

# Diffusion through the Interface between Viscous Liquids in a Laminar Flow

## (Diffusion in a Laminar Flow)

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Studies were carried out in order to know in some detail the transport phenomena through the interface in the viscous liquid moving in laminar flow.

Experiments were carried out using ca. 88% glycerin solution, one added with an acid, and the other with alkali together with a small amount of phenolphthalein. Acidic glycerin solution was supplied to a long transparent cuvette of rectangular cross section through which the liquid was made to move slowly enough to establish the laminar flow, thin cords of coloured basic solution were introduced in the direction normal to the axis of flow at regular time intervals. The so obtained patterns of bending cords shortening in regular succession were photographed also at regular time intervals.

The authors attribute the origin of the changing patterns of the cords to the velocity gradient existing in the acidic solution which accelerates the diffusion by increasing the concentration gradient near the cords as well as the increase of the interfacial area, and also the decrease of the thickness of the cords. Based on these idea a mathematical analysis was carried out and was obtained an equation which gives the change of the concentration distribution of two dimensional cords.

Fair agreement was obtained between the results of mathematical analysis and those of experiments.

Furthermore, the influence of the thickness of the cords, and that of the velocity gradient as well as of the diffusion coefficient on the concentration at the center of the cords were discussed.

### § 1. Introduction

Compared with the process of mass transfer through solid-liquid interface whose kinetics is already well established<sup>1)2)3)</sup>, that of the mass transfer through liquid-liquid interface is current topics being intensively studied<sup>4)5)6)7)</sup>.

Especially, the mass transfer under agitation is one of the most important problems in chemical engineering, and many contributions for example, to the efficiency of agitation, power required, design of stirrer and container have been made to date.

There are, however, many points left untouched, especially, as to the kinetics of the mass transfer through slowly flowing liquids of high viscosity although it would certainly give some sound bases for the design and operation of

glass tank furnaces<sup>8)</sup>. The present paper contains the results of experiments and mathematical formulations in the case of simple laminar flow.

### § 2. Experiments

**a) Liquid used:** Expecting that the results may be available for the model experiment of glass tank furnaces 88% glycerin solution was used, and the larger part which was to be used to realize the laminar flow was added with HCl to a certain concentration together with a small amount of phenolphthalein. The smaller part was added with NaOH up to the concentration of 0.17N and was coloured red by phenolphthalein. Moreover, the densities of the both were adjusted to exactly same values.

**b) Apparatus and procedure:** In Fig. 1 is shown the principal part of the equipment used

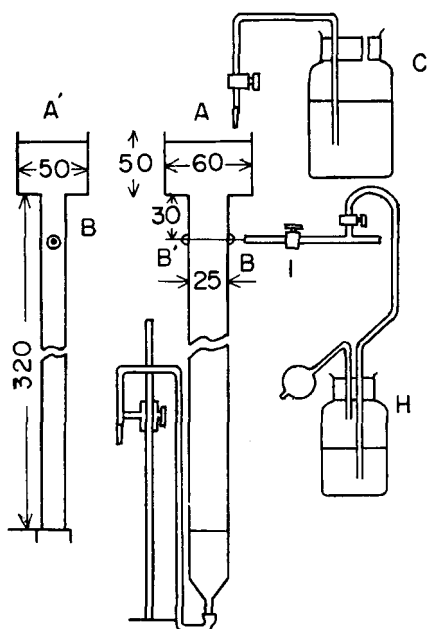


Fig. 1 Schematic reproduction of the apparatus used

A: Cuvette used for obtaining laminar flow of colourless glycerin

A': Side view of cuvette

B, B': Small hole used for injecting the coloured glycerin as a cord normal to the direction of flow

C: Reservoir bottle of colourless glycerin

H: Reservoir bottle of coloured glycerin

I: Injecting instrument

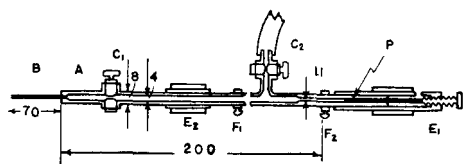


Fig. 2 Detail of injecting instrument (I in Fig. 1)

