The Separation of Solutes with Different Diffusion-coefficients by Two-layer Convection

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Synopsis. When a two-layer system which consists of water (upper layer) and an aqueous solution (lower layer) is heated from one side and cooled from the opposite side, a convection starts in each layer. The empirical formula for mass transfer between the convections was studied for a system of water containing a mixture of solutes; the flux of a solute in the mixture was found to be proportional to the square root of the diffusion coefficient of the solute. Therefore, solutes with different diffusion-coefficients can be separated by two-layer convection.

When a two-layer system which consists of water (upper layer) and an aqueous solution (lower layer) is heated from one side and cooled from the opposite side, a convection starts in each layer. We have already studied the system of a solution of one solute and have presented an empirical formula for mass transfer between convections.[1] From this formula, the flux of a solute in a mixture of solutes can be presumed, under certain conditions, to be proportional to the square root of the diffusion coefficient of the solute. Therefore, the separation of solutes may be done by the two-layer convection for a mixture of solutes. The purpose of this investigation is to discuss the possibility of the separation of solutes by this method.

Theoretical

In a previous paper[1] the empirical formula of mass transfer was presented for the two-layer convection in the case of a solution of one solute. Then, the flux, W_A, of a solute, A, was expressed by

$$W_A = a_1(\Delta\rho_1 - \Delta\rho_0)D^{0.5}(\Delta c_I/\Delta\rho_2). \quad (1)$$

Here, a_1 is the mass-transfer coefficient; $\Delta\rho_1$, the density difference between the liquid on the heated wall and that on the cooled wall; $\Delta\rho_0$, a constant; D, the diffusion coefficient of a solute; and Δc_I and $\Delta\rho_2$, the concentration difference and the density difference respectively between the solution of the upper layer and that of the lower layer.

In this paper we will discuss the mass transfer in the case of a mixture of two solutes. If the temperatures of cooling and heating are constant, $(\Delta\rho_1 - \Delta\rho_0)$ is approximately constant for a solution of different solutes. Then, the flux, W_x, of a solute, x, in a mixture may be expressed as follows:

$$W_x = a_2 D_x^{0.5}(\Delta c_x/\Delta\rho_2), \quad (2)$$

where a_2 is the mass transfer coefficient. The D_x[2] and the Δc_x are the values for a solute, x, while the $\Delta\rho_2$ is the density difference between the solutions. The $\Delta c_I/\Delta\rho_2$ was constant for the system of a solution of one solute. For that of two solutes, the $\Delta c_x/\Delta\rho_2$ will also be constant if the ratio of the amounts of solutes in a layer is constant while the two-layer convection is occurring, or if the amount of a solute, x, is very much larger than that of the other solute. Generally, the $\Delta c_x/\Delta\rho_2$ will be roughly constant for a small change of $\Delta\rho_2$. The ratio, W_x/W_y, of the fluxes of the two solutes is, then, expressed as follows:

$$W_x/W_y = (D_x D_y)^{0.5}(\Delta c_x/\Delta c_y). \quad (3)$$

When the Δc_x is equal to Δc_y, the W_x/W_y is expressed as follows:

$$W_x/W_y = (D_x/D_y)^{0.5}. \quad (4)$$

Experimental

The materials and apparatus used in this study were similar to those described in a previous paper.[1] The nitrates were used for the system of a solution of two electrolytes, while the chlorides were used for the other system (electrolyte-organic compound). The soluble starch was obtained from the Wako Pure Chem. Co. and was used without further purification. The temperatures of the heating and cooling water were 30 and 20 °C respectively, and the flow speed of those waters was 1.6 dm^3 min^{-1}. The concentration of the electrolyte was determined by atomic absorption spectrometry, while that of the organic compound was determined by colorimetry as reported by Dubois *et al.*[3] The samples (30—50 mm^3) for the determination of the solute concentration were taken out from the solution in the middle of the upper layer.

Results and Discussion

We examined the system of a solution of two solutes (mass ratio; 1:1) in order to separate the solutes, and investigated the relation between W_x/W_y and $(D_x/D_y)^{0.5}$. Figure 1 shows a case in which the concentrations in the lower layer are low, while the

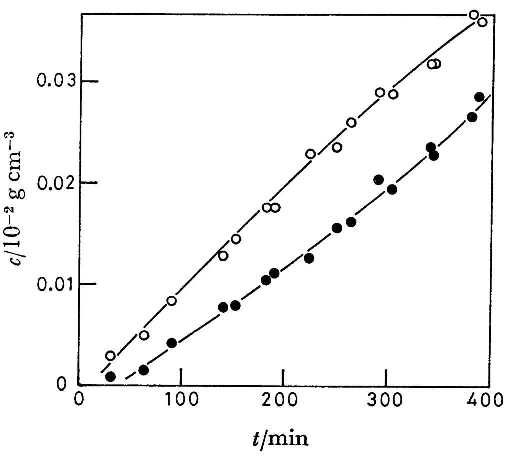

Fig. 1. Variation of concns in upper layer.
○: K^+, ●: Cu^{2+}.
Concns in lower layer at the start of convections; K^+: 0.1×10^{-2} g cm^{-3}, Cu^{2+}: 0.1×10^{-2} g cm^{-3}.

