Articles

The Complex Travelling Wave by Two Directional Differential Flow Induced Chemical Instability

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A new kind of differential flow induced chemical wave is introduced by theoretical calculation. A differential flow between the counter acting species of a dynamical activator-inhibitor system may destabilize its homogeneous reference state and cause the medium to self-organize into a pattern of travelling waves through the differential flow instability (DIFI). In a chemical system, also, the differential bulk flow may change the dynamics of the system, thus it has been refered to as the differential flow induced chemical instability (DIFICI). For DIFICI experiments, one directional flow has been commonly employed, resulting in periodic wave patterns generally. In this study, we considered two directional flow for the DIFICI wave by exchanging artificially the flow direction at some period.

Introduction

Differential flow between the counteracting species of a dynamical activator-inhibitor system may destabilize the system's homogeneous reference state and cause the medium to self-organize into a pattern of travelling wave through the differential flow instability (DIFI).[1] The homogeneous steady state of a chemical reaction system characterized by activator-inhibitor kinetics also may become unstable through the two similar differential transport mechanisms of its key species.[2,3] The Turing pattern[4] may be obtained by differential diffusion[5] between activator and inhibitor in chemical reaction systems, on the other hand, a differential flow between two chemical species may give rise to a travelling wave.[6]

The study of instabilities caused by the flow of matter constitutes a central task of hydrodynamics.[1,2] In this study, we focus on systems consisting of at least two distinct, interactive species. The flow field is assumed to be homogeneous throughout the system, *i.e.*, there are no gradients of the flow velocity. The different species, however, may travel with their individual flow velocitis. In this case, we say that there is a differential flow between the components.[1]

M. Menzinger *et al.* recently predicted theoretically[6] and verified experimentally[7,8] that such a differential bulk flow in chemical systems may change the dynamics of the system. The destabilizing mechanism by flow of activator and inhibitor at different flow rates, regardless of which one is faster, has been refered to as the differential flow induced chemical instability (DIFICI).[6,7,8]

In the experimental setup of one directional bulk flow chemical systems,[7,8] the differential flow between activator and inhibitor is made possible by the inhibitor of the metal ion catalyst of the Belousov-Zhabotinsky (BZ) reaction[9,10] immobilized on a cation-exchange resin by packing. The remaining reactant solution flows through a tubular column in which the flow rate is controlled by regulating the flow gas pressure.

In this paper, we report our investigations of calculations for a new kind of DIFICI in which a two directional differential flow system is considered for inducing complex chemical instabilities. For DIFICI experiments conducted up until now, one directional flow has been commonly employed, and the resulting periodic wave patterns are very apparent at some references.[1,7,8]

In this study, we considered the two directional flow induced chemical instability theoretically before the experimental research. The flow direction was exchanged by controlling the changing frequency artificially. From this experimental simulation-varying the flow rate of forward and reverse direction and exchanging the frequency of flow direction together-we were able to obtain complex travelling wave patterns.

Model and Procedure

Model. In order to consider the two directional differential flow induced chemical instability, we visualized a one-dimensional reactor model as shown in Figure 1. We assumed that the flow rate of forward and reverse is controlled by the regulation of gas pressure, and the exchanging of flow direction is accomplished by regulating RV(2) with RV(1) by cross opening and closing.

Procedure. For the simulation of DIFICI experiments composed of two species system of an activator and inhibitor, the inhibitor, represented in general by Y, is immobilized by a solid support, while the activator species X flows through the one-dimensional reactor with a constant velocitry v. This system has been described by the reaction-flow equation.[1,2]

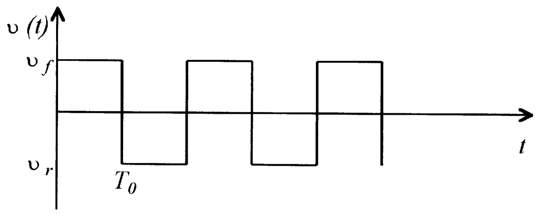
$$X = f(X, Y) + v\frac{\partial X}{\partial R} \qquad (1)$$

$$Y = g(X, Y)$$

Where f and g are reaction kinetic functions, and R is the one-dimensional flow direction coordinate.

