

NUMERICAL ANALYSIS OF INTER-PHASE MASS TRANSFER WITH CHEMICAL REACTION

Nigus Gabbiye, Nurelegne Tefera and Daggupati Venkata Narasaiah
Department of Chemical Engineering
Addis Ababa University

ABSTRACT

The numerical analysis in the present study simulates interphase mass transfer with chemical reaction of two immiscible liquids by simultaneously solving the Higbie Penetration model. The transport equations are solved numerically for concentration and temperature profiles at the inter-phase using finite volume method (FVM) for diffusion, and convection – diffusion equations with and without chemical reaction. The simulation results are validated using experimental data reported in the literature [1] for Cyclohexane - Acetic acid – Water system. The concentration variation along the horizontal direction is smaller compared to vertical direction.

Keywords: Inter phase mass transfer, mass transfer with chemical reaction, mass transfer without chemical reaction, finite volume method

INTRODUCTION

Reactions occurring at the inter phase between two immiscible liquids is very important in heterogeneous catalysis and separation processes. Such as in solvent extraction process, reactive distillation and phase transfer catalysis. This interfacial phenomenon is associated with momentum, energy and mass transfer at the interphase and they are attributed to local gradients of interfacial tension called Marangoni effects [1,2]. Gradients in interfacial tension are caused because of gradients in reactant and product or surfactant concentration and temperature changes within the interface [3].

Liquid-Liquid systems are hydrodynamically unstable leading to formation of wave's slugs and pulses. In addition, the interfacial instability generated near the gas-liquid or liquid-liquid interface results in the appearance of convective flows, which increase significantly the transfer coefficients [4, 5]. Knowledge about the parameter affecting the hydrodynamic instability in the fluid-fluid systems helps us in better design of reactors and separation columns. The parameters affecting the hydrodynamic instability are density difference and surface tensional changes due to concentration

gradients [3, 6] and the concentration gradients deepen with simultaneous mass transfer with chemical reaction.

Concentration gradients in the liquid-liquid system can be measured using the following experimental techniques namely, potentiometer or optical measurements (Laser Induced Fluorescence (LIF)) etc. These experimental methods are economically expensive and time consuming to get the concentration gradients at the liquid-liquid interface. Therefore with the help of high-speed computers one can adopt numerical solution method to simulate the concentration changes at the liquid-liquid interface.

It is aimed in the present study to simulate concentration and temperature profiles at the interface between two liquid-liquid systems for mass transfer with and without chemical reaction using one-dimensional diffusion and two-dimensional convection-diffusion equations.

THE TRANSPORT EQUATIONS

To explain the interface phenomena, capillary model is considered. The flow in the capillary is considered to be two-dimensional and the capillary hydraulic diameter is equivalent with a pipe of $d_h = Z = 2z$. It is also assumed that the flow is laminar and is caused by natural convection, which is generated mainly due to density variation, combined with gravity. Density variation and buoyancy driven flows can also result from solute concentration or temperature changes [7, 8].

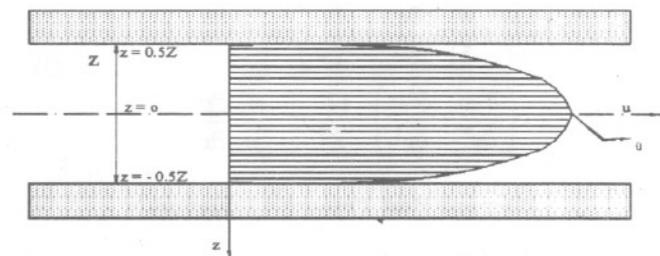


Figure 1 Velocity profile in capillary tube for laminar flow

The following transport equations are developed considering the capillary model and the well-

known mass transfer model, Penetration theory [9, 10].