A: Movable inner tube B: Injecting needle

C<sub>1</sub>, C<sub>2</sub>: tap

E<sub>1</sub>: Fixed outer tube having a wire P at the rear end

E<sub>2</sub>: Fixed outer tube F<sub>1</sub>, F<sub>2</sub>: Stopper ring

P: Stainless steel wire which acts as a piston

for the experiments which is composed of a long cuvette of rectangular cross section made by assembling the transparent plastic plates and two reservoirs, one for the colourless, and the other for coloured liquid. The lower end of the cuvette A was funneled, to which connected a glass tube narrowed at one end through a long rubber tube. The flow velocity of the solution in the cuvette was measured by counting the

number of drops coming out from the glass tube and was controlled by changing its position. The level of glycerin in the reservoir A was kept constant by supplying the solution from the bottle C.

B in this figure is a small hole bored in the side wall of the cuvette used for injecting the coloured liquid normal to the direction of flow. The hole was covered by a small piece of rubber to stop the leak. I represents an instrument used for introducing a cord of coloured glycerin normal to the direction of flow, whose detail is shown in Fig. 2. In the figure a brass tube A has an injection needle of 1 mm outer diameter, 7 mm length together with two taps C<sub>1</sub> and C<sub>2</sub>. The another end, 8 mm in outer diameter, was bored 1.1 mm capillary tube. A can move in front and rear between the stoppers F<sub>1</sub> and F<sub>2</sub> through two tubes E<sub>1</sub> and E<sub>2</sub>. At the centre of the outer tube was fixed a stainless steel wire P, of 1 mm diameter which is to be slipped into the capillary. When A moves forward, P acts as a piston and the coloured solution is discharged at the same rate as P enters into the capillary, while the coloured glycerin can be supplied from the bottle H (Fig. 1) through the tap C<sub>2</sub>.

The order of the manipulation is as follows: In the first place the rates of charge and discharge are controlled so that a steady laminar flow is established in the cuvette. After closing C<sub>1</sub> and C<sub>2</sub>, I is inserted into the holes through the rubber stoppers until it passes through B'. Then C<sub>1</sub> is opened, I is drawn backward with a suitable speed to form a red coloured cord. Closing C<sub>1</sub> and opening C<sub>2</sub> simultaneously the coloured solution was supplied to be ready for next operation which followed in a small interval.

### § 3. Results of experiment and discussion

After the injection the red cords bent gradually along with the parabolic velocity distribution of laminar flow. At the same time the lines faded away gradually from both ends as shown in Fig. 3 by line drawing certainly because of the progress of the neutralization reaction. By changing the concentrations of HCl as (a) 0.01, (b) 0.12, (c) 0.12, (d) 0.44, (e) 0.05N while that of NaOH was kept constant as 0.017N, and changing the flux values as (a) 1.0, (b) 0.8, (c) and (d) 0.1, (e) 0.8 cc/sec, the following observations were made: At the centre of the flow the thickness of the cords were appeared to be

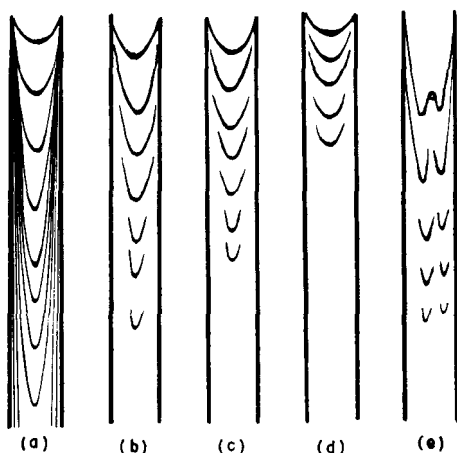


Fig. 3 Schematic reproductions obtained from the photographs showing the patterns of deforming and decolouring cords

	(a)	(b)	(c)	(d)	(e)
NaOH concentration of coloured glycerin (N)	0.017	0.017	0.017	0.017	0.017
HCl concentration of colourless glycerin (N)	0.01	0.12	0.12	0.44	0.05
Flux value of flow (cm <sup>3</sup> /sec)	1.0	0.8	0.1	0.1	0.8

rather broadend, probably due to the existence of the velocity gradient in the direction normal to the paper, although at the another part of the flow such trend was not noticeable. By comparing (b) with (c) in above examples, both having an identical concentration but different flux values, it was observed that the vanishing of cords parallels with the velocity gradient. In fact, the points of decolouration at the distance  $x$  from the side wall were pressed down with increasing flux values.

