

PARTITION OF BINARY LIQUID MIXTURES IN
THERMODIFFUSION COLUMNS WITH FILLERS

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An equation is derived which describes the transfer of a mixture mass with low concentrational expansivity in a thermodiffusion column with a filler, and a similar problem is analyzed with the concentrational expansivity taken into account, when $c(1-c) = \text{const}$. An expression is obtained for the partition index of a column. The considerable effect of lengthwise diffusion on the partition process is noted.

The partition of liquid mixtures by thermodiffusion is affected considerably by stray currents resulting from variations in the working clearance, in the temperature field, etc. [1], and making it possible in practice to attain the theoretically possible partition index [2, 3]. In order to raise the attainable partition index of thermodiffusion columns, a mesh grid has been placed in the working clearance [4], the inner cylinder has been rotated [5], and porous fillers have been placed in the active volume of columns [6, 7]. For a column operating in the intermittent mode, the use of porous fillers appears most promising. The partition of binary liquid mixtures in a thermodiffusion column with a porous filler has been treated theoretically in [8], but the analysis there contains a few inaccuracies. Specifically, two mutually exclusive viscous terms appear unjustifiably in the equation of motion. The authors of [8] have evidently used the two concepts of true and effective velocity at the same time. Furthermore, it is asserted in [8] that the effect of lengthwise diffusion on the partition process in a porous medium may be disregarded. With these objections in mind, we will solve the problem concerning the partition of a binary liquid mixture in a thermodiffusion column with a porous filler, and we will also analyze the effect of lengthwise diffusion on the partition process.

We consider the partition of a binary mixture in a flat column of height L , with a working clearance $2d \ll L$, and closed at both ends. The left-hand side of the column is maintained at temperature T_1 and the right-hand side at temperature T_2 , where $T_1 < T_2$.

The porous filler in the column is assumed porous and isotropic. The differential equations describing a quasisteady partition process in the column are

$$\begin{aligned} \frac{1}{\rho} \nabla P &= -\frac{\mu \mathbf{v}}{k\rho} + g[1 - \beta(T - T_0) - \gamma(c - c_0)], \\ \varepsilon(\mathbf{v}\nabla)c &= \nabla \frac{D\varepsilon}{\xi} \left[\nabla c - \frac{\alpha c(1-c)}{T} \nabla T \right], \\ (\mathbf{v}\nabla)T &= \frac{\kappa}{\xi} \Delta T, \\ \nabla \mathbf{v} &= 0. \end{aligned} \tag{1}$$

The first equation in system (1) is the filtration equation for a liquid through a porous medium and it has been derived by introducing into the Euler equation so-called Zhukovskii forces [9], which describe the interaction between the flowing viscous liquid and the porous medium.

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Parameters μ , β , γ , D , χ , ρ , and α in Eqs. (1) are considered constant and are calculated on the basis of average temperatures, pressures, and concentrations. We will consider the two-dimensional problem in (x, z) coordinates, deriving equation of mixture transfer, for which the concentrational expansion may be omitted. Noting that $d \ll L$ and disregarding the end effects, we may let $u = 0$. It will also be assumed that the temperature of the mixture does not vary along the vertical coordinate z . As is usually done, we write the thermodiffusion terms in the form $(\alpha/T_0)c(1-c)\nabla T$.

With all these assumptions, system (1) can be reduced to the following system of equations:

$$\begin{aligned} \frac{1}{\rho} \cdot \frac{dP}{dz} &= -\frac{v\nu}{k} + g[1 - \beta(T - T_0)], \\ \varepsilon v \frac{\partial c}{\partial z} &= \nabla \frac{D\varepsilon}{\zeta} \left[\nabla c - \frac{\alpha c(1-c)}{T_0} \nabla T \right], \\ \frac{dT^2}{dx^2} &= 0. \end{aligned} \quad (2)$$