Momentum Equations

In developing the momentum equation, Boussinesq approximation is used assuming that the variable density ρ can be replaced everywhere by the constant value ρ_o , except in the term $(\rho - \rho_o)g$. The two velocity component developed using capillary model for $u(z)$ and $v(z)$ are substituted in Navier-Stokes equations and evaluated in terms of z in the interval of $\left[-\frac{Z}{2}, \frac{Z}{2}\right]$ to obtain the following expressions [7,11].

$$\frac{\partial \bar{u}}{\partial t} + \frac{6}{5} \left(u \frac{\partial \bar{u}}{\partial x} + v \frac{\partial \bar{u}}{\partial y} \right) = \quad (1)$$

$$v \left(\frac{\partial^2 \bar{u}}{\partial x^2} + \frac{\partial^2 \bar{u}}{\partial y^2} \right) - \frac{12\nu}{Z^2} \bar{u} - \frac{1}{\rho_o} \frac{\partial p}{\partial x}$$

and

$$\frac{\partial \bar{v}}{\partial t} + \left(u \frac{\partial \bar{v}}{\partial x} + v \frac{\partial \bar{v}}{\partial y} \right) = \quad (2)$$

$$v \left(\frac{\partial^2 \bar{v}}{\partial x^2} + \frac{\partial^2 \bar{v}}{\partial y^2} \right) - \frac{12\nu}{Z^2} \bar{v} - \frac{1}{\rho_o} \frac{\partial p}{\partial x} + \frac{\rho}{\rho_o} g_y$$

The above Eqs. (1) and (2) were solved by employing the stream and vortices functions [7]. The pressure term was eliminated by differentiating each term in Eq. (1) in terms of y , and each term in Eq.(2) in terms of x and then subtracting one from the other using the vortices (ω) function. The final momentum equation in terms of vortices function becomes

$$\frac{\partial \omega}{\partial t} + \frac{6}{5} \left(u \frac{\partial \omega}{\partial x} + v \frac{\partial \omega}{\partial y} \right) = \quad (3)$$

$$v \left(\frac{\partial^2 \omega}{\partial x^2} + \frac{\partial^2 \omega}{\partial y^2} \right) - \frac{12\nu}{Z^2} \omega - \frac{g_y}{\rho_o} \frac{\partial p}{\partial x}$$

Mass and Heat Transport Equations

The differential equation of the mass transport with chemical reaction in a control volume for component k is described in a conservation form for constant density and diffusivity as follows.

$$\frac{\partial C_k}{\partial t} + \nabla \cdot (v C_k) = \quad (4)$$

$$\nabla \cdot (D_k \nabla C_k) + v_k M_k r_v$$

For two dimensional problems and constant diffusion coefficient Eq. (4) becomes

$$\frac{\partial C_k}{\partial t} + u \frac{\partial C_k}{\partial x} + v \frac{\partial C_k}{\partial y} = \quad (5)$$

$$D_k \left(\frac{\partial^2 C_k}{\partial x^2} + \frac{\partial^2 C_k}{\partial y^2} \right) + v_k M_k r_v$$

The heat transport equation is also described in conservation form as shown below

$$\frac{\partial(\rho c_p T)}{\partial t} + \nabla \cdot (\rho c_p v T) = \quad (6)$$

$$\nabla \cdot (\lambda \nabla T) + \Phi - \Delta H_R r_v$$

ΔH_R is the molar reaction enthalpy and Φ dissipation function.

In two-dimensional Cartesian coordinate with constant λ and neglected viscous dissipation Φ , the heat transport equation becomes

$$\frac{\partial(\rho c_p T)}{\partial t} + \frac{\partial(\rho c_p u T)}{\partial x} + \frac{\partial(\rho c_p v T)}{\partial y} = \quad (7)$$

$$\lambda \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - \Delta H_R r_v$$

Heat loss to the surrounding through both walls of the capillary can be described based on the reaction volume of the capillary and width Z by

$$q = -\frac{2U_o}{Z} (T_i - T) \quad (8)$$

The heat transport equation for constant specific heat capacity c_p and density ρ_o using Boussinesq approximation and continuity equation can be written as

$$\frac{\partial T}{\partial t} + u \frac{\partial T}{\partial x} + v \frac{\partial T}{\partial y} = a \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) \quad (9)$$

$$- \frac{1}{\rho_o c_p} \left[\Delta H_R r_v - \frac{2U_o}{Z} (T_i - T) \right]$$

The temperature coefficient is given as $a = \lambda / (\rho_o c_p)$

The above equations are developed for the two bulk phases (Fig.2) assuming that equilibrium is attained at the inter phase of the two liquids. The two bulk phase equations are coupled by a distribution coefficient for mass balance Eq. [12].