However, in order to consider the two directional flow DIFICI experiments, we used the time dependent flow velocity of $v(t)$ instead of the one directional constant v in Eq. 1. The flow direction is indicated by the sign of the flow rate in Figure 1 in which $v(t)$ is a positive value for forward direction and a negative value for reverse direction. The direciton of flow was exchanged by the period of T_0. We carried out this study by varying the T_0 value and by varying the absolute value of forward and reverse flow rate. Then, the two directional flow rate system is summarized as follows:

$$v(t) = |v_f| \text{ from } t = nT_0 \qquad n = 0, 2, 4 \cdots \qquad (2)$$
$$-|v_r| \text{ from } t = (n+1)\ T_0$$



To illustrate the spatial instability of the two-directional differential flow in this study, we used the Puschinator model[9] of the Belousov-Zhabotinsky (BZ) reaction[10,11] with the flow term,

$$\frac{\partial x}{\partial \tau} = \frac{1}{\varepsilon}\left[x(1-x) - \left\{2q\alpha\frac{y}{1-y} \cdot \beta\right\}\left[\frac{x-\mu}{x+\mu}\right]\right] + v(\tau)\frac{\partial x}{\partial r}$$

$$\frac{\partial y}{\partial \tau} = x - \alpha\frac{y}{1-y}$$

where $\varepsilon = \frac{k_1A}{k_4C}$, $\alpha = \frac{k_4K_fB}{(k_1Ah_0)^2}$, $\mu = \frac{2k_4k_7}{k_1k_5}$, $\beta = \frac{2k_4k_{13}B}{(k_1A)^2h_0}$,

$A = [BrO_3^-]$, $B = [CHBr(COOH)_2]$,
$C = [Fe(Phen)_3^{2+}] + [Fe(Phen)_3^{3+}]$,

$$y = \frac{Y}{C}, \quad Y = [Fe(Phe)_3^{3+}]$$

$$x = \frac{2k_4X}{k_1A}, \quad X = [HBrO_2]$$

$$r = R\left\{\frac{k_1CD_x}{(k_1A)^2h_0}\right\}^{1/2}, \quad \tau = \frac{(k_1A)^2h_0}{k_4C}t \qquad (3)$$

and h_0 is the acidity value of flowing solution, q is the stoichiometric factor of BZ reaction. We used the value of 0.5 for the stoichiometric factor. And k_1 and K_f are the rate constant and equilibrium constant of ferroin-catalyzed BZ reaction. Their definition and available values are well described by Rovinsky et al.[9,12] We used the diffusion coefficient value of D_x in the scaling process with 3×10^{-3} cm^2s^{-1} to adjust the length of one dimensional reactor for 10 cm. The parameters of the Puschinator model and the dimension scales of the reactor length, the flow rate, and the period of exchanging direction are summarized in Table 1.

The integration for the calculation of the differential equation Eq. 3 for one-dimensional reactor was conducted by the CVODE program using the Euler method, and we used a periodic boundary condition.[13] The initial perturbation of the homogeneous state was imposed at the middle of the one-dimensional reactor, with an amplitude equal to about 30% of the homogeneous steady state value.

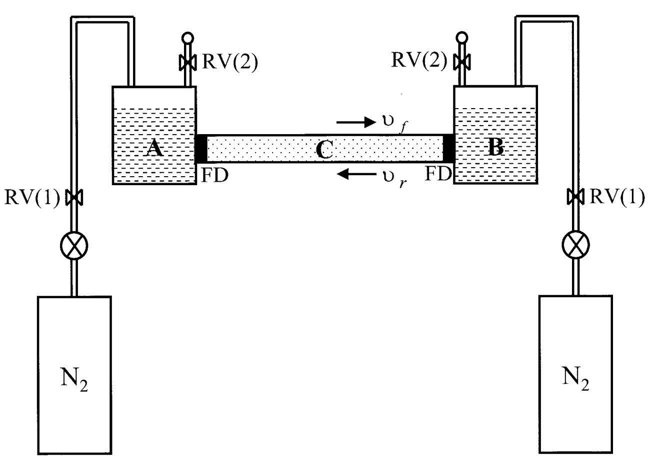


Figure 1. The model of schematic diagram for the two-directional flow DIFICI study. A and B, reaction flow solution; C, immobilized packed material such as cation exchange resin coated by metal catalyst; RV(1), regulating valve for flow rate control; RV(2), cross regulating valve with RV(1) for flow direction control; FD, fritted disk; v_f and v_r, the flow rate of forward and reverse.