The solution to the equation of heat conduction will be written as

$$T = T_0 + \frac{T_2 - T_1}{2d} x. \quad (3)$$

The effective velocity v is determined from the equation of motion in (2) with the single boundary condition $\int_{-d}^d v dx = 0$:

$$v = \frac{g\beta k(T_2 - T_1)}{2vd} x. \quad (4)$$

In order to determine the concentration distribution over a transverse column section, we temporarily neglect the lengthwise diffusion in (2) as being very small in comparison with the transverse diffusion. Then, with the aid of (4) and with $\partial c/\partial z$ assumed independent of x , we obtain for the transverse mass transfer j_x :

$$j_x = \frac{g\beta k\varepsilon(T_2 - T_1)}{4vd} \cdot \frac{dc}{dz} (d^2 - x^2). \quad (5)$$

In deriving (5) we used the boundary condition $j_x = 0$ at the walls. Using now (5) and the expression for the diffusion current j_x , we find an expression for $\partial c/\partial x$ which, after being integrated, will yield the horizontal concentration distribution:

$$c = c_0 + \frac{\alpha c(1-c)(T_2 - T_1)}{2dT_0} x - \frac{g\beta k\varepsilon(T_2 - T_1)}{12Dvd} \cdot \frac{dc}{dz} (3d^2x - x^3). \quad (6)$$

It has been assumed in this integration that $c(1-c)$ is not a function of x . Inserting (4) and (6) into the equation of lengthwise transfer for a mixture component, $\tau = B\rho\varepsilon \int_{-d}^d \left(vc - \frac{D}{\zeta} \cdot \frac{dc}{dz} \right) dx$, and then integrating,

we obtain the equation of transfer

$$\tau = Hc(1-c) - (K_c + K_d) \frac{dc}{dz}, \quad (7)$$

where

$$\begin{aligned} H &= \frac{\alpha\rho g\beta k\varepsilon(T_2 - T_1)^2 Bd}{6\nu T_0}, \\ K_c &= \frac{\rho g^2\beta^2 k^2 \varepsilon (T_2 - T_1)^2 Bd^3}{15D\nu^2}, \\ K_d &= 2D\rho \frac{\varepsilon}{\zeta} Bd. \end{aligned}$$

Integrating (7) over z will yield an expression for the steady-state partition index of a column with a filler:

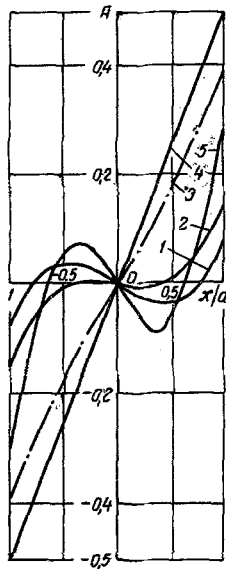


Fig. 1. Family of horizontal concentration profiles, calculated according to Eq. (6') for $Sm = 300$, $Gr = 385$, and various permeabilities k : 10^{-5} cm^2 (1), $4 \cdot 10^{-7} \text{ cm}^2$ (2), 10^{-7} cm^2 (3), 10^{-8} cm^2 (4), and the corresponding profile in a column without filler (5). $A = (c - c_0)T_0 / [\alpha c_0 (1 - c_0) (T_2 - T_1)]$.

$$\ln q_f = \frac{5\alpha DvL}{2g\beta k \zeta T_0 d^2 \left(1 + \frac{K_d}{K_c}\right)} \quad (8)$$

In order to compare the effectiveness of partition in a column with and without filler, we set up the ratio

$$\frac{\ln q_f}{\ln q_0} = \frac{5d^2}{63k\zeta \left(1 + \frac{K_d}{K_c}\right)} \quad (9)$$