Since the degree of deformation of cords at the position of  $x$  does not depend on the flux values but depends only on the vertical distance, it is possible to say that the difference of the position of decolouration point in Fig. 3 indicates the time used for the diffusion to which the flow flux affects directly. Moreover (e) in the same figure shows the effect of bubbles ascending upward giving a marked change to the velocity gradient surrounding them.

Curves in Fig. 4 represent the effect of acid concentration  $C$  (N) and of flux value,  $Q$  (cm<sup>3</sup>/sec) on the point of decolouration at the distance  $x$  from the side wall. Taking into account of the variation of the result of estimation of decolour-

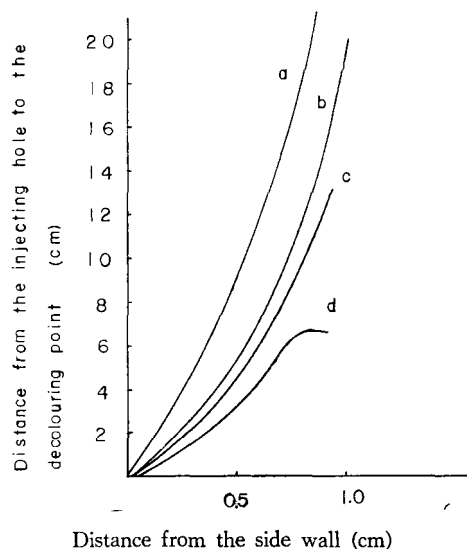


Fig. 4 Position of decolouration point of the cords  
NaOH concentration: 0.017N  
HCl concentration: (a) 0.44N, (b) 0.032N,  
(c) 0.12N, (d) 0.44N  
Flux value: (a) 1.0 cm<sup>3</sup>/sec,  
(b), (c), (d) 0.1 cm<sup>3</sup>/sec

ation points from photographic records these curves were drawn using the mean values of 2~6 separate measurements.

#### § 4. Distribution of velocity and velocity gradient

As the first step the velocity distribution,  $v(x)$ , was formulated in a power series as

$$v(x) = \frac{15Q}{7A} Q \left\{ 4 \left( \frac{x}{d} \right)^4 - 8 \left( \frac{x}{d} \right)^3 + 9 \left( \frac{x}{d} \right)^2 - 5 \left( \frac{x}{d} \right) \right\}, \quad (1)$$

where  $A$  is the cross sectional area of the cuvette, and  $d$  the distance between both walls. From eqn. (1) the velocity gradient,  $g(x)$  was expressed as

$$g(x) = \frac{15Q}{7Ad} \left\{ 16 \left( \frac{x}{d} \right)^3 - 24 \left( \frac{x}{d} \right)^2 + 18 \left( \frac{x}{d} \right) - 5 \right\}. \quad (2)$$

In Fig. 5 are compared the calculated velocity values when  $Q=1.0$ , with those obtained by experiment showing that the agreement is almost satisfactory. The velocity gradient was also calculated with a result shown in the same figure.

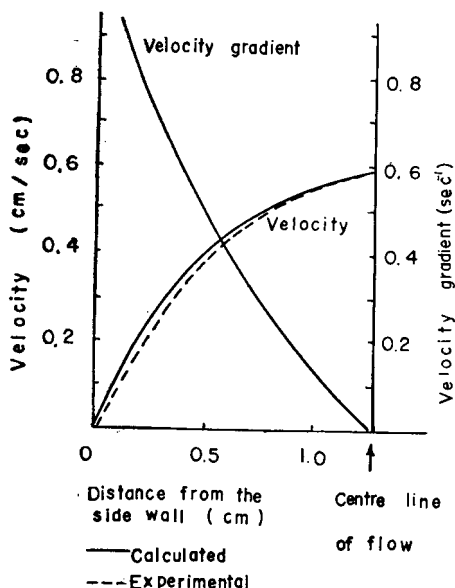


Fig. 5 Velocity and velocity gradient of a laminar flow when flux value  $Q=1\text{cm}^3/\text{sec}$