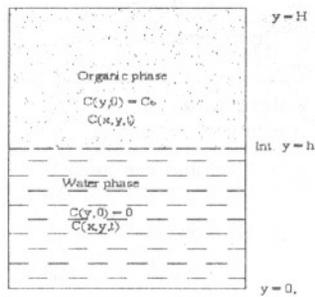


Figure 2 Two-dimensional representation of the capillary space

NUMERICAL SIMULATION

Various discretisation schemes are used depending up on the type of problem selected to discretise the transport equations namely central differencing, up-wind, hybrid and power law schemes. In the present study, first order backward differencing and central differencing scheme are used for time variation and momentum equations respectively. For mass and heat transport equations the discretisation equations are derived using the concept of up-wind differencing scheme and power law scheme over the control volume shown below [13,14].

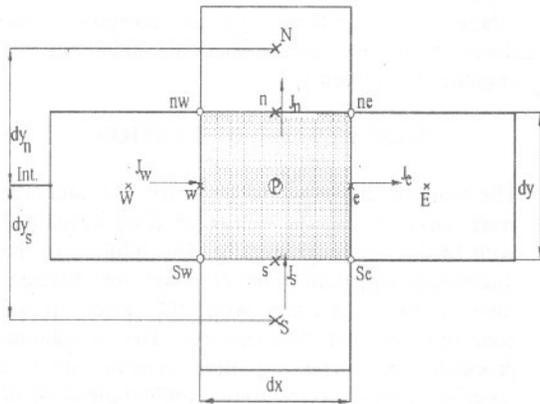


Figure 3 Control volume for the discretisation of mass and heat transport equations

After implementing the above discretisation techniques, the transport equations Eqs.(3), (5) & (9) have the following form.

Vorticity:

$$a_p \omega_p^m = a_E \omega_E^m + a_W \omega_W^m + a_N \omega_N^m + a_S \omega_S^m + a_{EE} \omega_{EE}^m + a_{WW} \omega_{WW}^m + a_{NN} \omega_{NN}^m + a_{SS} \omega_{SS}^m + a^{m-1} \omega_p^{m-1} + b \tag{10}$$

Mass:

$$a_p C_p^m = a_e C_e^m + a_w C_w^m + a_n C_n^m + a_s C_s^m + a^{m-1} C_p^{m-1} + b \tag{11}$$

Heat:

$$a_p T_p^m = a_e T_e^m + a_w T_w^m + a_n T_n^m + a_s T_s^m + a^{m-1} T_p^{m-1} + b \tag{12}$$

All the coefficients of the above equations are summarized in Appendix A. The solution of the resulted discretisation equations is dependent on the boundary and initial conditions. The boundary conditions for both vertical and horizontal boundaries are reported in Table 1. For mass and heat transport equations, the flux at the horizontal (bottom and top) sides of the capillary is considered to be zero, and constant value for stream function. At the vertical boundaries symmetrical boundary conditions were taken.

The solution of one-dimensional diffusion transient equation was used for initial conditions. But it is also possible to use any random values for iteration process in such a way that the selection of the initial value should facilitate the final iteration. The resulting discretisation equations are rearranged in the matrix form and shown in Eq. 4.

