

Ionic Mass Transport Correlation of Double-Diffusive Convection in Horizontal Fluid Layers

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Here is investigated the characteristics of double-diffusive convection in thermally-stable stratified horizontal fluid layer. By employing an electrochemical technique, and adopting aqueous $\text{CuSO}_4\text{-H}_2\text{SO}_4$ solution as electrolyte, experiments on ionic mass transfer have been conducted systematically. And, also a new mass transfer correlation in double-diffusive situations has been derived by extending the model of micro-scales of turbulence, which was proposed by Arpaci. The resulting correlation of the Sherwood number as a function of the thermal Rayleigh number and the solutal Rayleigh number was in good agreement with the present experimental results. The present study provides plausible understanding in controlling both mass and heat transfer rates for practical situations including double-diffusive convection.

Key Words : Double-Diffusive Convection, Ionic Mass Transfer, Micro-Scales of Turbulence

Nomenclature

C	: Concentration [mole m^{-3}]	Pe	: Peclet number ($=ud/\alpha_s$) [-]
c	: Concentration fluctuation [mole m^{-3}]	Ra	: Thermal Rayleigh number ($=g\beta d^3 \Delta T / \alpha \nu$) [-]
d	: Characteristic length, or cell depth [m]	Rs	: Solutal Rayleigh number ($=g\beta_s d^3 \Delta T / \alpha_s \nu$) [-]
F	: Faraday constant, 96485 [C/equiv]	Sh	: Sherwood number ($=k_c d / \alpha_s$) [-]
g	: Gravitational constant [m s^{-2}]	T	: Temperature [K]
I	: Current density [A m^{-2}]	u	: Velocity fluctuation [ms^{-1}]
k_c	: Individual mass transfer coefficient [m s^{-1}]	Subscripts	
Le	: Lewis number ($=\alpha_s/\alpha$) [-]	α	: Thermal diffusivity [m^2s^{-1}]
l	: Integral scale [-]	α_s	: Mass diffusivity [m^2s^{-1}]
n	: Valence of transferred ion [-]	β	: Thermal expansion coefficient [K $^{-1}$]
P	: Pressure [Pa]	β_s	: Solutal expansion coefficient [$\text{m}^3\text{mole}^{-1}$]
P_I	: Inertia production rate [m^2s^{-3}]	ϵ	: Dissipation rate [m^2s^{-3}]
P_β	: Solutal buoyant production rate	η	: Kolmogorov length scale [m]
		λ	: Taylor length scale [m]
		ν	: Kinematic viscosity [m^2s^{-1}]
		ρ	: Density [kg m^{-3}]

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1. Introduction

Buoyancy-driven convection in double-diffu-

sive systems has been studied extensively in connection with wide engineering applications such as crystal growth processing, solar ponds and natural gas storage tanks (Turner, 1973; Ostrach, 1983; Chen and Johnson, 1984). It enhances or reduces heat and/or mass transfer rates, of which magnitude depends on the direction of temperature and concentration gradients and the ratio of thermal to solutal diffusivity. But the inherent complexity in convective transport phenomena makes it very difficult to predict the convective fluxes. It is requisite to construct a reasonable model for an accurate prediction of convective transport rates in various double-diffusive systems.

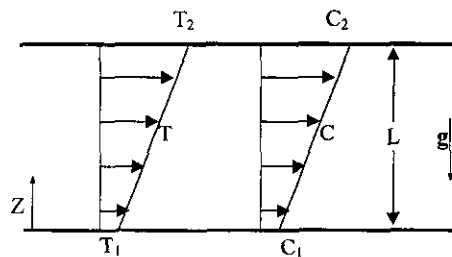
Early theoretical studies on double-diffusive convection focused on the onset of convective instabilities. Nield (1967) examined the linear stability theory to obtain the onset conditions of thermohaline convection in a horizontal fluid layer. Turner (1973) summarized the stability conditions of double-diffusive systems. Kaviany and Vogel (1986), and Yoon et al. (1996) analyzed the stability conditions of double-diffusive system under nonlinear, time-dependent temperature gradient by employing their amplification theory and propagation theory, respectively. In addition to the research activity on the onset of double-diffusive convection, the correlations of heat and/or mass transfer rates were studied experimentally. It can be expected that the transport characteristics of double-diffusive system is quite similar to the typical Rayleigh-Benard system, if the enhanced or reduced effects are taken into account in driving force. The theoretical analysis on transport characteristics in a Rayleigh-Benard system were studied extensively. Howard (1964) proposed the boundary-layer instability model in which the heat transport characteristics is governed by the narrow region near the heated surface for very high Rayleigh number. Busse (1967) improved Howard's concept and Long (1976) and Cheung (1980) proposed a backbone equation to predict heat transfer in horizontal fluid layers. Recently, Arpaci (1997) suggested a new transport model based on the micro-scales of turbulence.

