thermal distillation is negligible<sup>10,13,14</sup>.

From Eqs (6), (8) and (20) is obvious that the effect of hydrodynamic conditions, affecting in Eq. (6) only the ratio  $(\alpha/k)$ , will not be significant for the shape of  $\eta(y)$  with regard to values of other terms in the denominator and with regard to the form of dependence (20).

From Eqs (6) and (10) then results that nor the value of reflux ratio will affect significantly the shape of dependence  $\eta(y)$ .

### LIST OF SYMBOLS

$A$	interfacial area ( $m^2$ )
$C$	condensing vapours (mol/s)
$C_p$	specific heat at constant pressure (J/mol K)
$D$	distillate (Eq. (1)) (mol/s)
$D$	diffusivity ( $m^2/s$ )
$d$	linear dimension of the system (m)
$E$	evaporated liquid (mol/s)
$F(Sc)$	defined by Eq. (15a,b)
$f(Sc)$	defined by Eq. (17)
$f$	friction factor
$H$	molar enthalpy of vapours of composition $y$ at temperature $t_v$ (J/mol)
$H^*$	molar enthalpy of vapours $y^*$ at temperature $t_L$ (J/mol)
$H_{1v}, H_{mv}$	enthalpy of vapours of pure less volatile, or more volatile component of mixture at the temperature $t_L$ (J/mol)
$h$	molar enthalpy of liquid of composition $x$ at temperature $t_L$ (J/mol)

$h^*$	molar enthalpy of liquid of composition $x^*$ at temperature $t_L$ (J/mol)
$\text{ierfc } x = \int_x^\infty \text{erfc } \xi \, d\xi = (1/\sqrt{\pi}) \exp(-x^2) - x \text{erfc } x$	
$k$	mass transfer coefficient in vapour phase (mol/m <sup>2</sup> s)
$K$	mass transfer coefficient in vapour phase (m/s)
$L$	liquid flow rate (mol/s)
$M$	molar weight of vapour mixture (kg/mol)
$N$	defined by Eq. (8)
$N_D, N_T$	number of transfer units, defined by Eqs (21) or (22)
$Nu = \alpha d/\lambda$	Nusselt number for vapour
$P$	quantity defined by Eq. (9)
$Pr = C_p \mu/\lambda M$	Prandtl number for vapour
$R = L_2/D$	reflux ratio
$Re_\tau = u_\tau d \rho/\mu$	Reynolds number for vapour
$Sc = \mu/\rho D$	Schmidt number for vapour
$Sh = Kd/D$	Sherwood number for vapour
$t$	temperature (K)
$u$	velocity (m/s)
$V$	vapour flow rate (mol/s)
$x$	mole fraction of low boiling component in liquid
$x^*$	mole fraction of low boiling component in liquid in equilibrium with vapour having the composition $y$
$y$	mole fraction of low-boiling component in vapour
$y^*$	mole fraction of low-boiling component in vapour in equilibrium with liquid having the composition $x$
$\alpha$	heat transfer coefficient (J/m <sup>2</sup> s K)
$\delta_1$	thickness of laminar layer (m)
$\eta(y)$	defined by Eq. (7)
$\lambda$	coefficient of thermal conductivity (J/m s K)
$\lambda_p$	thickness of transition layer (m)
$\rho$	density of vapour mixture (kg/m <sup>3</sup> )
$\Phi(Sc)$	quantity defined by Eq. (16)
$\mu$	dynamic viscosity (kg/ms)

## Subscripts

$i$	interface
$L$	liquid phase
$V$	vapour phase
$r$	relative to liquid flow
$t$	total value
$1$	value at the vapour inlet
$2$	value at the vapour outlet

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