SECOND-ORDER APPROXIMATIONS TO CONCENTRATION
BOUNDARY LAYER IN A LIQUID-LIQUID SYSTEM

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This note is a supplement of our previous article\(^\text{10}\), in which similar solutions for concentration boundary layer based on linear velocity profile were given. But in that analysis effects of interfacial curvature on mass transfer were not allowed for. In second-order approximations it has been shown that effects of interfacial vorticity, longitudinal and transverse curvature of the interface are of the same order of magnitude\(^4,8,12\).

The present analysis concerns second-order approximations to concentration boundary layer in laminar liquid-liquid systems, and similar perturbation solutions for mass transfer are presented.

1. Analysis

1.1 Basic equations and their transformation

Figure 1 shows the coordinate system, where \( r \) and \( \kappa \) are defined as

\[
\begin{align*}
    r(x,y) &= r_0(x) + y \cdot \cos \theta \\
    \kappa \cdot \cos \theta &= -d^2 r_0(x)/dx^2
\end{align*}
\]

It is assumed that the solute concentrations, \( \omega_{AB} \) and \( \omega_{A,B} \), at the interface and in the bulk stream respectively, are constant. Mass transfer rate is assumed to be so small that it does not affect the flow pattern and that all physical properties are also constant. Our considerations are restricted to mass transfer resistance in the outer region around the interface in Fig. 1.

The steady incompressible velocity field within the concentration boundary layer is approximated by

\[
u = u_0(x) + b(x) \cdot y + c(x) \cdot y^2
\]

where \( b \) and \( 2c \) are the interfacial velocity gradients of the first and second order, respectively. All values of \( u_0 \), \( b \), and \( c \) are assumed to be given.

The linear velocity approximation \((c=0)\) gives sufficiently accurate estimates for mass transfer rates in the case of large \( u_0 \) and small \( D \), but not for small \( u_0 \) and large \( b \). The quadratic profile of the tangential velocity is appropriate for second-order approximation in general liquid-liquid systems.

Fig. 1 Coordinate system

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According to van Dyke\textsuperscript{11}, the boundary-layer equation for solute concentration is written as

\[
\frac{\partial}{\partial x} (r^2 u \omega_x) + \frac{\partial}{\partial y} (r^2 v (1 + \kappa y) \omega_x) = -D \frac{\partial}{\partial y} \left[ r^2 (1 + \xi y) \frac{\partial \omega_x}{\partial y} \right]
\]  

(4)

The continuity equation is

\[
\frac{\partial}{\partial x} (r^2 u) + \frac{\partial}{\partial y} (r^2 (1 + \xi y) v) = 0
\]  

(5)

where \( j=0 \) for two-dimensional and \( j=1 \) for axisymmetric systems. Dimensionless variables are introduced:

\[
\eta = \frac{y}{\delta(x)}
\]  

(6)

\[
\xi = \int_0^x \left( r^2 u_0 / L^3 U \right) dx
\]  

(7)

where \( \delta \) is an undetermined function of \( x \). By the use of Eqs. (3), (5), (6) and (7), Eq. (4) is rewritten as

\[
\phi''(1 + 2\eta) + \phi'(\alpha \eta + \beta \eta^2 + \gamma \eta^3 + \varepsilon \eta^4) + k_1 + k_2 (k_3 + k_4) \eta + k_5 (k_3 + k_4) \eta^3 = 0
\]  

(8)

where the primes denote partial differentiation with respect to \( \eta \), and \( \alpha, \beta, \gamma \) and \( \varepsilon \) are defined as

\[
\alpha = D u, \delta \beta = \int_0^x \frac{r^2 u_0}{r / w_x} \, dx
\]  

(9)

\[
\beta = \int_0^x \left( r^2 u_x \cos \theta / r \right) \delta \beta \, dx + \int_0^x \left( r^2 b + u_x \cos \theta / r \right) \delta \beta \, dx
\]  