In present study, ionic mass transfer rate in, double-diffusive system is analyzed theoretically and experimentally. We employ a micro-scale turbulence model, which is modified to consider the double-diffusive buoyant terms, as a backbone correlation form. The validity of this model is discussed in comparison with the experimental results in electrochemical ionic mass transfer system.

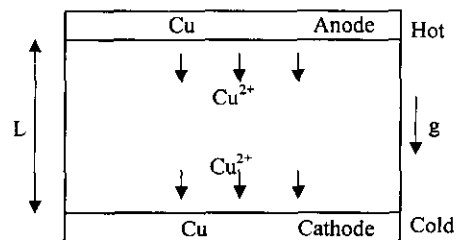
2. Double-Diffusive Convection System

2.1 Experiments

The system of double-diffusive convection used in the present experiments is that of the electrochemical redox reaction of copper ion in aqueous copper sulfate solution with stable thermal stratification. The present double-diffusive system is schematized in Fig. 1. This electrochemical system are widely used in studying buoyancy-driven phenomena because copper sulfate has a reasonable solubility in water and does not form soluble product on the electrode surface (Goldstein et al., 1990). Copper plates are used as both the cathode



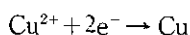
(a) CuSO₄-H₂SO₄ electrolyte cell



(b) Horizontal double-diffusive fluid layer with stable thermal stratification

Fig. 1 Schematic diagram of double-diffusive electrochemical system

and the anode. At the cathode the following reduction reaction occurs:



while the following oxidation reaction proceeds at the anode:



In these experiments sulfuric acid was added as a supporting electrolyte to lessen the migration effect.

The electrochemical cell was constructed as a cubic with two horizontal copper plates with the same area of $\text{cm } 5\text{cm} \times 5\text{cm}$ and four vertical acrylic plates with various depths of 3, 4 and 5cm. The fluid layer is initially quiescent at a constant concentration C_b and stably stratified by a uniform temperature gradient. For stable temperature gradient, the upper surface was heated uniformly with $20^{\circ}\text{C} + \Delta T$ while the lower one was cooled with 20°C by circulating constant temperature water through the copper plates. The electrolyte consists of 0.2M and 0.3M CuSO_4 solutions with 1.5M H_2SO_4 as a supporting electrolyte. Copper ion was deposited on the cathode electrode under the limiting current condition, and was dissolved from the anode one. The electrical informations in the cell were obtained by a PC controlling potentiostat (EG&G Parc.) on line. The calomel reference electrode was used to measure the potential difference between the electrolyte solution and the cathode. The experimental setup is given in Fig. 2.

The ionic mass transfer experiments were carried under the limiting current condition in horizontal electrolyte solution. The typical limiting current under the typical condition is shown in

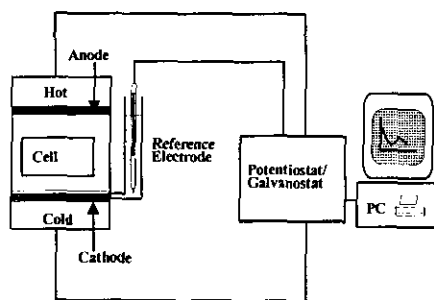


Fig. 2 Experimental setup

Fig. 3. As the potential difference increase, the current flowing between the two electrodes increase sharply at first until the limiting potential difference reaches a certain value. However, above this potential difference, the current rises again. At this stage, the hydrogen ions take part in electrochemical reaction and hydrogen gas bubbles evolve. The plateau where an increase in potential difference causes almost no increase in current is known as the limiting current. Experiments were repeated separately in two different modes of unstable (cathode facing upward) buoyancy-driven convection or stable (cathode facing downward) diffusion for various thermal gradients, cell depths and concentrations of bulk solution. Typical current-time curve is shown in Fig.

