Diffusion Action of Chemical Waves

Jirí Stávek
Laboratory of Diffusion Processes
Bazovského 1228
163 00 Prague, Czech Republic
e-mail: stavek@volny.cz

Diffusion actions of chemical waves are calculated as the product $Kkm\,l\,u = h$, where K is the diffusivity factor, k is the tortuosity factor, m is the particle mass, l is the wavelength, u is the propagation speed, h is a characteristic constant of the diffusion action. During evolution of successive LR (Liesegang ring) waves, BZ (Belousov-Zhabotinsky) waves, and cAMP (cyclic adenosine 3′,5′-monophospate) waves their diffusion actions showed a strong tendency to converge to a value 6.6 * 10^{-34} Js.

Keywords: chemical waves, diffusion action, self organization of matter

Chemical waves are known to travel at a propagation speed u that represents the product of the distance between the patterns λ and their frequency n (or its reciprocal value the period T). The dependence of the propagation speed u on the wavelength l (or the period T) is called the dispersion relation. Dispersion relations bring the additional information about the evolution of chemical waves in excitable reaction-diffusion systems.

Several groups of colloidal chemists have evaluated the dispersion relations for the Liesegang ring (LR) formation—the precipitation of periodic structures of sparingly soluble salts in the presence of a polymer in order to stabilize the formed structure in the reaction space [1,2,3]. They found that during the evolution of successive waves the product of instantaneous propagation speed u and the wavelength l converges to a constant value. It was found that this product ul depends on the type and the concentration of the polymer used. These authors have tried to characterize the diffusing front by a characteristic particle mass m that is needed for the estimation of the *diffusion action* of chemical waves. The product of the characteristic mass m, propagation speed u and the wavelength l is termed the diffusion action.

This approach to characterizing LR formation has been followed repeatedly several times since then. [4] More than one hundred different combinations of cations and anions have been employed for LR formation. Because of the difficulties in estimating the mass of diffusing particles (reaction between the molecules of outer and inner electrolytes, irreversible formation of clusters) the calculated values of the diffusion action of the order $\sim 10^{-34}$ Js could not be tuned to a certain constant value. Therefore, this concept has been considered very trivial [5]. Meanwhile, several theoretical physicists have contributed to this topic [6,7,8,9,10,11], too. Several decades of experimental and theoretical research can now be condensed into the following equation:

$$Kkm\,l\,u = h \tag{1}$$

where K is the diffusivity factor, κ is the tortuosity factor, m is the particle mass, l is the wavelength, u is the propagation speed, and h is a characteristic constant of the diffusion action. The parameter K—diffusivity factor—describes the geometrical arrangement of the experiment. For one-dimensional space (thin glass tubes) $K = 1$; for two dimensional space (thin layer in a Petri dish) $K = 2$; in the case of the three-dimensional experiment the value K depends on the space angle available for the diffusion of Brownian particles from their source. If the whole space is available for the propagation of the chemical waves, then $K = 4p$. Many studies of the dispersion relations have been performed in gels, membranes, resin beads, and glasses in order to prevent hydrodynamic disturbances from the reacting media. These media help to localize the propagating bands; however, they modify the diffusion path of ions. The diffusion field in these restricted environments changes by a tortuosity factor k that characterizes diffusivity in porous media.

Recently, many dispersion relations have been collected for Belousov-Zhabotinsky waves (BZ waves) and cyclic adenosine monophosphate waves (cAMP waves) for different reaction conditions. These enormous collections of experimental data offer a good opportunity to test this old concept, because in both cases the particle mass of chemical waves can be well defined.

The basic system of the BZ waves consists of one-electron redox catalyst [Ce(III)/Ce(IV)], an organic substrate that can be easily brominated and oxidized (citric acid), and bromate ions in the form of $KBrO_3$, all dissolved in sulfuric or nitric acid. For the evaluation of the diffusion action of BZ waves the mass of hydrogen ions H^+ will

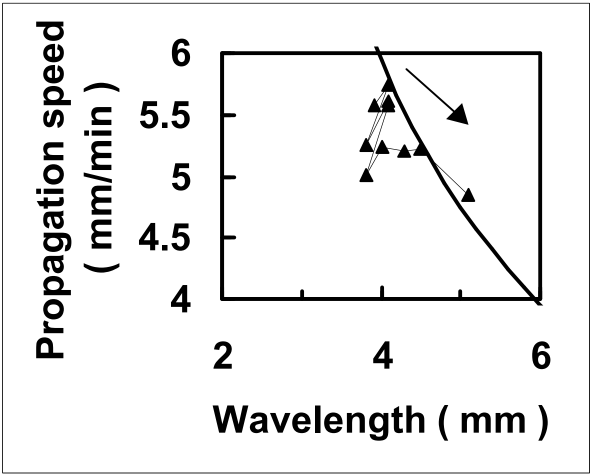

Figure 1 - Evolution of 1D BZ waves in plexiglass thin tube (▲), data from Tatterson and Hudson (Ref. 13), solid curve was calculated from Equation 1 for $K = 1$, $\kappa = 1$, $m = m_H$, h is the Planck constant, the arrow shows the tendency of successive waves to minimize their diffusion action.

be taken as the characteristic particle mass. Tockstein and Trondl [12] have reviewed many variations of the original BZ recipe and concluded that the presence of the H^+ cations was necessary for the appearance of these oscillations.