### § 5. Effect of the velocity on the rate of diffusion

It has been pointed out that the velocity gradient in flowing liquid plays a leading role in determining the rate of fading out of the red cords gradually from both ends. Fig. 6 is a

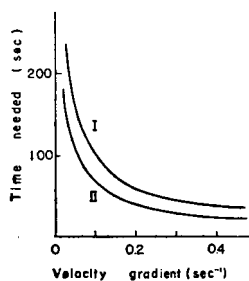


Fig. 6 Relation between the velocity gradient and time passing before the disappearance of the cords  
NaOH concentration of colourless glycerin: 0.17N  
HCl concentration of colourless glycerin:

{ 0.032N for curve I  
0.425N for curve II

qualitative representation of the relation between the velocity gradient and the time passing before the disappearance of cords. Furthermore the curves show that the cords in the solution having higher acid concentration vanish more rapidly than those in the solution containing weaker acid. It may be concluded that the elongation of the cords by the velocity gradient brings out (1) the increase of the interfacial area,

(2) the decrease of the thickness of the cords, and (3) the increase of the concentration gradient near the boundary of the liquids, hence profoundly accelerates the rate of diffusion.<sup>9)</sup>

### § 6. Measurement of apparent diffusion coefficient

Without coming into the details of molecular processes let us discuss the diffusion through the interface of moving liquid. In Fig. 7 (a) is shown an apparatus for measuring the rate of diffusion through the interface of stagnant liquids by measuring the rate of the displacement of the boundary,  $x_a$ , formed in this case, between the alkaline glycerin solution and the acidic solution of slightly smaller density. The apparent diffusion constant may be calculated by

$$C_D = \frac{1}{2} \left( 1 - \operatorname{erf} \left[ \frac{x_a}{2\sqrt{Dt}} \right] \right), \quad (3)$$

Where  $C_D$  is the apparent concentration at the neutral point as illustrated by Fig. 7 (c) and may be regarded as a constant determined by the given initial concentration values of both solutions.

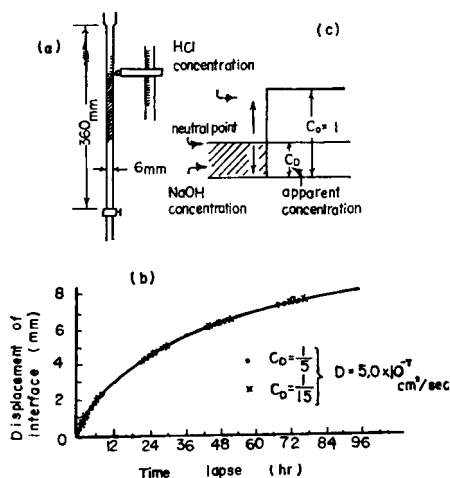


Fig. 7 Measurement of apparent diffusion constant  
(a) Method (b) Results  
(c) Definition of apparent neutral concentration  $C_D$

In Fig. 7 (b) is given the rate of the displacement of the boundary which shows the well known parabolic curve of diffusion. Multiplying  $x_a$  values of one of the curves by a constant the agreement of two experimental results with those obtained by direct observation were made to see more clear. The value of  $D=5.0 \times 10^{-7}$

cm<sup>2</sup>/sec was obtained for diffusion constant of glycerin solution. This value may be regarded as remaining constant at around the room temperature.

§ 7. Mathematical analysis for a simple two-dimensional model

a) Procedure of analysis: To simplify the problem the analysis was carried out for a two dimensional model. In Fig. 8(a) is shown a part

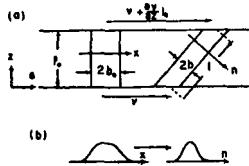


Fig. 8 Schematic reproduction showing deformation process of a cord in a part of a laminar flow

(a) Deformation

(b) Change of the concentration distribution

of the cord of width  $2b_0$  and length  $l_0$  (left) which after the time  $\theta$  was deformed to  $2b$  and  $l$  by the main flow (right). As  $l$  is represented by

$$l = l_0 \sqrt{\left[ \int_0^\theta \frac{\partial v}{\partial z} d\theta \right]^2 + 1}, \tag{4}$$

the width  $2b$  may be given by

$$2b = 2b_0 / \sqrt{\left[ \int_0^\theta \frac{\partial v}{\partial z} d\theta \right]^2 + 1}. \tag{5}$$

Taking into consideration that the diffusion occurs in the direction of the normal  $n$  to interface which in turn changes the direction as the cord is deformed, it is possible that Fick's equation

$$\frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial n^2}, \tag{6}$$

is applied with some modifications.