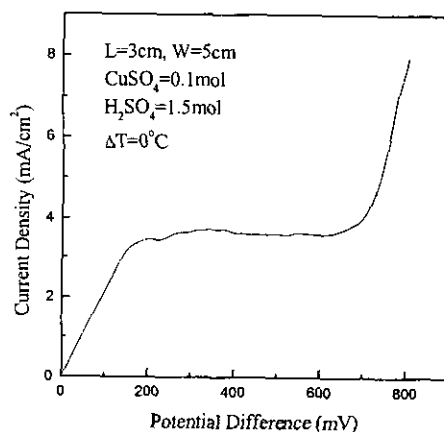


Fig. 3 Typical limiting current curve

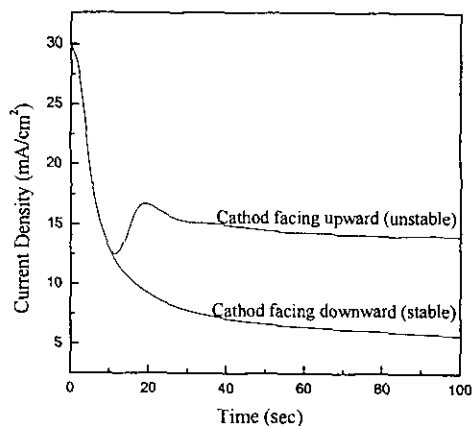


Fig. 4 Current-time behaviors of stable and unstable geometries

4. Two curves are coincident each other at a certain point, where buoyancy-driven motion due to the unstable concentration gradient sets in for unstable geometry. The upside down N-shape of current variations with time shows the peculiar behavior of natural convection in an ionic mass transport. It is considered that the convective flows start at the minimum point of each current curve in detectable manner.

Under the limiting current condition in the electrochemical system, the mass transfer coefficient can be obtained as

$$k_c = \frac{I_{lim}(1-t_n)}{2C_b n F} \tag{1}$$

where k_c is the mass transfer coefficient due to diffusion and convection, t_n is the transference number which explains a migration effect. I_{lim} , n , F and denote the limiting current density, the valence of the transferred ion, Faraday's constant and the bulk concentration of the transferred ion, respectively (Levich, 1962). The mass diffusivity, density and viscosity were calculated by using the correlation of Fenech and Tobias (1960), and Chiang and Goldstein (1991). Then the average Sherwood number Sh based on $(C_2 - C_1)$ with the top concentration $C_2 = C_b$ and the bottom concentration $C_1 = 0$ can be expressed as follows:

$$Sh = \frac{k_c d}{\alpha_s} = \frac{I_{lim}(1-t_n)d}{2C_b \alpha_s n F} \tag{2}$$

As long as the electrode surface is flat and the concentration of copper ion is dilute, a dimensionless correlation based on the boundary layer theory can be reasonably applied to the present double-diffusive convection (Mizushima, 1971).

2.2 Governing equations and parameters

For larger differences of concentrations overcoming thermal stratification between two horizontal boundaries, natural convection sets in due to buoyancy forces. Under this condition the density variation of fluid is assumed to follow the usual equation of state (Nield, 1967).

$$\rho = \rho_0 [1 - \beta(T - T_0) + \beta_s(C - C_0)] \tag{3}$$

where T and C represent temperature and solute concentration. ρ , β and β_s also represent the fluid density, the thermal expansion coefficient and the

solutal expansion coefficient, respectively. The subscript 0 denotes the basic state.

