

Spatial Structures Formed by Chemical Reactions at Liquid Interfaces: Phenomenology, Model Simulations, and Pattern Analysis

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1. INTRODUCTION. A remarkably wide-scope phenomenon has recently been revealed. Chemical reactions at liquid interfaces proceed in a patterned way; spectacular structures form and grow while matter or energy influx are maintained [1]. Despite its generality and experimental simplicity we could not find descriptions of the phenomenon other than a report by P. Möckel on some photochemical systems [2]. As it turned out, Möckel's observations, which initiated the research project described here, were only the tip of an iceberg; what we subsequently found was beyond any of our expectations.

2. THE PHENOMENON AND ITS GENERALITY. The majority of over 40 reactions we tested formed structures (some special cases in which structures did not form are described below). The initial efforts by us [1,3-6] and by Micheau et al. [7,8] were concentrated on photochemical processes. We found, however, that photochemistry is not a conditional factor: structures are formed also by gases diffusing through a liquid interface and reacting with solutes [5,6,9] and by ground state reactions at liquid/liquid interfaces (e.g., separated by a membrane) [1]. Various solvents were tested and it was found that if strong evaporation, high viscosity, excited state quenching and insolubility of product do not interfere, structure growth is observed.

We found that the phenomenon is quite general regarding the liquid interface: both free and rigid interfaces operate. Selected examples are the interfaces between liquid and air, gas, miscible or immiscible liquids, glass, plastic.

In view of earlier experimental results and models requiring highly complex and non-linear networks of chemical reactions for the formation of (temporal) dissipative structures [10,11], we find it interesting that the phenomenon we investigate shows low sensitivity to the type of reaction and its kinetics. The classes of reactions which produce structure range from complex redox chains [1-4,9], through moderately non-linear reactions of the type $A + B \rightleftharpoons C$ [7,9], to simple first order isomerizations! [7,12]. Examples are the photoreduction of Fe(III) [1,6] and the air oxidation of reduced methylene blue [5] (very complex), protonation of methylorange [9] (second or quasi-first order), and photochromic isomerization [7]. See Fig. 4.

3. A COMMENT ON THE MECHANISTIC APPROACH. The effort directed towards revealing the underlying mechanism(s) of this phenomenon was split into three directions, which are strongly correlated: a) Testing the response of the structure-growing process to changes in various physical parameters, especially in view of known instability phenomena in liquids [13]. b) Developing models of reaction/diffusion-coupled processes for computer simulation and subsequent experimental testing. c) Developing computerized pattern analysis tools for comparison of structures and for kinetic investigation of structure growth.

4. TESTED PARAMETERS. We describe now, phenomenologically, the effects of parameter changes. Due to space limitations the description is brief; details will be published elsewhere. There were two preliminary questions: first, is a chemical reaction necessary? Simple diffusion of a dilute solution of dye [1], and irradiation of photoproduct only, suggest a positive answer. Second, are convections a latter stage in the structure building process, or do they pre-

exist? We showed [1,4-6] that macroscopic convections are driven at a mature stage of the structure growth. No pre-existing convections were detected within the sensitivity of our tests (laser illumination of dusts and deflectometry [4]) when evaporation from the surface was excluded. Micheau et al. have shown [7,8] that if evaporation is allowed, then the pattern formed is a visualization of the evaporation process; this, however, is not the phenomenon we study: we have shown by a variety of experiments that structures form in the absolute absence of evaporation [1,5,6]. The following additional parameters were tested: a) Surface tension. In addition to the various interfaces mentioned above, silicon oil monolayer and addition of surfactants were tested. The structure formation process seems insensitive to this parameter. b) The insensitivity to addition of surfactants seems to exclude also a diffusion-limited aggregation mechanism. c) Depth and viscosity. Profound sensitivity was found at very shallow layers (<1 mm): induction time is increased even to the degree of no-pattern formation. Increase in effective viscosity is probably the reason. Indeed, increase in viscosity at a 1 cm layer produces the same changes [2,12]. A scaling law exists for the average distance between lines as a function of depth [6,7,12]. Structures do not form in a gel [9]. d) Concentration thresholds were searched. We have preliminary indications that these exist, but at very low values. e) Vibrations. It is very difficult to exclude a possibility that the fluctuations which are amplified to a full macroscopic structure are due to minute background vibrations. We went, however, in the other direction: ultrasonic vibrations destroy the structure; light vibrations such as caused by a nearby laboratory magnetic motor, do not seem to interfere. f) Temperature: Rayleigh-number calculations show that in our thin layer experiments, temperature difference should be at least 1 °C. In practice, the difference is <<1°C. Furthermore, structure forms also in a stabilized temperature gradient (cooling the bottom, warming to top). g) Gravity. Sensitivity to this parameter is suggested in thin layer experiments. The full picture of the effect of gravity will be obtained from an experiment in space, now in preparation.

5. TWO DIMENSIONAL SIMULATION MODELS WITH A NON-LINEAR DIFFUSION TERM. The accumulation of the experimental data suggests that the investigated phenomenon may indeed be an authentic non-linear reaction/diffusion coupling process. Furthermore, the low sensitivity to the type of chemical reaction suggests that non-linearities in the transport processes are the dominant factors. Therefore, many of our simulation efforts have been directed towards this type of non-linearity. We exemplify the approach with one model; others will appear elsewhere.

