

Effects of Mass Transfer Rate and its Expressions on Dynamics of Mass Transfer Operation

By

Takeichiro TAKAMATSU* and Eiji NAKANISHI**

(Received January 31, 1963)

In this paper, the dynamics with respect to mass transfer operation in a perfect mixing vessel is discussed. The transfer functions for the small change of concentrations or flow rates of input fluids are derived and the effects of residence time, stripping factor and number of transfer units, etc. on the dynamics are explained by using Bode diagrams.

In addition, the limitation on the use of the mass transfer capacity coefficient, the Murphree efficiency and the height per transfer unit in unsteady state are discussed, and it is concluded that only the mass transfer capacity coefficient gives reasonable results whereas the Murphree efficiency must not be used as a constant.

1) Introduction

Among studies on dynamics of mass transfer operations, of which not many have been published, most of them have been for stagewise operations and have been analyzed under an assumption of the ideal stage^{1,3,4,5}. It is, however, a well known fact that this assumption may not generally hold in industrial and practical mass transfer plants. In some published papers a concept of Murphree efficiency has been used to express deviation from the above assumption^{2,6}.

In order to express the degree of mass transfer rate in steady state the concept of mass transfer capacity coefficient, height per transfer unit and Murphree efficiency are widely used, and some mutualities exist among these concepts.

In this paper, the applicability of these concepts in unsteady states is discussed, and it is implied that a concept easily recognized in steady state operations can not always be used for the unsteady state.

In addition, the reasonability of neglecting the holdup of one fluid is checked.

* Department of Sanitary Engineering

** Department of Chemical Engineering

2) Transfer functions expressed by means of mass transfer capacity coefficient

Transfer functions for concentration change: Referring to Fig. 1, let us assume

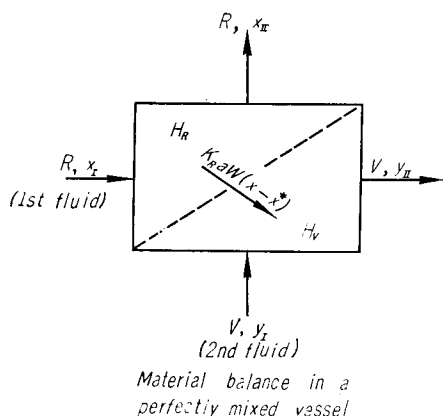


Fig. 1.

that $R, V, H_R, H_V, K_R a$ and an equilibrium relation between x and y are always constant, being independent of concentration change. From the material balances of one component the following relations are easily found.

$$H_R \frac{dx_{II}}{dt} + H_V \frac{dy_{II}}{dt} = R(x_I - x_{II}) + V(y_I - y_{II}) \quad (1)$$

$$H_R \frac{dx_{II}}{dt} = R(x_I - x_{II}) + K_R a W (x_{II}^* - x_{II}) \quad (2)$$

For simplicity, an equilibrium relation between x and y is assumed to be

$$y_{II} = mx_{II}^* + c \quad (3)$$

Based on Eqs. (1), (2) and (3), the following transfer functions for concentration change are obtained,

$$G_1(s) = \frac{X_{II}(s)}{X_I(s)} = \frac{1 + N_{0V} + \tau_V s}{H(s)} \quad (4)$$

$$G_2(s) = \frac{Y_{II}(s)}{mX_I(s)} = \frac{N_{0V}}{H(s)} \quad (5)$$

$$G_3(s) = \frac{mX_{II}(s)}{Y_I(s)} = \frac{N_{0R}}{H(s)} \quad (6)$$

$$G_4(s) = \frac{Y_{II}(s)}{Y_I(s)} = \frac{1 + N_{0R} + \tau_R s}{H(s)} \quad (7)$$

where

$$H(s) = (1 + \tau_R s)(1 + \tau_V s) + N_{0R}(1 + \tau_V s) + N_{0V}(1 + \tau_R s) \quad (8)$$

$$N_{0R} = \frac{K_R a W}{R} = \frac{x_I^0 - x_{II}^0}{x_{II}^0 - x_{II}^{0*}}, \quad N_{0V} = \frac{N_{0R}}{\lambda} \quad (9)$$