Results and Discussions

One-directional flow system. In order to justify our computational model of two-directional flow system in the DIFICI wave study, we first calculated for one directional system from the model by holding the reverse flow rate value at zero. Then, we compared our results with the experimental results obtained by M. Menzinger et al. using the one directional differential flow system.[7,8]

The calculated results in a tubular one dimensional reactor for a one directional system are shown in Figure 2. Figure 2(a) represents a sample calculation of travelling wave by a periodic peak of an arbitrary unit of an activator concentration change, which is represented as $U(x)$ vertically. The

Table 1. The used parameters of the Puschinator model and the used dimenhsion scales for calculation

Parameters of Puschinator model	Used dimensions for calculation
A 0.1249M	R (reactor length) 10 cm
B 0.2M	v_f or v_r 0-1.5 cm/sec
C 0.0003M	T_0 0-80 sec
h_0 = 0.3M	

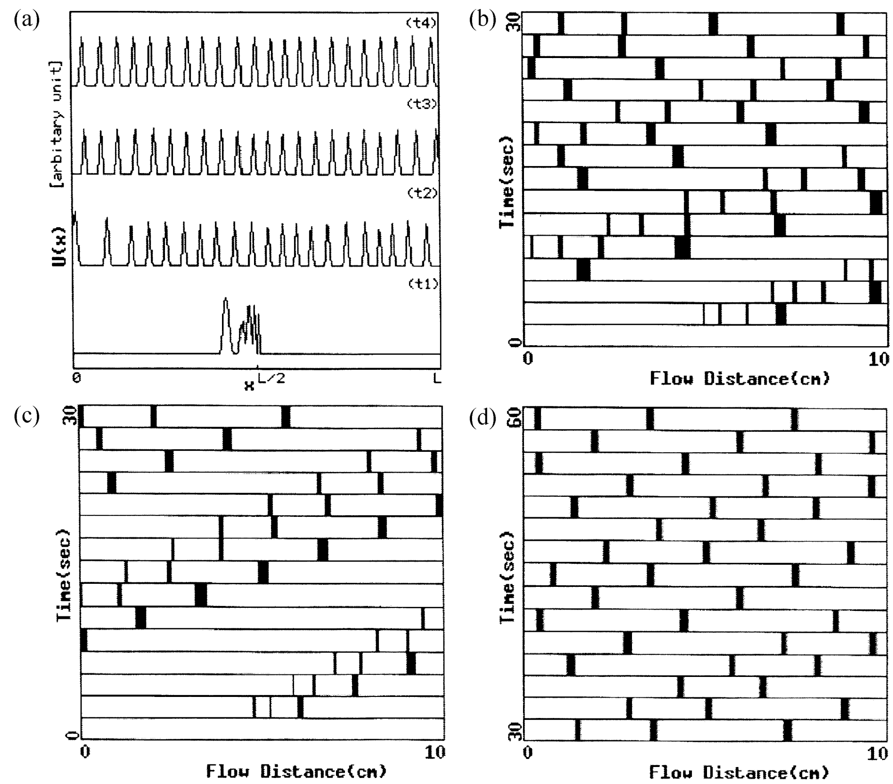


Figure 2. The calculational results of travelling wave patterns for one-directional flow systems. The forward flow rates are as follows: (a) $v_f = 0.57$ cm/sec. (b) $v_f = 0.86$ cm/sec. (c) $v_f = 0.43$ cm/sec. (d) $v_f = 0.43$ cm/sec.

