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DISSIPATIVE STRUCTURES IN SOLIDIFYING SOLUTIONS

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Structure formation during polymerization of polyacrylamide and gelatinization of gelatine in aqueous solutions are described. In both cases dissipative dynamic structures occur in the solutions due to convective flows and manifest in macroscopically visible structure patterns after solidification. Adverse vertical temperature gradients of maximal 2°C for polymer solutions and 1°C for gelatine solutions are assumed to be responsible for the instability of the systems and thus for their dynamic behaviour.

Introduction

The spontaneous formation and maintenance of ordered structures from originally homogeneous, undifferentiated media is one of the most fascinating phenomena in the natural and technical world. Static structures arise during equilibrium processes due to a temperature decrease (e.g. crystallization). On the other hand dynamic (or dissipative) structures occur spontaneously by the cooperative motion of particles in a thermodynamically open system if adverse gradients drive the system into an unstable state with a supercritical distance from equilibrium. In the first case the structure is conserved due to an entropy decrease of the system and a transition to a state of minimum potential energy, whereas in the second case the structure is maintained by an entropy export of the system via continuous flows of energy and mass through the system.

The occurrence of dissipative structures in physics, chemistry, biology, geology, meteorology and technology as well as the theoretical background are occasionally described in the literature [1–12].

In spite of their transient nature dynamic structures may transform to static ones if the convective motion within the system ceases without having any opportunity for equalizing the existing spatial structures. Such 'frozen' structures mainly arise from more or less viscous fluids solidifying as a fast

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process by a considerably evaporation or binding of the solvent. Among these are the surfaces of desiccating lakes or sandbanks, hardening lacquers, shrinking puddings and polygonal stone assemblies on mud flats in subpolar regions freezing and thawing several times every year ('rudemarks' in Iceland).

In the present paper we describe the formation of cellular patterns during the solidification of gelatine solutions firstly mentioned in 1914 by Leduc [13] and compare them to those obtained during the polymerization of acrylamide already described in [14].

Methods and Materials

Polymerization: A mixture of the following solutions was used in the proportions 4A, 3B, 10C and 1D: A =0.1% ammonium persulfate, B =1% N,N,N',N'–tetramethylethylenediamine, C =28% acrylic acid amide +0.75% N,N'–methylene–bis–acrylamide, D =concentrated methylene blue solution as dye. The mixture was poured into petri dishes of approximately 10 cm in diameter giving layers of 1 to 5 mm thickness. After about 15 min polymerization and structure formation was finished. Further details are given in [15].

Gelatinization: Gelatine solutions were prepared by heating a mixture of gelatine powder (Merck 4078) in concentrations between 2% and 5% in distilled water and adding concentrated solution of methylene blue or potassium hexacyanoferrate(III) as dyes. After coaling to room temperature (25^{o}) the mixture was pipetted into petri dishes of approximately 10 cm in diameter rendering layers of 1 to 5 mm thickness. The petri dishes remained uncovered at room temperature until gelatinization was finished after 2 to 4 h depending on the gelatine concentration and the initial temperature. Addition of concentrated NaCl–solution to the warm gelatine solution giving a final concentration of 3% enhanced the structure formation though the time was prolonged considerably.

Documentation: Photos of the polymer and gelatine structures were taken directly from the petri dishes under diffuse illumination from below. Photos of the gelatine structures were also taken from projection images under intensive transmitted light.

Results and discussion

Polymerization structures

Structure formation of various types of cell pattern (Figs 1 and 2) was obtained with fluid layers between 1 mm and 5 mm of thickness. Among these were vermiculated rolls, ribs and irregular polygons with side number from 4 to 7. Cell diameters were in the mm-range. The boundaries of the cells were more intensively stained by methylene blue than the concave surfaces of the intermediate cells. Maximum elevations of the boundaries above the cell centers amounted to 0.5 mm.

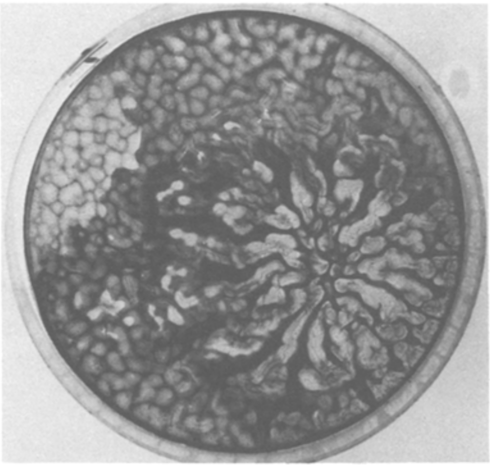

Fig. 1 Total view of the structures on polymerized acrylamide stained by methylene blue showing polygons (top left), rolls (top and bottom left) and a star-like superstructure (right). Direct photo of a petri dish illuminated from below

From calorimetric and thermometric measurements [15] a vertical temperature gradient of approximately 2^0 between the bottom and the upper surface of the layer was assumed to be accountable for the convective motion and the subsequent structure formation. The gradient is caused by the polymerization heat within the layer and the heat loss due to conduction as well as to evaporation of water at the upper surface. It could not be decided between a Rayleigh-Benard or a Marangoni convection because both numbers calculated for the specific experimental conditions exceeded the critical values cited in literature, for review see [1]. As an explanation a Rayleigh–Benard convection is based on density differences which are caused by a