These transfer functions can also be obtained from following equations which are based on the behavior of the second fluid.

$$H_V \frac{dy_{II}}{dt} = V(y_I - y_{II}) + K_V a W (y_{II}^* - y_{II}) \quad (10)$$

$$y_{II}^* = mx_{II} + c \quad (11)$$

It is easily found that the transfer functions obtained from Eqs. (1), (10) and

(11) are in complete agreement with Eqs. (4) to (7), respectively, if a well known relation

$$N_{0R} = \lambda N_0 V \quad (12)$$

with

$$N_0 V = \frac{K_v a W}{V} \quad (13)$$

is taken into account.

Transfer functions for flow rate change: The basic differential equation for flow rate change is not linear for most cases. But it may approximately be linearized, provided it can be assumed that the deviation of flow rate from a steady state, ΔR or ΔV , is very small. Then the outlet concentration change, Δx_{II} or Δy_{II} , is also very small by the same order of magnitude as that of the flow rate. Consequently products of two deviational quantities like $\Delta R \cdot \Delta x_{II}$ and $\Delta V \cdot \Delta y_{II}$ can be neglected in comparison with deviations in concentration and flow rate.

Under the above assumption the following basic equations for material balance and equilibrium relation are obtained.

$$H_R \frac{d\Delta x_{II}}{dt} + H_V \frac{d\Delta y_{II}}{dt} = (x_I^0 - x_{II}^0) \Delta R + (y_I^0 - y_{II}^0) \Delta V + (\Delta x_I - \Delta x_{II}) R^0 + (\Delta y_I - \Delta y_{II}) V^0 \quad (14)$$

$$H_R \frac{d\Delta x_{II}}{dt} = (x_I^0 - x_{II}^0) \Delta R + (\Delta x_I - \Delta x_{II}) R^0 + K_R a W (\Delta x_{II}^* - \Delta x_{II}) \quad (15)$$

$$\Delta y_{II} = m \Delta x_{II}^* \quad (16)$$

Taking the Laplace transformation of these equations without considering any inlet concentration change, the modified transfer functions for flow rate change are derived as follows.

$$g_1(s) = \frac{X_{II}(s)/(x_I^0 - x_{II}^0)}{R(s)/R^0} = \frac{1 + N_0 V + \tau_V s}{H(s)} \quad (17)$$

$$g_2(s) = \frac{Y_{II}(s)/(y_I^0 - y_{II}^0)}{-R(s)/R^0} = \frac{N_{0R}}{H(s)} \quad (18)$$

$$g_3(s) = \frac{X_{II}(s)/(x_I^0 - x_{II}^0)}{-V(s)/V^0} = \frac{N_0 V}{H(s)} \quad (19)$$

$$g_4(s) = \frac{Y_{II}(s)/(y_I^0 - y_{II}^0)}{V(s)/V^0} = \frac{1 + N_{0R} + \tau_R s}{H(s)} \quad (20)$$

Reasonability of obtained transfer function: In sum, when mass transfer capacity coefficient is used as the constant parameter that represents the mass transfer rate, all transfer functions obtained above are reasonable with respect to the following points:

i) Taking into account of the order of magnitude of s , $G_1(s)$ and $G_4(s)$ as well as $g_1(s)$ and $g_4(s)$ are dynamically analogous to each other, and the

same is true with respect to $G_2(s)$ and $G_3(s)$ as well as $g_2(s)$ and $g_3(s)$. This property will be called "correspondency" in this paper.

ii) When the mass transfer capacity coefficient is expressed based on the behavior of one of two fluids, both transfer functions are in perfect agreement with each other due to the well known relation Eq. (12). This property will be called "interchangability" in this paper.