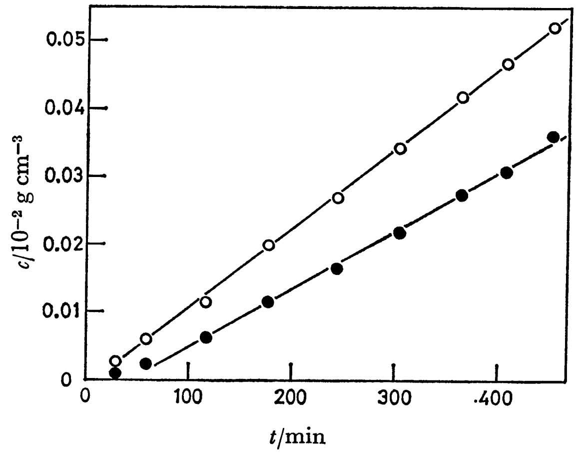

Fig. 2. Variation of concns in upper layer.
○: K^+, ●: Cu^{2+}.
Concns in lower layer at the start of convections; K^+: 0.25×10^{-2} g cm^{-3}, Cu^{2+}: 0.25×10^{-2} g cm^{-3}.

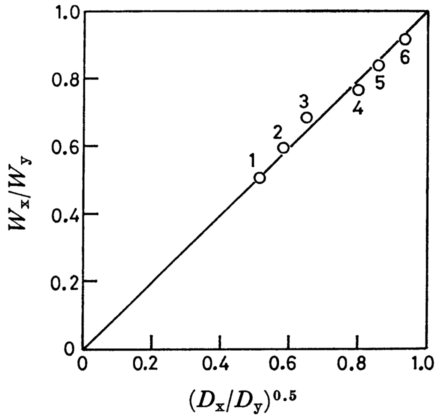

Fig. 3. Relation between W_x/W_y and $(D_x/D_y)^{0.5}$.
1: Sucrose–KCl, 2: D-glucose–KCl, 3: D-glucose–NaCl, 4: Cu^{2+}–K^+, 5: Pb^{2+}–K^+, 6: Cu^{2+}–Pb^{2+}.

relation between the concentration in the upper layer and the time is nonlinear. Figure 2 shows a case in which the concentrations in the lower layer are high and the relation is linear. If the relation is linear, the W_x or W_y can easily be evaluated. Therefore, subsequent experiments were carried out on the systems with the high concentrations.

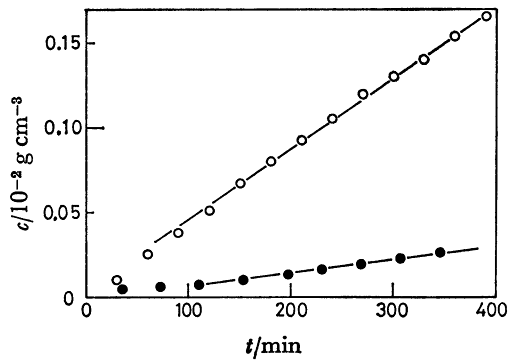

Fig. 4. Variation of concns in upper layer.
○: KCl, ●: starch.
Concns in lower layer at the start of convections; KCl: 1×10^{-2} g cm^{-3}, starch: 1×10^{-2} g cm^{-3}.

As Fig. 3 shows, W_x/W_y is equal to $(D_x/D_y)^{0.5}$.[2] Therefore, Eq. 4 seems to be proper and the separation of solutes is possible.

Figure 4 is the plot for the system of a solution containing an electrolyte (low molecular weight) and a starch. The electrolyte mainly moves from the lower layer to the upper layer. Nevertheless, the starch gradually moves to the upper layer. The diffusion coefficient of the starch was calculated by means of Eq. 4 from the two slopes for each solute. The value thus obtained, 0.72×10^{-6} cm^2/s, agreed with the order of the data (0.8×10^{-6} cm^2/s) in the literature.[4]

In view of the above results, we conclude that the separation of solutes is possible by this method.

References

1) K. Kamakura, *Bull. Chem. Soc. Jpn.*, **52**, 2175 (1979).

2) The diffusion coefficients (D_x or D_y) used in this paper were the values at an infinite dilution for a solution of one solute; the values of the electrolytes were calculated by means of the equation of Nernst-Hartley; those of sucrose and D-glucose were 0.523×10^{-5} and 0.673×10^{-5} cm^2 s^{-1} respectively.

3) M. Dubois, K. A. Gilles, J. K. Hamilton, P. A. Rebers, and F. Smith, *Anal. Chem.*, **28**, 350 (1956).

4) "International Critical Tables," Mcgraw-Hill (1929), Vol. 5, p. 71; for example, the diffusion coefficient of starch (powder-like) in a 1.25% solution at 20 °C is 0.8×10^{-6} cm^2 s^{-1}.