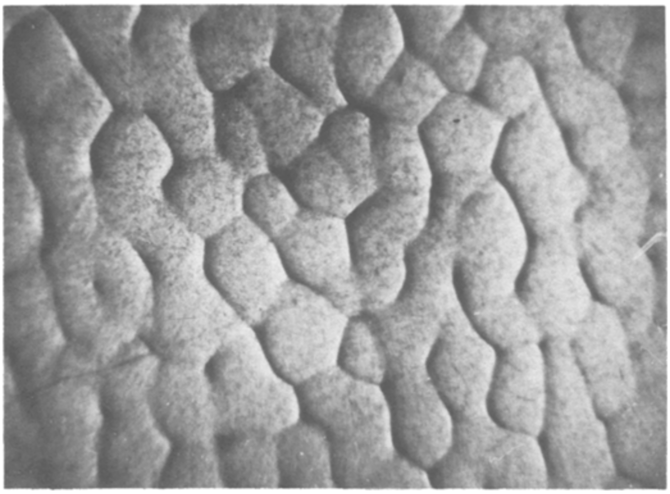

Fig. 2 Enlarged part of the surface structure of a polyacrylamide layer showing irregular polygons with diameters of 1 to 2 mm. Illumination from below, the polymer was stained by methylene blue

temperature gradient over the sample volume, or in other words it is a buoyancy driven convection. The Marangoni convection, however, is induced by a temperature gradient which gives rise to differences of the surface tension over the sample under investigation. The concave cell surfaces indeed point more to a convection which is driven by the surface tension, i.e. a Marangoni mechanism.

Gelatinization structures

Structure pattern of different species of cells (polygons, ribs, streamers and rolls, cf. Fig. 3) could be recognized directly by eye against an intensive illumination under low angular incidence or as a projection image by transmitted light. In lower and higher concentrated gelatine solutions than given above no visible formation of structures occurred. Predominantly polygons were found in solutions mixed with NaCl. In the extreme case of a very thin gel layer of less than 0.5 mm which completely dried in during three days the NaCl crystallized at the boundaries of the structure cells and enhanced the shape of the polygons (Fig. 4). Cell sizes were mostly not larger than 1 mm with boundaries elevated less than 50 μm. Methylene blue itself did only enhance the visibility of the cell boundaries if added as a concentrated older solution with obviously precipitated small crystals. Freshly prepared solutions of methylene blue or potassium hexacyanoferrate stained the gels homogeneously and enhanced the visibility of the structures only in opposite light because of their darker contrast. During the gelatinization period the weight of the petri dishes was followed any yielded a loss of 0.29 mg H_2O/s or 4.5 μg $H_2O/(s \cdot cm^2)$ in the mean. This loss was obviously due to the evapora-

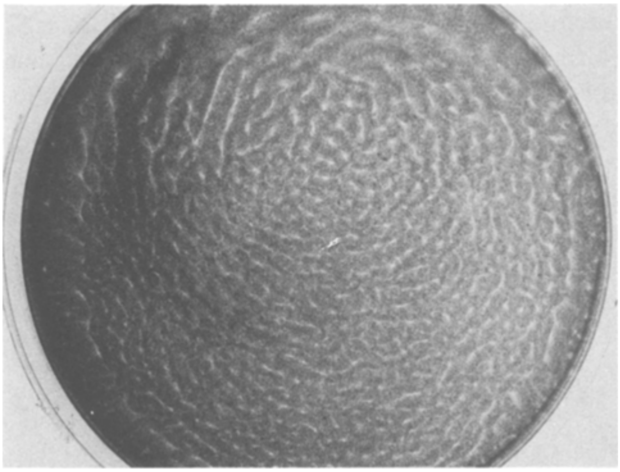

Fig. 3 Total view of the cell pattern of a solidified gelatine solution stained by potassium hexacyanoferrate. Direct photo of a petri dish illuminated from below

Fig. 4 Total view of a 0.5 mm-layer of gelatine plus 3% NaCl. The methylene blue stained layer is completely desiccated and NaCl crystallized within the network of the former cell structures. Direct photo of a petri dish under illumination from below

tion of water from the upper surface and requires a heat power 10.6 mW/cm^2 if an evaporation heat of 40.7 kJ/mol is assumed for water at 25°.

Thus, evaporation at the surface of the petri dish, resting at a constant temperature of 25°, gives rise to a heat flow through the gel layer and establishes a temperature gradient of 0.2 to 1° between the lower and upper surface. In contrast to the experiments with polyacrylamide where the polymerization process creates a significant heat source lasting for more than 15 min, in gelatine systems no further sources or sinks of heat were detectable. It could be shown by calorimetric measurements that the mixing of the gelatine powder with water gave a heat of 15.6 J/(g of gelatine) ceasing after about 12 min. But the actual solidification of the solution as coming off during the structure formation was not recognized in the calorimetric response.

A Rayleigh–number of $R_a = 12.3 \cdot \Delta T \cdot d^3$

and

a Marangoni-number of $M_a = 1050 \cdot \Delta T \cdot d$

(ΔT = temperature difference in °C, d = layer thickness in mm) calculated for a mainly aqueous solution were adopted from [15]. These formula yield R_a–values between 12 and 1538 and M_a–values between 1050 and 5250 for a maximum temperature gradient of 1° and layers of 1 mm to 5 mm. Both ranges cover the critical values of 658 for a Rayleigh-Benard mechanism and 4000 for a Marangoni mechanism [1]. Thus it remains open which of these mechanisms is responsible for the structure formation.

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Zusammenfassung — Die Bildung von geordneten Strukturen während der Polymerisation von Polyacrylamid und der Gelatinisierung von wässerigen Gelatinelösungen wird beschrieben. Diese sogenannten dissipativen Strukturen entstehen bei beiden Prozessen durch Konvektionen in der flüssigen Phase, die sich nach der Verfestigung als makroskopisch sichtbare Muster darstellen. Die Konvektion beruht auf vertikalen Temperaturgradienten, die unter den hier vorgegebenen Bedingungen mit 1 bis 2°C aus den exothermen Reaktionswärmen abgeschätzt werden können.