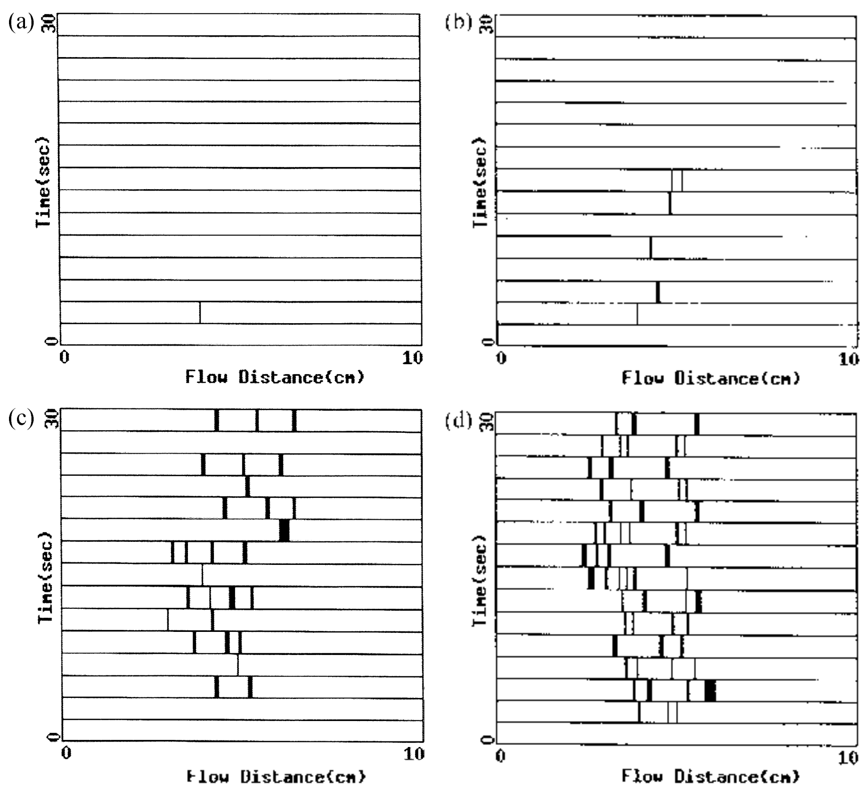


Figure 3. The calculational results of travelling wave patterns for two-directional flow systems with the same forward and reverse value. The flow rate and the direction exchanging frequencies are as follows: (a) $v_f = 0.36$ cm/sec, $v_r = 0.36$ cm/sec, $f(1/T) = 0.33$ sec^{-1}. (b) $v_f = 0.43$ cm/sec, $v_r = 0.43$ cm/sec, $f = 0.33$ sec^{-1}. (c) $v_f = 0.50$ cm/sec, $v_r = 0.50$ cm/sec, $f = 0.33$ sec^{-1}. (d) $v_f = 0.71$ cm/sec, $v_r = 0.71$ cm/sec, $f = 0.33$ sec^{-1}.

time of (t1) in this diagram indicates the perturbed point in the middle of the reactor. The time scale (t1)-(t4) is about 900 seconds, which is a very large value compared with the 30 seconds of other systems (b)-(d) in Figure 2. In Figure 2(b) and 2(c), the travelling waves are represented by a dark band, similar to the experimental results in which the concentration change of activator species show periodic band[7,8] with the flow solution. The flow direction of one dimensional tubular reactor is manifested at a horizontal axis from 0 to 10 cm. The tubular reactor is represented as a rectangular surface in the diagram. The initial perturbed wave in the middle of the reactor changes into a travelling wave with flow time indicated at a vertical axis with discontinuous time scale. The travelling waves at an early stage are aperiodic in which the intervals between the dark bands are irregular, as shown in (b) and (c) of Figure 2, while the wave gradually becomes periodic with flow. The difference between (b) and (c) in Figure 2 is the value of flow rate, *i.e.*, the absolute flow rate of (c) is the half value of (b). Thus, the intervals between bands are longer than in (b). The change into periodic travelling wave with flowing time is well shown in (d) in Figure 2. This result agrees well with previous experimental results of periodic wave using one directional flow rate by M. Menzinger *et al.*[7,8]

Two-directional flow system. When we calculate using the model for the two directional flow system as shown in Figure 1, we can consider other control parameters, including the flow rate of forward and reverse direction separately, and the frequency of exchanging flow direction. In one directional systems only the flow rate value can be varied. To investigate the effects of the control parameters in the two directional travelling waves in more detail, we also varied the calculation time, which corresponds to the flow time of the travelling wave.