Table 2: Parameter used for the numerical analysis

Component	Diffusivity (m^2s^{-1})	Thermal conductivity (w/m.k)	Heat capacity (J/kg.k)	Viscosity (Ns/m^2)
Water solution	0.88×10^{-9}	0.609	4186	0.9×10^{-3}
Cyclohexane	1.17×10^{-9}	0.135	1263	1.7×10^{-3}
Heat of reaction ($\Delta H = -1067 kJ/kg^{-1}$)	Distribution Coefficient ($N = 168$)			

Validation of the Simulation Results

The numerical simulation results obtained in the present study were validated comparing with the experimental results reported in the literature [1] and also with the analytical solution for one-dimensional diffusion equation. The validation results are shown in Figs. 5 and 6 for literature data [1] and for analytical solution respectively. It is observed from the figures that the numerical results obtained in the present study are in good agreement with the experimental data reported in the literature as well as analytical solution. The average absolute error is less than 2 percent in both the cases.

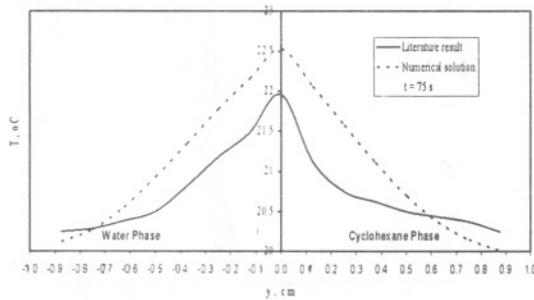


Figure 5 Comparison of temperature profiles at the inter phase with literature data [1].

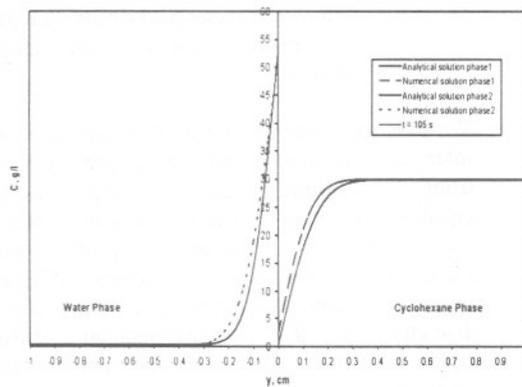


Figure 6 Comparison of concentration profiles at the inter phase with one-dimensional diffusion equation for mass transfer without chemical reaction with an analytical solution.

Simulation of Concentration Profiles:

Mass Transfer without Chemical Reaction

The numerical results were simulated for the concentration profiles at the inter phase with one-dimensional and two-dimensional diffusion equations without reaction term for mass transfer without chemical reaction. The numerical results with one-dimensional diffusion are shown in Fig. 7 and with analytical solution in Fig. 8. One-dimensional diffusion equation was considered because the variation of concentration along the horizontal direction is small compared to the vertical direction. It was assumed that there is no acetic acid in the water phase initially and the acetic acid transfers through the interface from cyclohexane phase to the water phase. The concentration of the diffusing component (acetic acid) decreases from its initial concentration (C_o) in the bulk phase of cyclohexane to the interface and starts increasing its concentration in the water phase with time. It is also observed from the figures that the analytical and numerical results shows similar trend for different time intervals.

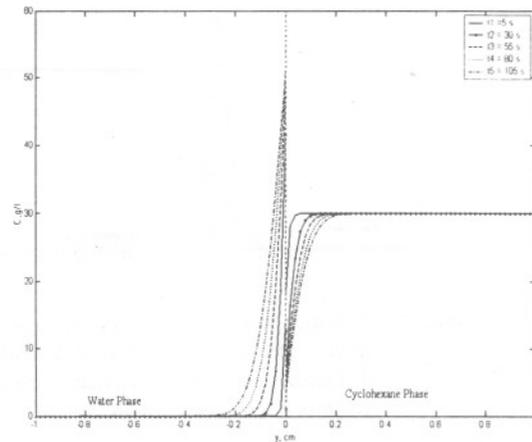


Figure 7 Numerical simulation of concentration profiles at the inter phase with one-dimensional diffusion equation for mass transfer without chemical reaction.