3) Transfer functions expressed by means of Murphree efficiency

Transfer functions for concentration change: The Murphree efficiency based on the first fluid is defined as follows.

$$E_{MR} = \frac{x_I - x_{II}}{x_I - x_{II}^*} \quad (21)$$

Assuming that a value of E_{MR} is constant even in the period of the unsteady state, the transfer functions for inlet concentration change are derived from Eqs. (1), (3) and (21) as follows,

$$G_1(s) = \frac{X_{II}(s)}{X_I(s)} = \frac{[(E_{MR} - \lambda E_{MR} + \lambda) + \lambda(1 - E_{MR})\tau v s]}{H_1(s)} \quad (22)$$

$$G_2(s) = \frac{Y_{II}(s)}{mX_I(s)} = \frac{[E_{MR} - (1 - E_{MR})\tau_R s]}{H_1(s)} \quad (23)$$

$$G_3(s) = \frac{mX_{II}(s)}{Y_I(s)} = \frac{\lambda E_{MR}}{H_1(s)} \quad (24)$$

$$G_4(s) = \frac{Y_{II}(s)}{Y_I(s)} = \frac{\lambda}{H_1(s)} \quad (25)$$

where

$$H_1(s) = (\lambda + E_{MR}) + (E_{MR}\tau_R + \lambda\tau v)s \quad (26)$$

If the Murphree efficiency based on the second fluid E_{MV} is used, the following transfer functions are obtained,

$$G_1(s) = \frac{X_{II}(s)}{X_I(s)} = \frac{1}{H_2(s)} \quad (27)$$

$$G_2(s) = \frac{Y_{II}(s)}{mX_I(s)} = \frac{E_{MV}}{H_2(s)} \quad (28)$$

$$G_3(s) = \frac{mX_{II}(s)}{Y_I(s)} = \frac{\lambda[E_{MV} - (1 - E_{MV})\tau v s]}{H_2(s)} \quad (29)$$

$$G_4(s) = \frac{Y_{II}(s)}{Y_I(s)} = \frac{[(1 - E_{MV} + \lambda E_{MV}) + (1 - E_{MV})\tau_R s]}{H_2(s)} \quad (30)$$

where

$$H_2(s) = (1 + \lambda E_{MV}) + (\tau_R + \lambda E_{MV}\tau v)s \quad (31)$$

$$E_{MV} = \frac{y_{II} - y_I}{y_{II}^* - y_I} \quad (32)$$

Looking through the above eight transfer functions, the following unreasonable characteristics are found.

i) In either case, “correspondency” can not be found between $G_1(s)$ and $G_4(s)$ or between $G_2(s)$ and $G_3(s)$.

ii) Even if the wellknown relation

$$\frac{E_{MR}}{1-E_{MR}} = \frac{\lambda E_{MV}}{1-E_{MV}} \quad (33)$$

is considered, there is no “interchangability” between Eqs. (22) to (25) and Eqs. (27) to (30), respectively.

To sum up generally, since the transfer functions derived from the assumption of constant E_{MR} or E_{MV} have no “correspondency” and “interchangability”, it is not exactly reasonable to use E_{MR} or E_{MV} as a constant parameter.

Transfer functions for flow rate change: Using the assumptions and procedures similar to those for the case of $K_R a$ expression, the following transfer functions are obtained. From the E_{MR} expression,

$$g_1(s) = g_3(s) = \frac{E_{MR}}{H_1(s)} \quad (34)$$

$$g_2(s) = g_4(s) = \frac{\lambda}{H_1(s)} \quad (35)$$

and from the E_{MV} expression,

$$g_1(s) = g_3(s) = \frac{1}{H_2(s)} \quad (36)$$

$$g_2(s) = g_4(s) = \frac{\lambda E_{MV}}{H_2(s)} \quad (37)$$

Inspecting these transfer functions, the following characteristics are found.

i) There is no “correspondency” between $g_1(s)$ and $g_4(s)$ or between $g_2(s)$ and $g_3(s)$ in both cases, since the numerators of $g_1(s)$ and $g_4(s)$ or $g_2(s)$ and $g_3(s)$ are not of the same order in s .