(10)

\[
\gamma = \int_0^x \left( c + r b \cos \theta / r \right) \delta \gamma \, dx + \int_0^x \left( r^2 c + r b \cos \theta / r \right) \delta \gamma \, dx
\]  

(11)

\[
\delta = \int_0^x \left( r^2 \delta \right) / r \, dx + \int_0^x \left( r^2 b + u_x \cos \theta / r \right) \delta \beta \, dx
\]  

(12)

The primes in Eqs. (9) to (12) denote differentiation with respect to \( x \). The parameters, \( k_i \) and \( k_r \), in Eq. (8) are of longitudinal and transverse curvatures and \( k_i \) and \( k_r \) are of the velocity gradients of the first and second order, respectively. They are:

\[
k_i \equiv \int_0^x \left( r^2 u_0 / L^3 U \right) dx
\]  

(13)

\[
k_r \equiv \int_0^x \left( r^2 u_0 / L^3 U \right) dx
\]  

(14)

\[
k_i \equiv \delta \beta / b
\]  

(15)

\[
k_r \equiv \delta \beta / b
\]  

(16)

As \( \delta(x) \) is an undetermined function, one can assign an arbitrary constant to \( \alpha \) and can define by Eq. (9). We set \( \alpha = 1/2 \), then:

\[
\delta \equiv \sqrt{D} \left( \int_0^x r^2 u_0 dx \right)^{1/2} / (r u_x)
\]  

(17)

The parameter, \( \delta \), is a measure of the thickness of the concentration boundary layer if \( u = u_x \).

By the use of Eq. (17), \( \beta, \gamma \) and \( \varepsilon \) in Eqs. (10) to (12) are rewritten as

\[
2\beta = (k_3 + k_4)(1 + p_i)
\]  

(18)

\[
3\gamma = k_3 (k_5 + k_4)(1 + p_i + p_e + p_i)
\]  

(19)

\[
4\varepsilon = k_3 k_5 k_4 (1 + p_s + p_e + p_i)
\]  

(20)

where

\[
p_{me} = \frac{2e}{k_m + k_a} \cdot \frac{d}{d\xi} (k_m + k_a)
\]  

(21)

when \( n = m \), we set \( p_{me} = p_m \).

1.2 General similar equation and perturbation equations

We consider a flow pattern and the shape where all \( k_i \)'s are constant. Then \( \phi \) can be a function only of \( \eta \). Under the boundary conditions, \( \phi = 0 \) at \( \eta = 0 \) and \( \phi = 1 \) at \( \eta \to \infty \), Eq. (8) becomes:

\[
\phi''(1 + 2\eta) + \phi'(\beta \eta + \gamma \eta^3 + \varepsilon \eta^4) + k_1 + k_2 (k_3 + k_4) \eta + k_5 (k_3 + k_4) \eta^3 = 0
\]  

(22)

In general, the orders of magnitude of \( k_i \)'s are not known. By the use of order of \( \delta \), we assume the following asymptotic expansion:

\[
\phi = \phi_0 + k_3 \phi_1 + k_4 \phi_2 + O(\delta^3)
\]  

(23)

In Eq. (23), \( k_3 \) is included in \( \phi_0 \), the first approximation. It is the reason that we want to incorporate not only the penetration theory\textsuperscript{9} but the Lighthill solution\textsuperscript{10} into the first order approximation.

The perturbation equations on the basis of Eq. (23) are derived from Eq. (22):

\[
\phi'' + (\gamma / 2)(1 + k_3 \eta) \phi_1 = 0
\]  

(24)

\[
\phi'' + (\gamma / 2)(1 + k_3 \eta) \phi_2 = -\phi_0 \eta - \phi_0 (1 + \eta)^2 / (2 \eta + k_3 \eta)^2
\]  

(25)

\[
\phi'' + (\gamma / 2)(1 + k_3 \eta) \phi_3 = -k_1 \phi_0 \eta / (2k_3 \eta)
\]  

(26)

\[
\phi_0 = 0, \phi_0 (\infty) = 1
\]  

(27)

The boundary conditions are:

\[
\phi_0 (0) = 0, \phi_0 (\infty) = 0
\]  

(28)

The linear equations (24) to (27) can be converted to initial value problems\textsuperscript{7} and numerical solutions readily obtained.