Tatterson and Hudson [13] substantially improved both the recipe of BZ reaction and the technique for a well-documented observation of the dispersion relation in 1D reaction space. They used a stirred tank as an oscillating source whose frequency could be controlled by the intensity of stirring. The waves emitted from this tank penetrated into the attached glass or Plexiglass tubes and 1D propagation of waves was observed and measured potentiometrically. Their experimental arrangement served as a reproducible and controllable source for the waves from outside into the diffusion tube. Their experimental results are summarized in the Figure 1 together with a

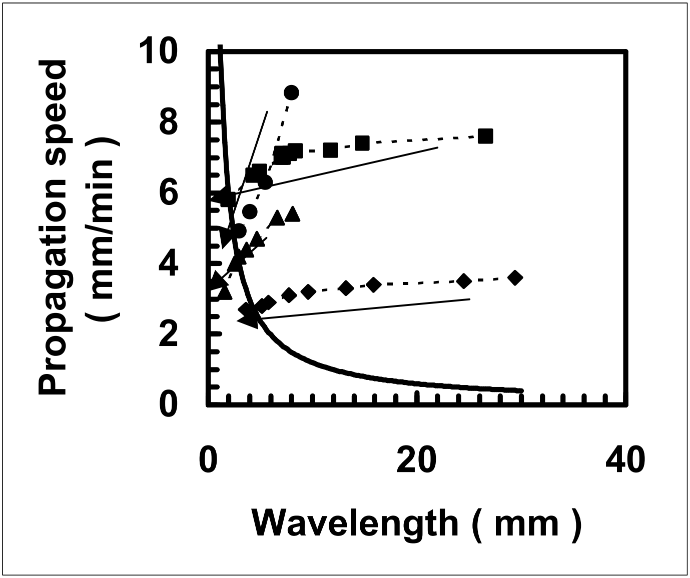

Figure 2 - Evolution of 2D BZ waves in water non-restricted media, data taken from Ševcíková and Marek (Ref. 15), solid curve was calculated from Equation 1 for K = 2, κ = 1, m = m_H, h is the Planck constant, arrows show the tendency of successive waves to minimize their diffusion action.

theoretical curve calculated from Equation 1 (*h* is the Planck constant, *m* represents the mass of H^+, λ is the distance between following patterns, *u* is the propagation speed, the diffusivity factor $K = 1$, the tortuosity factor is $\kappa = 1$). There is an observable tendency of the successive waves to minimize their diffusion action to a certain constant value close to the $6.6 * 10^{-34}$ Js [14]. The further evolution of wave propagation can be described by fluctuations of the diffusion actions around the attractor value $6.6 * 10^{-34}$ Js.

In the absence of stirring, periodic propagation of concentration waves occurs also in a two dimensional system and its investigation brings new evidences about the world of Brownian particles. Dispersion relations for propagating 2D BZ waves were reported by Marek with Ševcíková [15], Pagola *et al*. [16], Jahnke *et al*. [17], and Nagy-Ungvárai with Hess [18]. Their dispersion relations are given in Figure 2 with a relation calculated from Equation 1 for the diffusivity factor $K = 2$, and tortuosity factor $\kappa = 1$ (water non-restricted media). The target patterns are continuously changing, with new patterns of lower propagation velocity and shorter wavelengths replacing their predecessors. The velocity and wavelength of successive waves decrease until they reach a constant value of their product $u\lambda$, and the next waves keep this value for a long time. There is a strong tendency for all four sequences of propagating target waves to self-organize their diffusion fields in such a way that their diffusion actions approach the attractor value $6.6 * 10^{-34}$ Js. Diffusion actions of the next waves fluctuate around this attractor value.

Numerous dispersion relations of BZ waves were measured in the presence of gels, resin beads, glasses, etc. In this case the network of restricted media influences both the propagation speed and wavelength of penetrating waves, and the tortuosity factor k has to be inserted into Equation 1. However, the dispersion relations in these restricted media show the same tendency: minimization of the diffusion action to a certain constant value. Steinbock and Muller [19] have introduced a powerful technique for manipulation of wave propagation. In the ruthenium catalyzed BZ reaction the laser beam can modify the parameters of waves. When the laser source is switched off, the perturbed spiral waves minimize their diffusion action to the lowest value again.