ii) A common time constant T_R for Eqs. (34) and (35) is given by

$$T_R = \frac{E_{MR}\tau_R + \lambda\tau_V}{\lambda + E_{MR}}$$

and a common time constant T_V for Eqs. (36) and (37) is

$$T_V = \frac{\tau_R + \lambda E_{MV}\tau_V}{1 + \lambda E_{MV}}$$

Two time constants are not equal except for a special case of $E_{MR} = E_{MV} = 1$. That is, there is no “interchangability” between the E_{MR} and E_{MV} expression methods.

Therefore, E_{MR} or E_{MV} must not be used as a constant for the purpose of calculating the dynamics for the change of flow rate.

4) Transfer functions expressed by means of height per transfer unit

Even in a perfectly mixed vessel, it is conceptually possible to use the so called "H.T.U.", H_{0R} or H_{0V} which is usually used for the purpose of expressing the degree of mass transfer rate in such continuous contacting equipments as the packed tower and the wetted wall tower.

From the definition of H.T.U.,

$$K_R a W = \frac{l_R \cdot R}{H_{0R}}, \quad K_V a W = \frac{l_V \cdot V}{H_{0V}} \quad (38)$$

where l_R, l_V are the travelling length of the first and the second fluids, respectively. It is easily seen that the transfer functions expressed in terms of H.T.U. for concentration change are in perfect agreement with Eqs. (4) to (7), assuming that H.T.U. and the travelling length are constant.

In §2, the mass transfer capacity coefficient is assumed to be constant for the change of flow rate. However, mass transfer capacity coefficient and H.T.U. are generally considered as a function of flow rate, and hence the transfer functions for flow rate change should be derived by taking account that mass transfer capacity coefficient or H.T.U. undergoes a change with a variation of flow rate. Supposing that the deviational quantity of flow rate from a steady state is sufficiently small for the purpose of linearization, the variation in mass transfer capacity coefficient or H.T.U. from a steady state value will be approximately proportional to $\Delta R, \Delta V$, as expressed below.

$$\left. \begin{aligned} \frac{\Delta(K_R a W)}{(K_R a W)^0} &= \alpha_R \frac{\Delta R}{R^0} + \beta_R \frac{\Delta V}{V^0} \\ \frac{\Delta(K_V a W)}{(K_V a W)^0} &= \alpha_V \frac{\Delta R}{R^0} + \beta_V \frac{\Delta V}{V^0} \end{aligned} \right\} \quad (\text{for } K_R a, K_V a) \quad (39-a, b)$$

$$\left. \begin{aligned} \frac{\Delta(H_{0R})}{(H_{0R})^0} &= \gamma_R \frac{\Delta R}{R^0} + \delta_R \frac{\Delta V}{V^0} \\ \frac{\Delta(H_{0V})}{(H_{0V})^0} &= \gamma_V \frac{\Delta R}{R^0} + \delta_V \frac{\Delta V}{V^0} \end{aligned} \right\} \quad (\text{for } H_{0R}, H_{0V}) \quad (40-a, b)$$

The transfer functions for flow rate change are, for example, derived by $K_R a$ expression from Eqs. (1), (2), (3) and (39-a) as follows:

$$g_1(s) = \frac{N_0 V + (1 - \alpha_R)(1 + \tau_V s)}{H(s)} \quad (41)$$

$$g_2(s) = \frac{N_0 R + \alpha_R(1 + \tau_R s)}{H(s)} \quad (42)$$

$$g_3(s) = \frac{N_0 v + \beta_R(1 + \tau v s)}{H(s)} \quad (43)$$

$$g_4(s) = \frac{N_0 R + (1 - \beta_R)(1 + \tau_R s)}{H(s)} \quad (44)$$

Obviously the transfer functions (17) to (20) are just in agreement with the above transfer functions for $\alpha_R = \beta_R = 0$. The analogous results are obtained also by K_{va} , H_{0R} and H_{0V} expressions, and in the dynamic analysis with flow rate change the following relations should be satisfied between four kinds of expressions of mass transfer rate, because the transfer functions expressed by the four methods must essentially give the same equation for only one dynamic phenomenon.