1.3 For negative \( b \)

When \( b \) is negative, e.g., the potential flow over a sphere, the tangential velocity, \( u \), here assumed, \( u = u_x \) may become negative for large \( y \) and the integration of Eq. (24) would not converge. To avoid this difficulty, when \( b < 0 \), we set \( u = 0 \) in \( y > y^* \), where \( y^* = u_x / b \).

\[
u = u_x + by + cy^2 (y > y^*)
\]  

(29)

This approximation yields

\[
\phi''(1 + 2\eta) + \phi'(\beta \eta + \gamma \eta^3 + \varepsilon \eta^4) + k_1 - k_2 (2k_3 \eta) - (k_3 + k_4) = 0
\]  

(30)

The perturbation equations are for \( k_3 < 0 \) and \( y > y^* \):

\[
\phi'' + \phi'((4k_3) - \phi_0 (1 + (2k_3) \eta)
\]  

(31)

\[
\phi'' + \phi'((4k_3) - \phi_0 (1 + (2k_3) \eta)
\]  

(32)

\[
\phi'' + \phi'((4k_3) - \phi_0 (1 + (2k_3) \eta)
\]  

(33)
These are to be solved with Eqs. (24) to (27) for \( y \leq y^* \).

2. Results and Discussion

The initial value problem of the perturbation equations was numerically solved by the Runge-Kutta procedure. Numerical results are shown in Fig. 2 for \( b > 0 \) and in Fig. 3 for \( b < 0 \), respectively. Asymptotic solutions for large and small \( k_b \) can analytically obtained and their values well agree with numerical results. Numerical empirical equations were derived by combinations of these limiting solutions and numerical results (see Appendix).

Contribution of the quadratic term in the velocity profile to \( \phi'(0) \) is significant only when \( k_b \) is sufficiently large, while the contribution may be of higher order approximation and negligible for small \( k_b \). For zero interfacial velocity (solid-fluid systems) Chao has proposed non-similar universal functions, which improve Lighthill’s solution.

The second order solutions given here may be usually small in liquid-liquid mass transfer, because diffusivities in liquid phases are small. However, the interfacial velocity may be appreciably retarded when the adjacent phase is highly viscous. Then the penetration theory is not suitable and at least the effect of \( k_b \) on mass transfer should be taken into account. This correction was incorporated into the first order approximation, \( \phi'(0) \), in the present analysis.

Similar solutions cannot be applied exactly to most actual cases, especially to liquid-liquid systems. But the similar solutions make the first term in asymptotic expansion of Merk’s type in non-similar systems. The hypothesis of local similarity, which is a direct application of the similar solutions to non-similar systems, often gives good results.

Conclusion

If the shape of interface and the velocity profile over the interface are given, we can calculate mass transfer rates for similar systems, using Figs. 2 or 3. The parameters, \( k_i \)'s and \( \sigma \), can be calculated for a given shape and velocity profile.

Appendix: Numerical Empirical Equations of the First- and Second-Order Approximations

Using Churchill and Usagi’s method we obtain the first-order approximations:

\[
\phi_i(0) = (1 + 0.717/k^3_b)^{3/7} (k_b \geq 0) \quad (A-1)
\]

\[
\phi_i(0) = (1 + 5.64/k^3_b)^{8/17} (k_b < 0) \quad (A-2)
\]