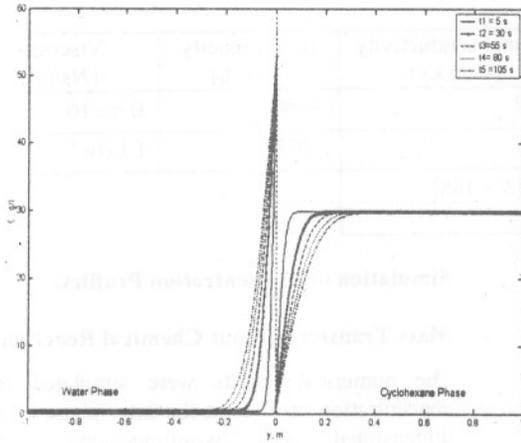


Figure 8 Analytical solution of concentration profiles at the inter phase with one-dimensional diffusion equation for mass transfer without chemical reaction.

The average concentration profiles at the interphase with two-dimensional diffusion equation for mass transfer without chemical reaction are shown in Fig. 9. The average concentration profiles were taken averaging the concentration distribution along the vertical direction. It is observed from the Figs. 7 and 9 that with two-dimensional diffusion equation, the concentration profiles are flat and this is due to the lateral diffusion of the diffusing component on the concentration distribution.

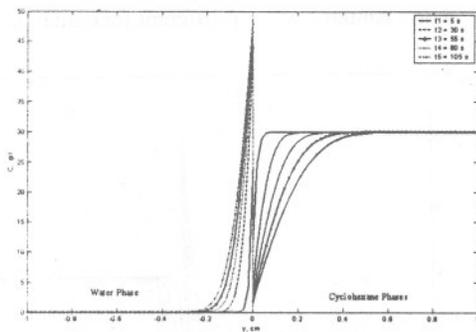


Figure 9 Average concentration profiles at the inter phase with two-dimensional diffusion equation for mass transfer without chemical reaction

Mass Transfer With Chemical Reaction

The reaction considered in the present study has the Hatta number of 10 for mass transfer with chemical reaction. Reactions are considered to be fast, if the value of Hatta number is greater than 2. Hence, the possibility of the diffusing component to penetrate the second phase compared to mass transfer with out chemical reaction is very small. The simulated results for the concentration profile at the inter phase with two-dimensional diffusion equation is shown in Fig. 10 assuming that the reaction occurs only at the inter phase. It is observed from the Figs 9 and 10 that the concentration distribution in the water phase is smaller with chemical reaction compared to mass transfer without chemical reaction.

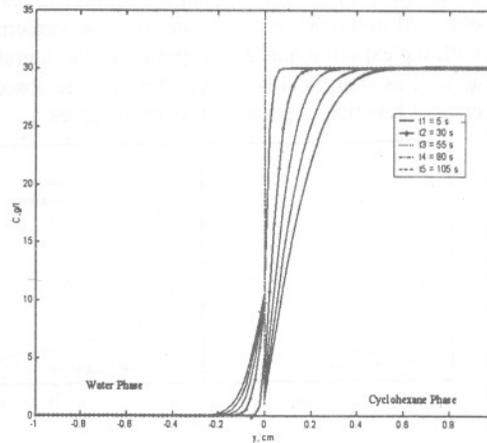


Figure 10 Concentration profiles at the inter phase with one-dimensional diffusion equation for mass transfer with chemical reaction.

The average concentration profiles simulated at the inter phase for mass transfer with chemical reaction using two-dimensional convection-diffusion equation are shown in Fig.11. It is observed from the figure that the concentration profile obtained for diffusion - convection discretisation equations is not as smooth as the profile obtained from the discretisation of two-dimensional diffusion equations. This is due to the incorporation of the convective term in the discretisation equations.

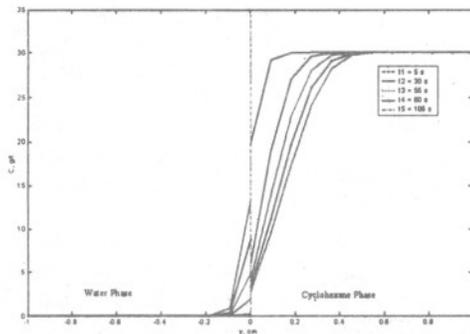


Figure 11 Average concentration profiles at the inter phase with two-dimensional convection-diffusion equation for mass transfer with chemical reaction.