Upon and after the onset of convection, the governing equations of flow and temperature fields are expressed employing the Boussinesq approximation:

$$\nabla \cdot \vec{U} = 0 \tag{4}$$

$$\rho_0 \left(\frac{\partial}{\partial t} + \vec{U} \cdot \nabla \right) \vec{U} = -\nabla P + \mu \nabla^2 \vec{U} + \rho g \vec{k} \tag{5}$$

$$\left(\frac{\partial}{\partial t} + \vec{U} \cdot \nabla \right) T = \alpha \nabla^2 T \tag{6}$$

$$\left(\frac{\partial}{\partial t} + \vec{U} \cdot \nabla \right) C = \alpha_s \nabla^2 C \tag{7}$$

where \vec{U} and P are the velocity vector and pressure. And μ , g , α and α_s denote the viscosity of fluid, the gravitational acceleration, the thermal diffusivity, the mass diffusivity, respectively. The important dimensionless parameters to describe the present system are the solutal Rayleigh number Rs , the thermal Rayleigh number Ra , the Schmidt number Sc , and the Lewis number Le , defined by

$$Rs = \frac{g \beta_s \Delta C d^3}{\alpha_s \nu}, Ra = \frac{g \beta \Delta T d^3}{\alpha \nu}, Sc = \frac{\nu}{\alpha_s}, \text{ and } Le = \frac{\alpha}{\alpha_s} \tag{8}$$

For the present double-diffusion system, it is well-known that the stationary convection can be set in only if $Rs - LeRa > 1708$.

3. Mass Transfer Correlation

3.1 Turbulent mass transfer correlation

For the fully developed turbulent buoyant convection regime, we assume that the buoyancy-driven convection can be described by the two-layer model. The mass transfer resistance is mainly confined within the sublayer next to the each plate. The turbulent properties of flow belong to the core region between the sublayers. The sublayer thickness is assumed to be the Kolmogorov scale, and diffusion in the a core is characterized by the Taylor scale. The schematic diagram of this model is given in Fig. 5. The mean mass flux in the sublayer may be written as

$$m \sim \alpha_s \frac{c}{\eta_c} \sim uc \tag{9}$$

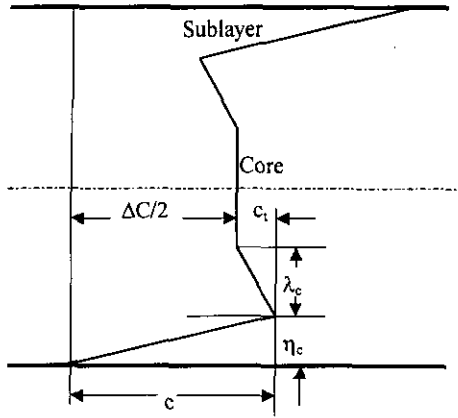


Fig. 5 Schematic diagram of concentration field.

where η_c is the concentration Kolmogorov scale. The above relation means that the order of magnitude of mass flux due to diffusion and convection is nearly same. In the core region, we may neglect the diffusion mass flux with respect to convection mass flux and write the mass flux as follows:

$$m_t \sim u_t c_t \tag{10}$$

where the subscript "t" means the turbulent core region. At the interface of two layers, the heat flux must be continuous, then the following relation can be obtained.

$$m \sim m_t \tag{11}$$

From the turbulent model of Arpaci, the following relation can be assumed:

$$c - c_t = \Delta C \tag{12}$$

By rearranging the above relations, we can derive the following relation

$$Sh = \frac{md}{\alpha_s \Delta C} \sim \frac{(d/\eta_c)}{1 - (d/\eta_c)} \cdot Pe^{-1} \tag{13}$$

where $Pe = u_t d / \alpha_s$ is the turbulent Peclet number.

Based on the micro-scale turbulence model (Arpaci, 1997), we derive a model for the turbulent mass transport of double-diffusive convection in the horizontal fluid layers. From the balance of the mean kinetic energy of velocity fluctuation, the following relation can be obtained.

$$P_\beta \sim P_1 + (-\epsilon) \tag{14}$$

where P_β , P_1 and ϵ denote the solutal buoyant

production, the inertia production and the dissipation term, respectively. This relation means that the buoyant production is partly converted into inertial production and partly into viscous dissipation. The balance of the root mean square of concentration fluctuations has the following form:

$$P_c \sim \epsilon_c \tag{15}$$

In the present double-diffusive system with stable thermal stratification, the balances are adjusted as follows:

$$(g\beta_c C - g\beta\Delta T)u \sim \frac{u^3}{l} + \nu \frac{u^2}{\lambda^2} \tag{16}$$

$$u \frac{c^2}{l} \sim \alpha_s \frac{c^2}{\lambda_c^2} \tag{17}$$

where λ denote the Taylor scale. u , c , θ and l denote the rms-values of velocity fluctuation, concentration fluctuations, temperature fluctuation and the integral scale. From the Squire postulate, it is assumed that $\lambda \sim \lambda_c$. Then the following relation can be obtained;

$$Pe \sim \left(\frac{l}{\lambda_c}\right) \sim \left(\frac{1}{1+Sc}\right) \left(\frac{g\beta_c c - g\beta\Delta T}{\alpha_s^2}\right)^{1/2} \tag{18}$$

