Available online at www.sciencedirect.com

ScienceDirect

Colloids and Surfaces A: Physicochem. Eng. Aspects 319 (2008) 218–225

COLLOIDS AND SURFACES A

www.elsevier.com/locate/colsurfa

Formation and role of colloid material structures and surfaces in chemical reaction system: Part II

F. Mogyoródi

University of Miskolc, Department of Chemistry, 3515 Miskolc-Egyetemváros, Hungary

Received 18 July 2007; received in revised form 1 October 2007; accepted 18 November 2007
Available online 4 March 2008

Abstract

In a thermodynamically open, non-isotherm, non-continuous, multicomponent, initially homogeneously distributed chemical reaction system far from equilibrium, quasi-stationary states and a heterogeneous spatial structure divided by surface boundaries may emerge spontaneously by self-organisation. This structure emerges, evolves and devolves over time as chemical reactions are completed. During this process, reactants segregate themselves in space, the rate of the mass transport and the chemical process partly decreases, both processes become periodic, new types of material exchange mechanisms unusual in inanimate nature arise, and feedback and self-regulation occur which promote the survival of the structure produced. Roles of boundary surfaces and solubility in generation of new type periodic or cyclic phenomena were discussed.

Keywords: Structures; Self-organisation; Periodic phenomena; Self-regulation

---

1. Introduction

Early works on non-equilibrium thermodynamics studied mostly homogeneous steady states and systems evolving monotonously toward the final equilibrium. Later on it was realised that chemical and diffusional instabilities can lend to so-called dissipative structures, that is to a symmetry breaking and pattern formation in time and space, especially in non-continuous, non-isotherm, thermodynamically open, far from equilibrium systems (references are listed in Part I [1–20]). After the description of a methyl-chloroformate (MCF)–methanol–water reaction system [1], a report is given of new and interesting periodic surface phenomena, forms of physical and chemical mass transports and exchange mechanisms observed in chloroformate–alcohol–water systems.

2. Experimental

Materials, reactors and analysis methods were the same as were used in Part I, except the next ones.

2.1. Materials

EtCF (C_2H_5OCOCl) and DEC ($C_2H_5OCOOC_2H_5$) purities were >99.0% (w/w) (North-Hungarian Chemical Works).

2.2. Reactors

Different type closed and open reactors were used. The phenomenon on liquid/liquid interface studied in a two-dimensional reactor (Pyrex glass Petri dish with different diameter and high), on the solid/liquid interface in a column reactor made of Pyrex glass, with 1800 mm high and 200 mm diameter, with four external electric tubes radiating violet light.

2.3. Analysis

Solubility was determined by turbidity titrations and in other usual ways. Temperature was measured continuously by termistor or by Fe/Konstantal bimetal or liquid-phase thermometers.

Front or reaction heat wave front propagations were studied by video camera and/or by infrared (IR) thermo camera.

E-mail addresses: fkmmf@uni-miskolc.hu, barthaz@freemail.hu.

doi:10.1016/j.colsurfa.2007.11.052

3. Results and discussion

3.1. *Description of the phenomena (continuation of Part I [1])*

It seemed interesting to test how the methyl-chloroformate–methanol–water reaction proceeded on liquid/liquid interface.

In a three-dimensional (cylindrical glass tube) reactor [1], methyl-chloroformate was layered under the methanol–water reactant solution with the same reaction parameters as reported in Part I [1].

The reaction process was similar. In the initially two-phase reaction system new phases, layers and trips emerged step by step in a substantially higher number than in the initially mixed reaction solution. The phases and phase boundaries were “multiplied”.

Occasionally 10–12 phases, layers and trips developed, but most of the phase boundaries were less sharp than in the initially mixed starting solution.

3.2. *Gradients, fronts and phase separations*

After looking at the aforementioned phenomena [1] and at point 3.1 the question arises what the driving forces in the development of these phenomena are?

The effect of driving forces on diffusive flux, convection, chemical waves and propagating fronts was extensively studied in other systems [2–7].