$$\text{i) } \alpha_R = \alpha_V, \beta_R = \beta_V \quad (\text{between } K_{Ra} \text{ and } K_{Va} \text{ expressions}) \quad (45)$$

$$\text{ii) } \gamma_R - \gamma_V = 1, \delta_R - \delta_V = -1 \quad (\text{between } H_{0R} \text{ and } H_{0V} \text{ expressions}) \quad (46)$$

$$\text{iii) } \alpha_R + \gamma_R = 1, \beta_R + \delta_R = 0 \quad \text{or} \quad \alpha_V + \gamma_V = 0, \beta_V + \delta_V = 1$$

$$(\text{between } K_{Ra}, K_{Va} \text{ and } H_{0R}, H_{0V} \text{ expressions}) \quad (47)$$

In §2, the same results are fortunately obtained by both K_{Ra} and K_{Va} expressions for flow rate change, in which K_{Ra} or K_{Va} is always constant. This is, however, a matter of course since Eq. (45) is satisfied in this case ($\alpha_R = \alpha_V = 0$, $\beta_R = \beta_V = 0$).

In sum, the transfer functions by any expression with respect to mass transfer rate are essentially the same, if the above relations (45) to (47) are taken into account.

5) Effect of neglecting holdup of one fluid

In the dynamic analysis of mass transfer operations in which one of the fluids is gas or vapor, the holdup of the gas or vapor may often be neglected in comparison with that of liquid. Several studies carried out with such an approximation have been published. It is, however, doubtful whether such an approximation is reasonable for any case.

Substituting $\tau_V = 0$ into Eqs. (4) to (7), it is seen that each of $G_1(s)$, $G_2(s)$ and $G_3(s)$ becomes a perfect first order type and only $G_4(s)$ takes a different form as follows.

$$G_4(s) = \frac{\lambda}{\lambda + \lambda N_{0R} + N_{0R}} \cdot \frac{1 + N_{0R} + \tau_R s}{1 + T s} \quad (48)$$

where

$$T = \frac{\lambda + N_{0R}}{\lambda + \lambda N_{0R} + N_{0R}} \tau_R$$

Obtaining an indicial response from Eq. (48) by Laplace-inverse-transform

and substituting $t=0$ in it, the result is

$$\Delta y_{II}(0) = \frac{\lambda}{\lambda + N_{0R}} \bar{\Delta y}_I \neq 0$$

where $\bar{\Delta y}$ is a value of step change of the inlet concentration of the second fluid. This result is unreasonable for a reason that the value of $\Delta y_{II}(0)$ should be zero from an initial condition. This fact implies that neglecting the holdup of one fluid may cause a considerable error in the dynamics for such a fluid.

6) Numerical consideration and reconfirmation by frequency response analysis

Fig. 2 shows Bode diagrams of $G_1(j\omega)$ and $G_2(j\omega)$ by using K_{Ra} (or K_{Va}), E_{MR} and E_{MV} expressions, respectively, for a process. They are identical from the statical view point. Dynamically, however, as these curves show, they become different depending on which one of K_{Ra} (or K_{Va}), E_{MR} and E_{MV} is used for the calculation. It is especially noticed that the E_{MR} expression markedly differs from the K_{Ra} (or K_{Va}) expression. These results are truly unreasonable. It will be easily seen that the result from the E_{MV} expression is extremely different from the others with respect to $G_3(s)$ and $G_4(s)$. In addition, these differences mentioned above increase with the increase in mass transfer resistance.