Maximum errors of these equations were estimated to be less than 1\%. The second order equations are:

for \( k_b \geq 0 \)

\[
\phi_1(0) = 0.424 + 0.0472(1 + 0.679/k^3_b) - \frac{6}{5} \quad (A-3)
\]

\[
\phi_2(0) = 0.189(1 + 0.716/k^3_b) - \frac{6}{5} \quad (A-5)
\]

for \( k_b < 0 \)

\[
\phi_1(0) = 0.212(1 + 9.24|k_b|^{12/5}) - \frac{5}{6} \quad (A-7)
\]

\[
\phi_2(0) = -(6k_b)^{-4}(1 + 0.136/k^3_b)^{-1.16} (k_b < -0.1) \quad (A-8)
\]

\[
\phi_2(0) = 0.282k_b(1 - 2.57k_b) (-0.1 < k_b < 0) \quad (A-9)
\]

Maximum errors of these equations were estimated to be less than 1\%, except for \( \phi_2(0) \). Maximum error of Eqs. (A-5, 8, 9) is about 5\%.

Acknowledgment

The authors wish to thank the Computer Center of University of Osaka Prefecture. All the numerical calculations in this study were carried out with the TOSBAC 5600-120 at the Center.

Nomenclature

- \( b \) = \( \frac{\partial u}{\partial y} \) \[1/\text{sec}\]
- \( c \) = \( \frac{\partial^2 u}{\partial y^2} \) \[1/\text{cm} \cdot \text{sec}\]
- \( D \) = diffusivity \[\text{cm}^2/\text{sec}\]
- \( j \) = \( j \) for two-dimensional and 1 for
- \( k_b \) = velocity gradient parameter
- \( k_2 \) = second order velocity gradient parameter
- \( k_3 \) = longitudinal curvature parameter
- \( k_t \) = transverse curvature parameter
- \( L \) = characteristic dimension \[\text{cm}\]
- \( Pe \) = Peclet number
- \( p_m \) = non-similar parameter, defined by Eq. (21) \[\text{cm}\]
- \( r \) = defined by Eq. (1)
CREEP CONSTANTS IN EXPRESSION OF COMRESSIBLE SOLID-LIQUID MIXTURES

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Introduction

Increasing interest in filter-cake dewatering1,5,6 has been shown in industry. In expression of solid-liquid mixtures, dewatering proceeds rather rapidly at the beginning of expression and becomes slow with elapsed time. Especially in the later period, deliquoring proceeds at a very slow speed which is mainly dependent upon the creep effects of the solid materials in the mixture. In recent studies5-8 of constant-pressure expression, it has been shown that the whole process of expression of solid-liquid mixtures can be accurately analysed by introducing the empirical creep constants \( B \) and \( \eta \) on the basis of an elaborate consolidation theory based upon the so-called Terzaghi-Voigt combined model. For a better understanding of the intrinsic nature of expression mechanisms based upon the Terzaghi-Voigt model, further experimentation on the creep constants of \( B \) and \( \eta \) may be needed.

The objective of this paper is the experimental investigation of the effects on the creep constants \( B \) and \( \eta \) of operating factors in expression operations.

1. Experiments

For studying the changes in the values of \( B \) and \( \eta \) due to applied pressure \( p \) and initial average void ratio \( e_{1,AV} \) of expression materials, expression experiments with both filter cakes and semi-solid materials are conducted under constant-pressure conditions. Three kinds of materials, Korean kaolin, 50 wt. % Mitsukuri Gairome clay-50 wt. % Standard Super-Cel mixture, and Solka Floe (BW-200), are used, their properties being tabulated in Table 1. Compression permeability cells (6.0 and 5.4 cm inside diameter) are used, and the decrease in thickness \((L - L_x)\) at a time \( t \) is measured by dial gauges. The expression pressure used in this work ranges from 0.4 up to 196 Kg-force/cm².

2. Experimental Results and Discussion

Consolidation mechanisms occur in two phenomena of void decrease3,4,8. In view of the fact that the decrease in a local void ratio consists of the so-called primary and secondary consolidation and that the rheological constitution can approximate to the