Propagating cAMP waves (cyclic adenosine 3′,5′-monophospate with $M_w = 329.22$) controlling chemotactic aggregation of starving cells of the social amoebae *Dictyostelium discoideum* may serve as an another interesting example of chemical waves. The cAMP waves are

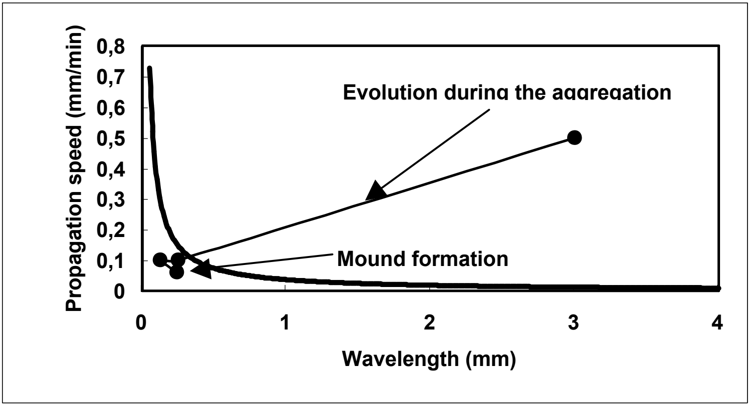

Figure 3 - Evolution of 2D cAMP waves in 1% agar, data taken from Rietdorf *et al*. (Ref. 24) and Dormann *et al*. (Ref. 25), solid curve calculated from Equation 1 for $K = 2$, $\kappa = 1$, $m = m_{cAMP}$, h is the Planck constant, the arrow shows the tendency of successive cAMP waves to minimize their diffusion action.

periodically relayed by cells in aggregation centers and are visible as outward-moving target or spiral waves. The dispersion relations of these cAMP waves during the early stages of aggregation were measured by Alcantara and Monk [20], Gross *et al*. [21], Tomchik and Devreotes [22], Siegert and Weijer [23], Rietdorf *et al*. [24], Dormann *et al*. [25].

In the typical experimental arrangement cells are placed at density of $5 * 10^5$ cells/cm^2 on 1% KK2 (20 mM potassium phosphate buffer, pH 6,8) agar plates and incubated at 22° C for 6 hours. After 6 hours of development the aggregation starts and dark-field wave propagation can be observed. After the onset of aggregation of cells the successive cAMP waves start to decrease both their period and the wave propagation speed during aggregation. The period of cAMP waves decreases from 6 min at the begin of the cell aggregation to 2.5 min (or 1.25 min) after the evolution of 20–30 waves when streams

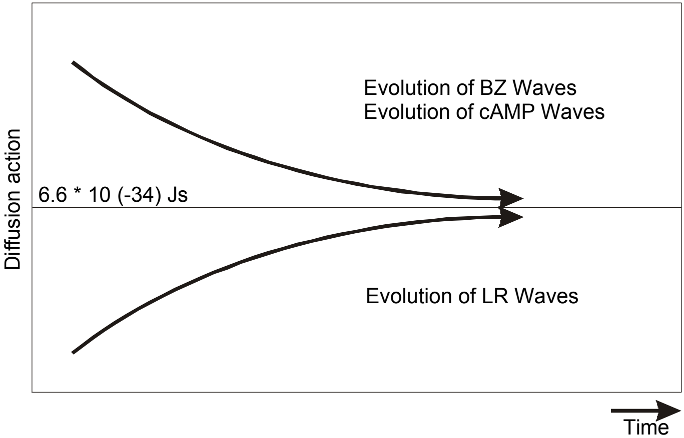

Figure 4 - Temporal evolution of diffusion actions of LR (Liesegang ring) waves, BZ (Belousov-Zhabotinsky) waves, and cAMP (cyclic adenosine 3´,5´-monophospate) waves.

are still flowing into the forming mound. At the same time the wave propagation speed decreases from 600 to 100 μm/min. In late stages after mound formation wave propagation speed stays low and slowly decreases to about 60 μm/min, while the wave period increases to about 4 minutes.

The product of the propagation speed and the wavelength remains approximately constant during mound formation. This situation is depicted on Figure 3. The diffusion action of cAMP waves decreases in value during the early aggregation and remains approximately constant during mound formation. The diffusion of cAMP molecules occurs in the presence of 1% agar and therefore, the tortuosity factor influences the resulting propagation speed and wavelength.

Figure 4 summarizes the evolution of the diffusion actions of Liesegang ring formation, Belousov-Zhabotinsky waves and cAMP waves. The main trend for all three types of chemical waves is similar. During evolution the successive chemical waves show a strong tendency to self-organize their diffusion fields in such a way that the diffusion actions converge to a constant value of about $6.6 * 10^{-34}$ Js. Diffusion actions of the following waves fluctuate around this quantity of action.

The earlier studies of chemical waves revealed several interesting properties that are similar to the effects observed with photon waves (Snell law, reflection, refraction). This diffusion concept may contribute to the explanation of many observed effects from the microworld (including the famous double-slit experiment when single particles create a pattern structure as a diffusion process).

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