Using the relation

$$n = x / \sqrt{\left[ \int_0^\theta \frac{\partial v}{\partial z} d\theta \right]^2 + 1}, \tag{7}$$

the eqn. (6) may be expressed as

$$\frac{\partial C}{\partial \theta} = \left\{ \left[ \int_0^\theta \frac{\partial v}{\partial z} d\theta \right]^2 + 1 \right\} D \frac{\partial^2 C}{\partial x^2}, \tag{8}$$

which states that the diffusion constant  $D$  is being modified by the function of the velocity gradient  $\partial v / \partial z$ .

If  $v(z)$  and  $\partial v / \partial z$  may be regarded as the function of  $z$  only, there exists the relation

$$\frac{\partial v(z)}{\partial z} = g(z), \tag{9}$$

and

$$\left[ \int_0^\theta g(z) d\theta \right]^2 = g(z)^2 \theta^2. \tag{10}$$

Accordingly, eqn. (8) may be transformed to

$$\frac{1}{g(z)^2 \theta^2 + 1} \cdot \frac{\partial C}{\partial \theta} = D \frac{\partial^2 C}{\partial x^2}, \tag{11}$$

and putting

$$\eta = \frac{1}{3} g(z)^2 \theta^2 + \theta, \tag{12}$$

the eqn.

$$\frac{\partial C}{\partial \eta} = D \frac{\partial^2 C}{\partial x^2}, \tag{13}$$

may be obtained.

Putting the initial condition of the concentration distribution  $C(x)$  in and around the cords,

$$\left. \begin{aligned} \text{at } \theta = 0 \quad \eta = 0 \\ C(x) = 1 \quad (-b_0 \leq x \leq b_0) \\ C(x) = 0 \quad (x < -b_0) \\ C(x) = 0 \quad (x > b_0) \end{aligned} \right\}, \tag{14}$$

and the boundary condition,

$$C(x) = 0 \quad \text{at } x = \pm \infty, \tag{15}$$

into the eqn. (11) the formula

$$C = \frac{1}{\pi} \int_{-\frac{b_0+x}{2\sqrt{D\eta}}}^{\frac{b_0-x}{2\sqrt{D\eta}}} e^{-\beta^2 d\beta}, \tag{16}$$

may be obtained, where  $\beta$  is a new parameter.

In order to know the actual concentration distribution  $x$  should be converted to  $n$  using the relation

$$x = n \sqrt{g(z)^2 \theta^2 + 1}. \tag{17}$$

To carry out the actual calculation it may be convenient to expand the eqn. (16) as a series, namely,

$$C(x) = \frac{2}{\sqrt{\pi}} \left[ \frac{b_0}{2\sqrt{D\eta}} - \frac{b_0^3 + 3b_0x^2}{3(2\sqrt{D\eta})^3} + \frac{b_0^5 + 10b_0^3x^2 + 5b_0x^4}{5 \cdot 2!(2\sqrt{D\eta})^5} \dots \right]. \tag{18}$$

Putting  $x=0$  in above eqn. the concentration at the centre of the cords may expressed as

$$C_n = \frac{2}{\sqrt{\pi}} \left[ \frac{b_0}{2\sqrt{D\eta}} - \frac{b_0^3}{3(2\sqrt{D\eta})^3} + \frac{b_0^5}{10(2\sqrt{D\eta})^5} \dots \right]. \tag{19}$$

### b) Discussion on the calculated results :

The eqn. (19) makes it possible to calculate the influences of diffusion coefficient and velocity gradient on the concentration  $C_n$  at the centre of the cords of various width, and the results of calculation are shown in Fig. 9 by a group of curves representing the relation of  $C_n$  vs.  $\theta$  giving different values of  $2b_0$  and  $g(z)$  when  $D=5 \times 10^{-7} \text{ cm}^2/\text{sec}$ .