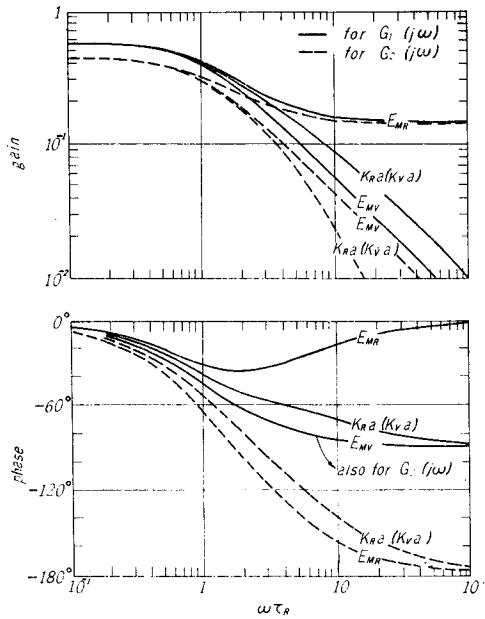
Fig. 3 shows the effect of the ratio of τ_V to τ_R on $G_1(j\omega)$, and it is seen that the dynamic behavior of $G_1(j\omega)$ is not seriously affected by $\kappa (= \tau_V/\tau_R)$ when $\kappa < 1$. On the other hand, $G_2(s)$, $G_3(s)$ and especially $G_4(s)$ are affected by κ . Fig. 4 shows the effect of κ on $G_4(j\omega)$, and it is obviously found that both dynamic behaviors for the cases of $\tau_V=0$ and $\tau_V \neq 0$ are essentially different from each other even if the value of τ_V is negligibly small compared with the value of τ_R . Moreover, it will be expected that $G_1(s)$ is strongly affected by κ when $\kappa > 1$.

It is easily predicted that N_{0R} affects more directly the transfer of a signal from one fluid to another. Fig. 5 shows one numerical example, and it is seen that the dynamics for signals between the different kinds of fluid is considerably affected by N_{0R} .

7) Conclusion

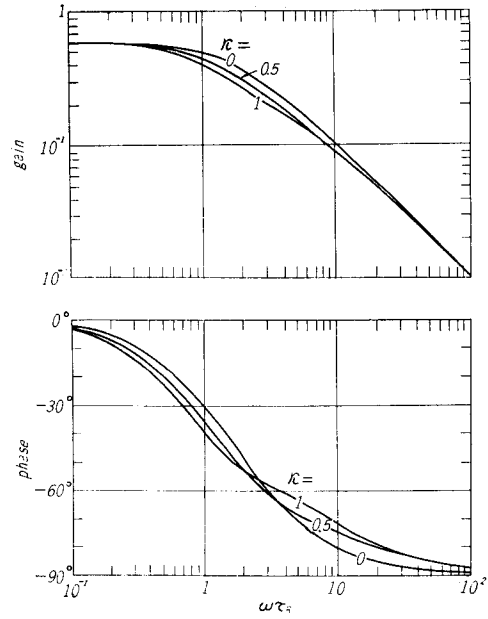
It seems that some assumptions which are certainly reasonable from the statical viewpoint have been similarly used in analysis of dynamics of mass transfer processes without question.

In this paper theoretical and numerical considerations are carried out with respect to the dynamic performance of mass transfer operations in a perfectly



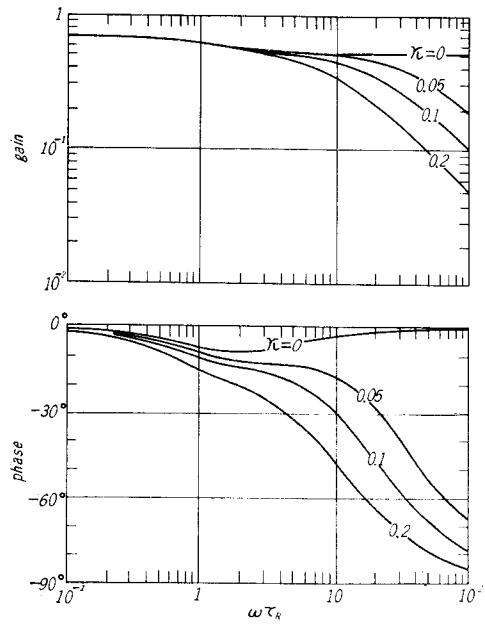
Variations in gain and phase due to $KRa(KVa)$, EMR and EMV expressions
($\lambda=1$, $\kappa=1$, $N_{OR}=N_{OV}=3$, $EMR=EMV=0.75$)

Fig. 2.