Simulation of Temperature Profile

The temperature distribution is resulted due to the heat generated at the interface of the two liquids by chemical reaction. The heat generated at the interphase has to be transported to the two bulk phases by diffusion as well as convection mode of heat transfer. One-dimensional simulation of heat equation for temperature distribution at the inter phase is shown in Fig. 12 for different time intervals. It is seen from the figure that the temperature profile increases with increasing time. This is because the heat generated by the reaction is greater than the heat lost to the surrounding in the capillary space considered.

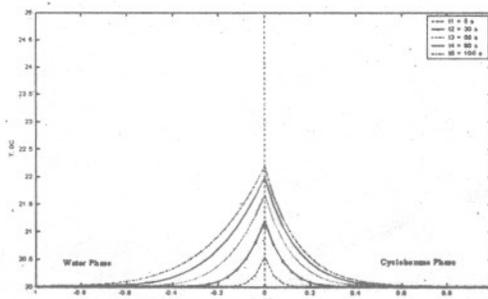


Figure 12 Temperature profiles at the inter phase with one-dimensional diffusion equation for mass transfer with chemical reaction.

The temperature distribution in both the phases is similar because the thermal diffusivity coefficients of the two fluids are nearly equal. It is also observed from the figure that there is a difference on the growth rate of the temperature distribution and the difference increases as the thermal

diffusivity differences of the two liquids become higher and higher.

The temperature distribution of two-dimensional discretisation equations is shown in Fig.13. It is observed from the figure that the temperature distribution is not the same for the two coordinate systems, i.e. the temperature variation along the vertical direction is higher than the temperature variation along the horizontal direction.

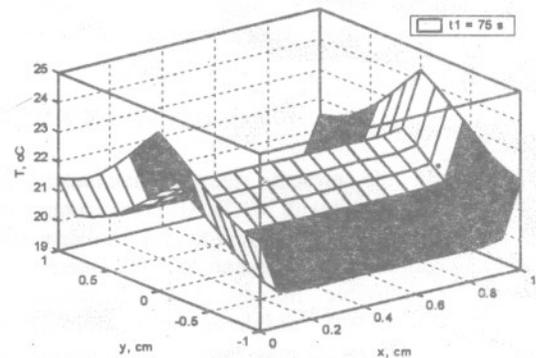


Figure 13 Temperature profiles at the inter phase with two-dimensional equation for mass transfer with chemical reaction. The water phase is in the negative and the Cyclohexane phase is in the positive side of the axis.

Averaging the temperature variation along the horizontal direction for each row along the vertical direction for two dimensional discretisation equations is shown in Fig. 14. It is observed from the figures that the temperature profile for one dimension is sharper than that of two-dimensional discretisation equations. On the other hand, the temperature distribution of two dimensional discretisation equations is flat compared to the distribution of one dimensional discretisation equation. This may be due to the incorporation of convective term in the heat transport equations. The convective mode of heat transport is much faster than the conductive transport. Due to this the temperature distribution in two dimensional discretisation equations becomes flat. The maximum temperature occurs at the interphase of the two liquids for both one and two dimensional discretised equations.

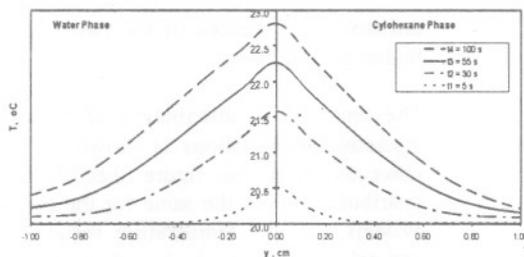


Figure 14 Average temperature profiles at the interphase with two-dimensional equation for mass transfer with chemical reaction.

CONCLUSIONS

In the present study, a computer code was developed with MATLAB programming to analyze the concentration and temperature distribution of a diffusing component at the interface of two immiscible liquids. Two-dimensional capillary space was considered to develop the transport equations for mass, heat and momentum equations. The analysis has been made using numerical discretised technique; the finite volume method and based on the observations the following conclusions were drawn.