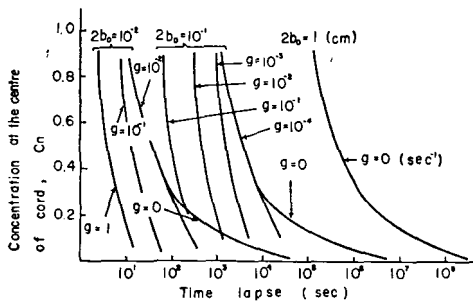


Fig. 9 Results of calculation which indicate the relation among  $C_n$ ,  $2b_0$  and velocity gradient  $g(z)$  when  $D=5 \times 10^{-7} \text{ cm}^2/\text{sec}$

To put the problem concretely let us give some examples: The time necessary for reducing  $C_n$  of a cord of  $2b_0=1 \text{ mm}$  to half value is  $7 \times 10^3 \text{ sec}$  when  $D=5 \times 10^{-7} \text{ cm}^2/\text{sec}$  without any velocity gradient while it reduces to  $1/100$  even if the velocity gradient as small as  $0.1 \text{ sec}^{-1}$  does exist.

Furthermore, when  $2b_0$  decreases from  $1 \text{ mm}$  to  $0.1 \text{ mm}$  the time reduces to the value  $7 \times 10^2 \text{ sec}$ . As to the influence of diffusion coefficient the another result of calculation shows that the time decreases to about  $1/10$  when the diffusion coefficient decreases to  $5 \times 10^{-6} \text{ cm}^2/\text{sec}$  for the  $2b_0=1 \text{ mm}$  and  $g(z)=0.1 \text{ sec}^{-1}$ . It is also indicated that the larger the value  $2b_0$  the more becomes noticeable the effect of the velocity gradient.

In Fig. 10 are shown the curves representing the calculated position of ends of coloured cords. For comparison the experimental values shown in Fig. 4 are inscribed by dashed curves. It may be seen that all curves have the similar trend except near the centre of the flow where the velocity gradient in another direction is remarkable. Thus we may use the eqns. (18) and (19) to draw a picture which indicates approximately the effect of flow on the material transfer whose rate is controlled by diffusion.

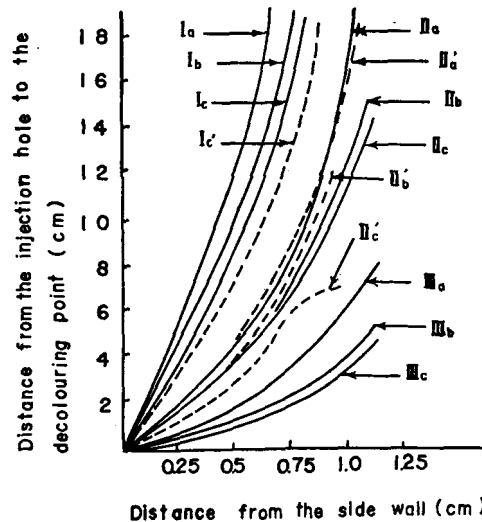


Fig. 10 Position of decolouration points obtained from the calculation

$Ia'$ ,  $Ib'$ ,  $Ic'$ ; Experimental results corresponding to  $Ia$ ,  $Ib$ ,  $Ic$ , respectively

Flux value of flow: I;  $1.0 \text{ cm}^3/\text{sec}$ ,

II;  $0.1 \text{ cm}^3/\text{sec}$ , III;  $0.01 \text{ cm}^3/\text{sec}$

Concentration value at the neutral point (C):

a;  $C_D=0.65N$  b;  $C_n=0.87N$ , c;  $C_n=0.96N$

### § 8. Summary

1. Deformation and decolouration processes of the cords of red alkaline glycerin introduced normally to the laminar flow of acidic glycerin have been indicated by a series of experiments.
2. The rate of diffusion which controls the decolouration process of the cords were markedly accelerated by the existing velocity gradient.
3. The influence of the velocity gradient could be attributed to the increase of concentration gradient near the cords as well as the interfacial area, and also the decrease of the thickness of the cords.
4. Mathematical analysis was carried out obtaining an equation which gives the change of the concentration distribution of simple two dimensional cords.
5. Results of the calculation indicated fair agreement with those of experiments.

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