Figure 3 shows the calculational results of the travelling waves for this two directional flow systems. We used the same value of an exchanging frequency in (a)-(d) with a different flow rate. In this system, the forward flow rate equals the reverse rate, but the absolute value increases from (a) to (d). We could confirm from this result in Figure 3 that the travelling wave pattern is very dependent on the absolute value of the flow rate in this two-directional DIFICI system of fixed frequency. In (a) and (b) of Figure 3, the time span of the travelling wave was relatively short, especially in the case of (a) where only one perturbed wave was shown. This result can be explained by the slow flow rate in comparison with the exchanging frequency. When the flow rate was increased gradually, aperiodic travelling waves were obtained as shown in (c) and (d).

Figure 4 shows the computational results of the travelling waves that describe the frequency effect of exchanging flow direction in two directional flow systems. In (a) and (b) of Figure 4, the same rate and frequency value were used. The periodic bands at the begining of flow times as shown in (a) change gradually into an aperiodic travelling wave as shown in (b) of Figure 4. The frequency value of Figure 4(c) is

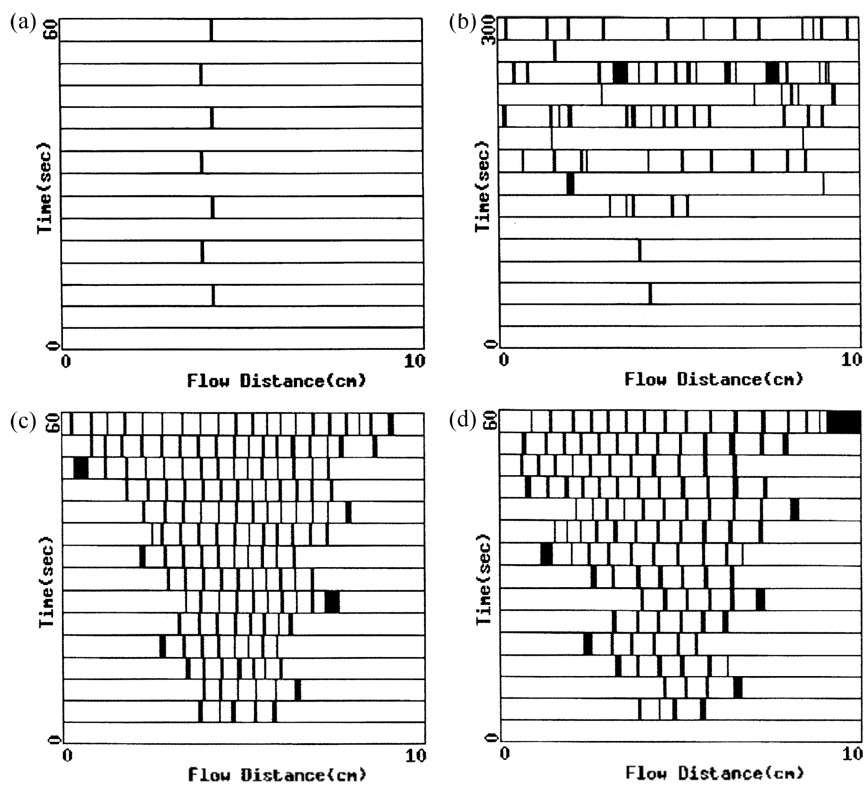


Figure 4. The calculational results of travelling wave patterns of two-directional flow systems for the frequency effects of exchanging flow: (a) $v_f = 0.57$ cm/sec, $v_r = 0.57$ cm/sec, $f = 0.50$ sec^{-1}, (b) $v_f = 0.57$ cm/sec, $v_r = 0.57$ cm/sec, $f = 0.50$ sec^{-1}, (c) $v_f = 0.57$ cm/sec, $v_r = 0.57$ cm/sec, $f = 0.17$ sec^{-1}, (d) $v_f = 1.05$ cm/sec, $v_r = 1.05$ cm/sec, $f = 0.17$ sec^{-1}.