It was found that in our experimental system [1] during the induction period vertical differences or gradients evolve in the reaction solution in a spontaneous process without any external intervention (Fig. 1a and b).

Density gradients caused by thermal and solutal gradients often cause instabilities in propagating fronts [2,8].

These gradients (density, concentration, temperature and electric conductivity) initiate chemical reaction fronts or waves with a downward or upward direction in the reaction mixture. The density and concentration gradients (Fig. 1a and b) are formed through diffusion and convective upward and downward mass motion, or through fluid flow due to the different densities of the reaction components.

$$\rho_{\mathrm{MCF}} > \rho_{\mathrm{DMC}} > \rho_{\mathrm{H_2O}} > \rho_{\mathrm{MA}} \qquad (1)$$

In the upper part of the vertical tube reactor a reaction mixture with a high MA concentration and a high MA/MCF ratio forms. That is the reason why here reaction is continuing with a higher reaction rate and propagates downwards as a reaction heat wave front, and causes the temperature gradient (Fig. 2b and d) which, with the help of thermodiffusion, contributes to the development of the concentration gradient (Fig. 1b). The use of digital image processing is a useful technic for the measurement of concentration gradients [9].

With the help of an infrared thermo camera this process can be followed well. Initially, the thermo image is homogeneous and the vertical temperature profile is linear, then the temperature in the upper part of the reactor is always higher and warming is faster than in the lower part.

The thermal and H^+-ion autocatalytic front, which propagates in a downward direction, initiates the reaction with proton and heat addition to layers which are lower and have lower concentrations of MA and H^+-ions and lower temperatures than upper reacting layers have.

All this happens with increasing delay.

This is basically not only heat transport through conduction or diffusion, but the rate of the exothermic reaction and the rate of heat production are shifted in time and space. In the beginning these thermal reaction fronts propagate downwards without difficulty with a rate of 5.7 cm/min, then with 2.8 cm/min and with 2.5 cm/min. In the vertical temperature profiles waves can be observed later with temperature differences of several degrees Celsius (Fig. 2b and d) and on the continuous pictures of the infrared thermo camera decelerations and accelerations can be detected. These indicate the appearance of phases (layers) and phase boundaries (Fig. 2a, c and e). Sharp regional heat producing layers can also be observed appearing after the probable local explosion of the thermal and H^+-ion autocatalytic reaction front (Fig. 2e). No layers and strips can be observed visually yet, however, the image of the thermo camera shows their appearance (Fig. 2).

The formation of layers begins at the end of the induction period, when there is not enough MA to hold soluted the H_2O and the DMC produced.

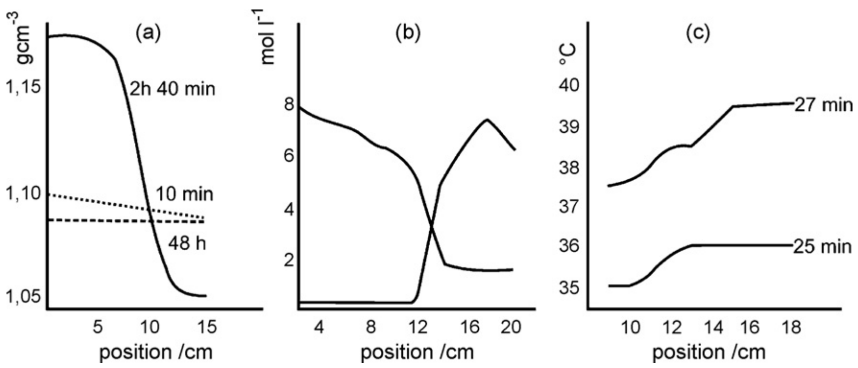

Fig. 1. Density and concentration gradients (differences) in different time in reaction mixture in a 30 cm cylindrical glass tube reactor with 5 cm inside diameter. (a) Density gradients in 10th and 160th minutes and in 48th hour of the reaction. (b) Concentration gradients of reactants in 190th (1) MCF and (2) MA minutes of reaction. (c) Temperature gradients in 25th and 27th minutes.