Under the assumption of isotropic properties of mechanical and concentration dissipation, the length scales of λ_c and l are replaced with the Kolmogorov scale η_c as;

$$\eta_c \sim (1+Sc)^{1/3} \left(\frac{\alpha_s^2}{g\beta_c - g\beta\Delta T}\right)^{1/3} \tag{19}$$

where the rms-values of concentration fluctuation is assumed to be proportional to the concentration difference ($c \sim \Delta C$). By combining Eqs. (13), (18) and (19), the correlation of the Sherwood number in the layers which experiences simultaneous double-diffusive convection can be obtained as follows:

$$Sh \sim \frac{A(Rs - Le \cdot Ra)^{1/3}}{1 - B(Rs - Le \cdot Ra)^{-1/3}} \tag{20}$$

where A and B are constants which depend on the Schmidt number Sc and should be determined by experiments.

3.2 Correlation of experimental results

An example of double-diffusive convection is demonstrated in Fig. 6 for which electrodeposition of copper ions is carried out at constant

electrostatic potential of each own limiting current in various copper sulfate concentration and temperature difference. As mentioned previously, the geometric position of anode plate determines the occurrence of solute-driven convection regardless of thermal stratification. Comparing these experimental results with a theoretical one, a new correlation of the Sherwood number is proposed for the double-diffusive convection:

$$Sh = \frac{0.0714(Rs - Le \cdot Ra)^{1/3}}{1 - 1.4910(Rs - Le \cdot Ra)^{-1/9}} \quad (21)$$

The coefficients in the above equation have been obtained through the regression analysis of experimental results. Figure 7 shows the comparison of experimental results described by symbols and theoretical ones by curves. It is seen that the

predictive model for the Sherwood number explains the experimental results fairly well.

4. Conclusions

The correlation of the Sherwood number of double-diffusive ionic mass transfer has been proposed in a horizontal fluid layer with stable thermal stratification. For a double-diffusive system the correlation equation has been obtained deterministically by the microscales of turbulence model, and the experiments have been carried out using the electrochemical techniques systematically. In comparison with experimental results the present correlation looks very promising.

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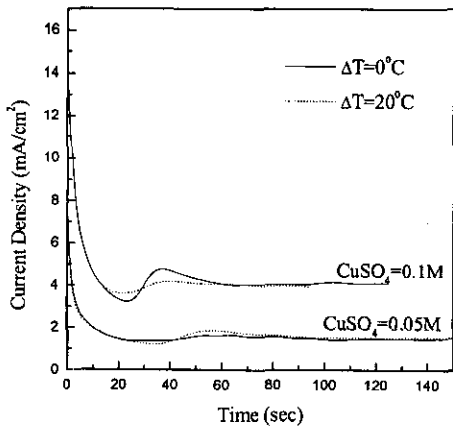


Fig. 6 Effect of thermal stratification on the current density for the unstable geometry

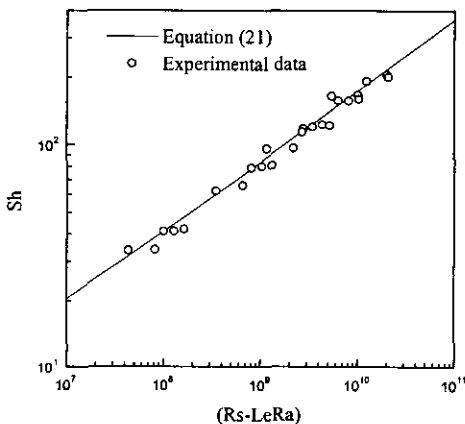


Fig. 7 Comparison of correlation with experiments

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