three times smaller than that of (a) and (b). The resulting wave is nearly periodic and the interval between bands is shorter than the interval of wave bands in (a) and (b). Figure 4(d) shows the wave result when the flow rate value is higher than the value of (c) at the same frequency value. The obtained pattern is similar to that of Figure 4(c). This means that the flow rate value in the two directional system does not have much effect on the periodic wave pattern if the frequency value is smaller than some limit value compared with the flow rate value. This phenomenon is silmilar to the one directional flow system of periodic wave.

We observe some interesting results in the travelling waves by using a different value for the forward and reverse flow rate as shown in (a)-(c) of Figure 5. The result of Figure 5(a) is similar with those of Figure 3(a) and Figure 3(b). The forward flow rate of Figure 5(a) is larger than the value used in Figure 3(c), though the reverse flow rate is the same as that in Figure 3(b). This result means that the wave by using a different forward and reverse flow rate value in the two directional flow system is highly dependent on the small difference between the two flow rate values. In Figure 5(b) and 5(c), the values of the forward and reverse flow rate were larger than the value in 5(a), and aperiodic travelling wave patterns were obtained. We used a time scale in 5(c) that was twice the value compared with 5(b) to extend the observation of aperiodic wave character. The aperiodicity is well shown in Figure 5(d), where the calculation time is extended ten times. The frequency value of Figure 5(d) is twice that of Figure 5(c).

In Figure 6, variance of the travelling wave pattern by controling the flow rate and the exchanging frequency is summarized in the result of repeated calculations varying the flow rate value and the exchanging frequency value. In Figure 6(a), the boundary is a wave pattern roughly. No pattern formation in the region of C can be described by the fact that the frequency value goes beyond limits for the propagation of flow wave. The variance of the travelling wave pattern by controling the flow rate and frequency is well shown in Figure 6(b). The diagram was obtained by the same method of Figure 6(a), *i.e.*, repeated calculations. The boundary represented by the small circles was obtained by the observation of the differences in the wave pattern formation when the parameter values were varied slightly around a given point. The boundary of wave pattern formation meets our expectations on the whole. When a small frequency value is used, the periodic wave is obtained generally as in the region (1). The periodic travelling wave observed in the region (1)-A differed somewhat from that of region (1). The periodic wave did not continue for an extended length of time in the case of region (1)-A. However, when a large value of frequency rate is used, the travelling wave is not formed since the wave does not progress due to the interference of direction change as shown in region (4). The characteristics of a two directional differential flow system are well shown in