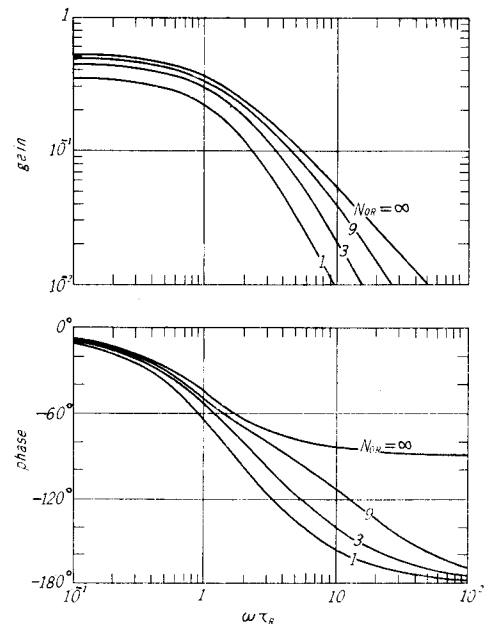
Effect of κ on $G_1(j\omega)$
($\lambda=1$, $N_{OR}=N_{OV}=3$)

Fig. 3.



Effect of κ on $G_2(j\omega)$
($\lambda=1$, $N_{OR}=N_{OV}=3$)

Fig. 4.



Effect of N_{OR} on $G_2(j\omega)$ or $G_3(j\omega)$
($\lambda=1$, $\kappa=1$)

Fig. 5.

mixed vessel and the discussions are focused on the expression of mass transfer rate and the neglecting of holdup of one fluid, and the following is concluded:

i) Among the mass transfer capacity coefficient, the height per transfer unit and Murphree efficiency, the former two expressions give reasonable results in every case, while Murphree efficiency must not be used as a constant.

ii) Only when the dynamic concerning a fluid whose holdup is not negligible is being discussed, the holdup of another fluid may be neglected.

Notations

E_{MR}, E_{MV}	: Murphree efficiencies based on the 1st fluid and the 2nd fluid, respectively
H_{0R}, H_{0V}	: overall height per transfer unit based on the 1st fluid and the 2nd fluid, respectively
H_R, H_V	: holdups of the 1st fluid and the 2nd fluid in a vessel, respectively
j	: $=\sqrt{-1}$
K_{Ra}, K_{Va}	: overall mass transfer capacity coefficients based on the 1st fluid and the 2nd fluid, respectively
l_R, l_V	: travelling length of the 1st fluid and the 2nd fluid through a vessel, respectively
N_{0R}, N_{0V}	: overall number of transfer units based on the 1st fluid and the 2nd fluid, respectively
R, V	: flow rates of the 1st fluid and the 2nd fluid, respectively
$\Delta R, \Delta V$	: deviational quantities of R, V , respectively
$R(s), V(s)$	: Laplace-transformed quantities with time t of $\Delta R, \Delta V$, respectively
s	: complex parameter for Laplace transformation
t	: time
x, y	: concentrations of the 1st fluid and the 2nd fluid, respectively
$\Delta x, \Delta y$	: deviational quantities of x, y , respectively
$X(s), Y(s)$	: Laplace-transformed quantities with time t of $\Delta x, \Delta y$, respectively
W	: volume of a vessel
κ	: ratio of τ_V to τ_R
λ	: stripping factor ($=mV/R$)
τ_V, τ_R	: residence time of the 1st fluid and the 2nd fluid, respectively
ω	: angular frequency
superscripts	
◦	: value in steady state
*	: equilibrium value

subscripts

- I : value at inlet
II : value at outlet

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