An analysis of this ratio shows that in columns with fillers the partition increase substantially. In a column with a 0.12 cm clearance and filled with glass wool ($k \approx 4 \cdot 10^{-7} \text{ cm}^2$), for instance, the ratio is $\ln(q_f)/\ln(q_0) \approx 10^2$. From expressions (6) and (7) we can find the steady-state transverse concentration profile:

$$c = c_0 + \frac{\alpha c (1 - c)(T_2 - T_1)}{T_0} \left[\frac{1}{2} \left(\frac{x}{d}\right) - \frac{5}{24} \cdot \frac{3 \left(\frac{x}{d}\right) - \left(\frac{x}{d}\right)^3}{1 + \frac{K_d}{K_c}} \right],$$

where the ratio K_d/K_c can be expressed as

$$\frac{K_d}{K_c} = \frac{15}{2 Gr^2 Sm^2 k^2}$$

In Fig. 1 a family of steady-state horizontal concentration profiles according to Eq. (6') is shown, having the permeability k as the parameter. For comparison, a corresponding profile in a column without filler is also shown here. An analysis of the curves indicates a strong dependence of the partition process on the permeability and, consequently, on the K_d/K_c ratio characterizing the effect of lengthwise diffusion. We note that, when the permeability is low, the horizontal concentration profile of a liquid mixture in a column with a filler is identical to the analogous profile of a gas mixture in a column without filler.

The transient time in a column with a filler can be calculated by the formulas in [10], where the transient transfer equation is solved without considering the specific form of the transfer coefficients H , K_c , and K_d .

We will next consider the case where concentrational expansion may not be disregarded. As before we let $u = 0$ and $T = T(x)$. We will assume, in addition, that the thermodiffusion term in Eq. (1) can be written as $(\alpha/T_0)c_0(1 - c_0)(dT/dx)$. With the introduction of new variables $v' = v$, $c' = c - c_0$, $T' = T - T_0$, and $P' = P - g\rho z$, this system of equations becomes

$$\frac{dP'}{dz} = Gr T' + Rc' - \frac{v'}{k},$$

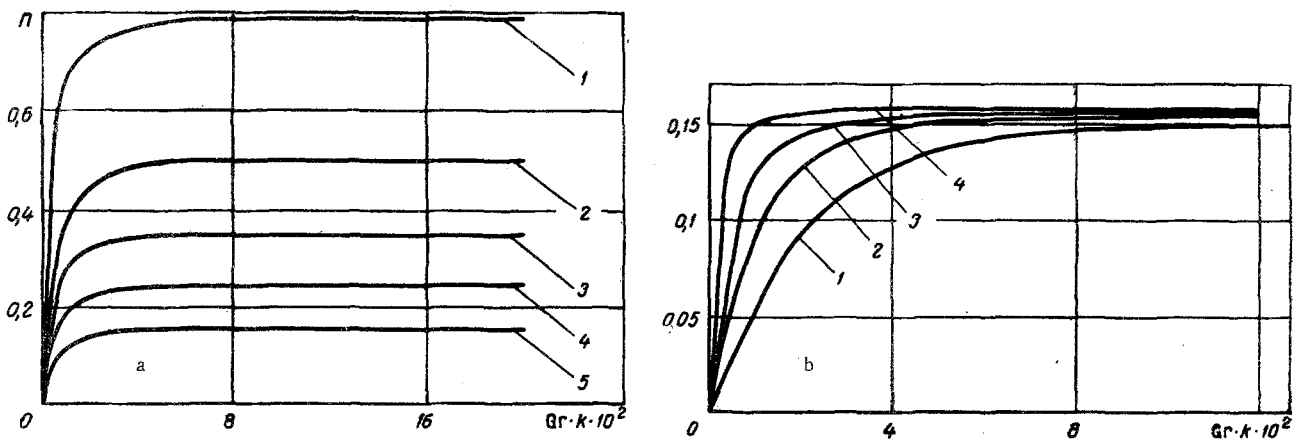


Fig. 2. The value of n as a function of $Gr \cdot k$ according to Eq. (16): a) for $Sm = 350$ and $Rs/Gr = 0.25$ (1), 0.1 (2), 0.05 (3), 0.025 (4), 0.01 (5), and b) for $Rs/Gr = 0.01$ and $Sm = 100$ (1), 350 (2), 500 (3), 1000 (4).