The concentration profile of the diffusing component (acetic acid) obtained from the numerical solution is in good agreement with the analytical solution of one dimensional diffusion equation.

The concentration variation along the horizontal direction is very small compared to vertical direction and also the concentration profiles are flat two-dimensional convective-diffusion equation than without convective term. This leads to the conclusion that the diffusing component is dominantly transferred in the direction perpendicular to the interface.

The maximum temperature occurs at the interface of the two fluids because the heat is being generated at the interface due to chemical reaction.

The temperature gradient of one dimensional discretisation equation is sharper than two dimensional discretisation equations.

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APPENDIX A

A1. The discretisation coefficients for the vorticity Eq. (10).

$$a_E = \frac{\nu}{\delta x^2} + \frac{12}{5\delta x} \max(-u_p, 0),$$

$$a_W = \frac{\nu}{\delta x^2} + \frac{12}{5\delta x} \max(u_p, 0),$$

$$a_N = \frac{6(\delta y_N + \delta y_{NN})}{5\delta y_N \delta y_{NN}} \max(-V_p, 0)$$

$$+ \frac{2\nu}{\delta y_N(\delta y_S + \delta y_N)},$$

$$a_S = \frac{6(\delta y_S + \delta y_{SS})}{5\delta y_S \delta y_{SS}} \max(V_p, 0)$$

$$+ \frac{2\nu}{\delta y_S(\delta y_S + \delta y_N)}$$

$$a_{EE} = -\frac{3}{5\delta x} \max(-u_p, 0)$$

$$a_{WW} = -\frac{3}{5\delta x} \max(u_p, 0)$$

$$a_{NN} = -\frac{6}{5} \frac{\delta y_N}{\delta y_{NN}(\delta y_N + \delta y_{NN})} \max(-V_p, 0)$$

$$a_{SS} = -\frac{6}{5} \frac{\delta y_S}{\delta y_{SS}(\delta y_S + \delta y_{SS})} \max(V_p, 0)$$

$$a_P^{m-1} = \frac{1}{\delta t}$$

$$a_P = a_E + a_W + a_N + a_S + a_{EE} + a_{WW}$$

$$+ a_{NN} + a_{SS} + a^{m-1} + \frac{12\nu}{Z^2}$$

$$b = -\frac{g_P}{\rho_{e*}} \left(\frac{\rho_e - \rho_w}{\delta x} \right)$$

A2. The discretisation coefficients for mass transport Eq.(11).

$$a_E = \frac{D\delta y}{\delta x} A(|Pe_e|) + \max(-Fe, 0)$$

$$a_W = \frac{D\delta y}{\delta x} A(|Pe_w|) + \max(F_w, 0)$$

$$a_N = \frac{D\delta x}{\delta y_N} A(|Pe_n|) + \max(-Fn, 0)$$

$$a_S = \frac{D\delta x}{\delta y_S} A(|Pe_s|) + \max(Fs, 0)$$

$$a^{m-1} = \frac{\delta x \delta y}{\delta t}$$

$$b = \nu M_T$$

$$a_P = a_E + a_W + a_N + a_P^{m-1}$$

A3. The discretisation coefficients for heat transport Eq. (12).

$$a_E = \frac{a\delta y}{\delta x} A(|Pe_e|) + \max(-F_e, 0)$$

$$a_W = \frac{a\delta y}{\delta x} A(|Pe_w|) + \max(F_w, 0)$$

$$a_N = \frac{a\delta x}{\delta y_N} A(|Pe_n|) + \max(-F_n, 0)$$

$$a_S = \frac{a\delta x}{\delta y_S} A(|Pe_s|) + \max(F_s, 0)$$

$$a^{m-1} = \frac{2\delta x \delta y}{\delta t}$$

$$a_P = a_E + a_W + a_N + a_S + a^{m-1} + \frac{2U_o \delta x \delta y}{\rho_o c_p Z}$$

$$b = \frac{2U_o \delta x \delta y}{\rho_o c_p Z} T_s$$