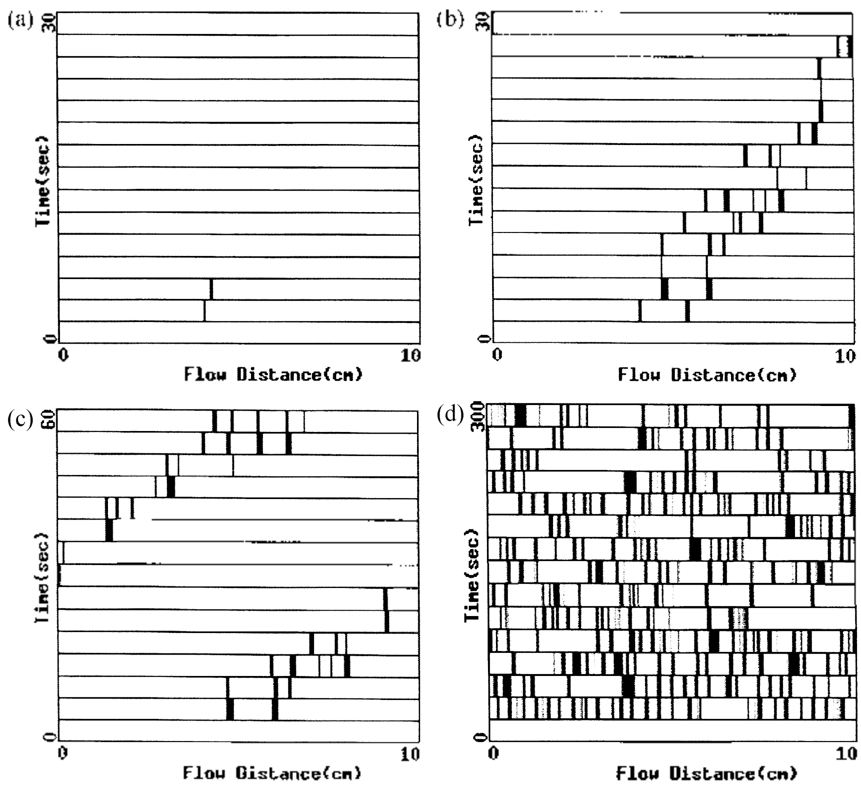


Figure 5. The calculational results of travelling wave patterns of two-directional flow systems with a different rate of forward and reverse value. and the systems of an extended time scale: (a) v_f = 0.57 cm/sec. v_r = 0.43 cm/sec. f = 0.33 sec^{-1}. flow time = 30 second. (b) v_f = 1.05 cm/sec. v_r = 0.57 cm/sec. f = 0.33 sec^{-1}. flow time = 30 second. (c) v_f = 1.05 cm/sec. v_r = 0.57 cm/cec. f = 0.33 sec^{-1}. flow time = 60 second. (d) v_f = 0.57 cm/sec. v_r = 0.57 cm/sec. f = 0.67 sec^{-1}. flow time = 300 second.

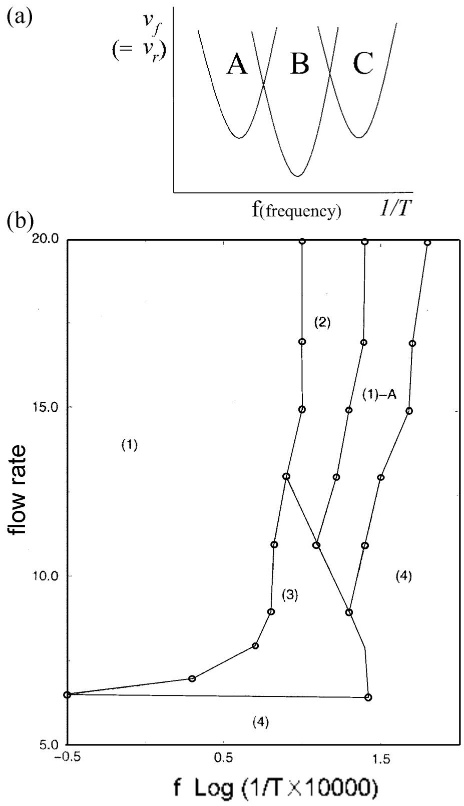


Figure 6. The diagram being summarized for the dependency of the DIFICI travelling wave patterns on the two-directional flow system. (a) The rough dependency on the flow rate and the direction exchanging frequency: A; Aperiodic and chaotic wave. B; Periodic wave. C; No wave formation. (b) The diagram for dependency of DIFICI travelling wave patterns on the two-directional flow system in detail on the base of some calculational points. The used dimension scale for the flow rate and the period is unitless where the flow rate value of 10 equals to 0.71 cm/sec and the direction exchanging period(T) of 10000 equals to 25 second. The dependency is as follows: (1) and (1)-A: Periodic wave. (2): Aperiodic wave. (3): Complex wave. (4): No wave formation.

the region of (2) and (3). Aperiodic or complex wave patterns are not observed by the control of the flow rate alone in one directional differential flow systems.

Conclusion

These calculational results suggest that we can obtain various travelling wave patterns, including a periodic and an aperiodic wave pattern, by controling some parameters in a two directional flow system of differential flow induced chemical instability (DIFICI).

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