We study the reaction $2A \xrightarrow{k} C$ in two dimensions. For low concentration of C, $\mu_C = \mu_C^0 + RT \ln C$, so that in Onsager equations $\nabla \mu_C = (RT/C) \nabla C$. To remove the singularity of diffusion rate $\rightarrow \infty$ as $C \rightarrow 0$, we replace RT/C by $RT/(C+\alpha)$, where LRT/α is the diffusion constant at zero concentration. Using this assumption and Gauss theorem we obtain:

$$\frac{\partial c}{\partial t} = L_{CC} RT \nabla \left(\frac{1}{C+\alpha} \nabla c \right) + kA^2 \quad (1)$$

$$\frac{\partial A}{\partial t} = \frac{L_{AA} RT}{A_0} \nabla^2 A - kA^2 \quad (2)$$

where we assumed $L_{CA} = L_{AC} = 0$ and that the reactant A concentration does not change during the period of study. Eq. (2) is the standard linear diffusion case; Eq. (1) is the novel non-linear approach. To the best of our knowledge, no previous attempts were made in coupling non-linear diffusion terms with chemical reactions. Numerical solution of reaction-diffusion problems have been carried out so far mainly by the finite difference method, limiting the studies to one dimension. One of us (R.K.) has recently developed an efficient computational tool which makes multidimensional simulation feasible [14]. The first stage in the numerical solution is surface discretization on an evenly spaced two dimensional grid (64x64 points) with periodic boundary conditions (other boundary conditions could be used as well). Spatial derivatives are calculated using a Fourier

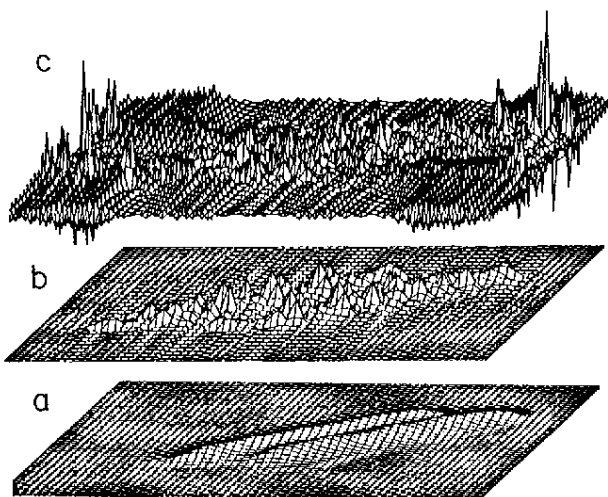


Fig. 1: Simulated pattern growth for $2A \rightarrow C$ (see text). Reaction rate: 10^3 [mole⁻¹ sec⁻¹]; Diffusion rates of A and C: 0.10 [cm² sec⁻¹]; α (eq. 1) = $[0.01]M$; Initial fluctuation: 5%. a) $t=0$ [sec.], b) $t=5000$ [sec.], c) $t = 18000$ [sec.]

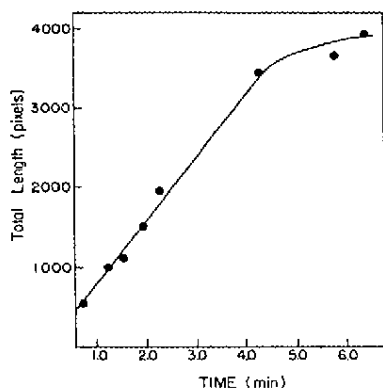


Fig. 2: Total length of pattern skeletonized lines as a function of time

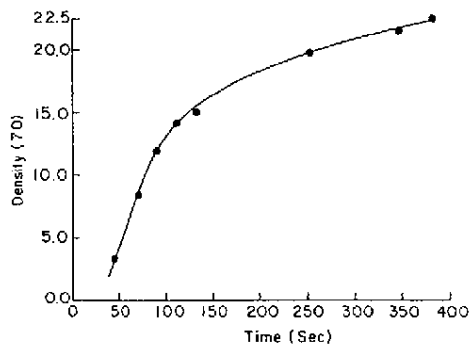


Fig. 3: Growth rate of total product density at shade value of 70

method [14] which gives very accurate values. A first order propagation scheme is used for advancing in time. Initial conditions were chosen such that the concentration of C was zero everywhere and the concentration of A was uniform except for two line-like fluctuations. The pattern-growth is depicted in Fig. 1. Three-dimensional calculations are in progress.

6. COMPUTERIZED IMAGE ANALYSIS OF COMPLEX PATTERNS. The effects of various physical parameters on the process of pattern growth, cannot be fully studied unless tools are developed for quantitative description of spatial structures and their growth kinetics. Computerized image analysis proved to offer solutions [15] some of which are briefly listed in this volume [16]. Two illustrative results are described in Fig. 2 (total length of lines) and Fig. 3 (non-

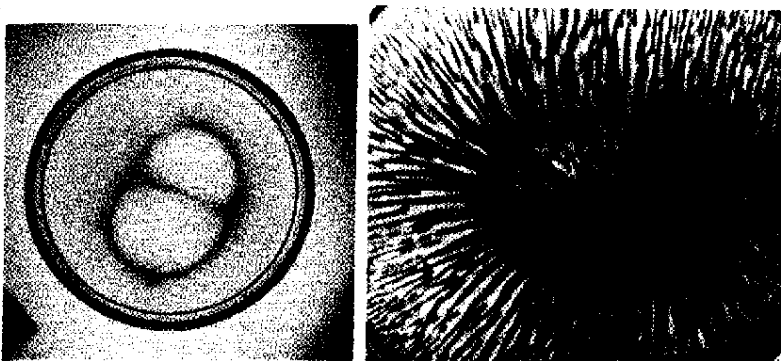


Fig. 4: Simple and complex structures formed by a chemical reaction at an interface. left: photo-oxidation of I^- [2,3]; right: photoreduction of Fe(III) [1].

destructive densitometry), typical of structure formation during photo-oxidations of anilines. Detailed description of the image analysis method will appear elsewhere.

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