$$v' \frac{\partial c'}{\partial z} = Sm^{-1} \left(\frac{\partial^2 c'}{\partial x^2} + \frac{\partial^2 c'}{\partial z^2} \right), \quad (10)$$

$$\frac{d^2 T'}{dx^2} = 0.$$

Here d , v/d , $\theta = (T_2 - T_1)/2$, and $\rho v^2/d^2$ have been used as the scale quantities for distance, velocity, temperature, and pressure, respectively. The boundary conditions under the given assumptions are

$$\int_{-1}^1 v' dx = 0,$$

$$T'(-1) = -1, \quad T'(1) = 1,$$

$$\left(\frac{\partial c'}{\partial x} - s \frac{dT'}{dx} \right)_{\pm 1} = 0, \quad (11)$$

$$\int_{-1}^1 \left(v' c' - Sm^{-1} \frac{\partial c'}{\partial z} \right) dx = 0.$$

The solution to Eqs. (10) with the boundary conditions (11) will be written out in the form:

$$T' = x, \quad (12)$$

$$v' = \frac{k(Gr + Rs)}{n \operatorname{ch} n} \operatorname{sh} nx, \quad (13)$$

$$c'(x; z) = \kappa z + \frac{\frac{Gr}{R} + s}{n \operatorname{ch} n} \operatorname{sh} nx - \frac{Gr}{R} x. \quad (14)$$

The magnitude of the lengthwise concentration gradient appears to be constant and it is determined from the last boundary condition:

$$\int_0^1 v' c' dx = \frac{2\kappa}{Sm}; \quad (15)$$

Integrating (15) gives

$$\frac{1}{n^4} \left[\left(1 + \frac{Rs}{Gr} \right) \left(\operatorname{th}^2 n + \frac{\operatorname{th} n}{n} - 1 \right) + 2 \left(\frac{\operatorname{th} n}{n} - 1 \right) \right] = \frac{2}{Gr^2 \left(1 + \frac{Rs}{Gr} \right) Sm^2 k^2}. \quad (16)$$

For low values of n expression (16) can be rewritten as

$$n^2 = \frac{\frac{Rs}{Gr}}{\frac{3}{\left(1 + \frac{Rs}{Gr}\right) Gr^2 Sm^2 k^2} + \frac{2}{5} \left(1 + 2 \frac{Rs}{Gr}\right)} \quad (17)$$

Unlike columns without filler, columns with a filler have a lengthwise concentration gradient κ which, in the case of liquids, depends on θ and this is explained by the lengthwise diffusion evident in such columns.

The transcendental equation (16) has been solved numerically on a computer. The value of n as a function of the Grashof number is shown in Fig. 2a for various values of the parameter Rs/Gr and in Fig. 2b for various values of the parameter Sm .

NOTATION

v	is the effective velocity of the mixture;
u	is the horizontal component of the velocity;
v	is the vertical component of the velocity;
T	is the absolute temperature;
$T_0 = (T_1 + T_2)/2$	is the average temperature of the mixture;
c	is the concentration;
c_0	is the initial concentration;
P	is the pressure;
ρ	is the density of the mixture;
μ	is the dynamic viscosity;
ν	is the kinematic viscosity;
$\beta = (1/\rho)(\partial\rho/\partial T)$	is the thermal expansivity;
$\gamma = -(1/\rho)(\partial\rho/\partial c)$	is the concentrational expansivity;
D	is the diffusivity;
α	is the thermal diffusivity;
χ	is the thermodiffusion coefficient;
k	is the permeability;
ζ	is the sinuosity;
ε	is the clearance ratio;
x	is the horizontal coordinate;
z	is the vertical coordinate;
g	is the acceleration of free fall;
B	is the width of working clearance;
q_f	is the partition index of a column with a filler;
q_0	is the partition index of a column without filler;
H, K_c, K_d	are coefficients in the transfer equation (7);
$Gr = g\beta d^3 \theta / \nu^2$	is the Grashof number;
$R = g\gamma d^3 / \nu^2$;	
$Sm = \nu\zeta/D$	is the Schmidt number;
$s = \alpha \theta c_0(1 - c)/T_0$;	
$\kappa = \partial c/\partial z$;	
$n^2 = g\gamma d^3 \kappa \zeta / \nu D$.	

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