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Transition between circular fronts and spiral waves in marginally excitable media

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Belousov–Zhabotinsky (BZ)-type waves are studied on a polysulfone membrane loaded with bathoferroin catalyst. The membrane is placed on a glass-fibre filter-disc soaked with a BZ medium containing no catalyst. Waves are periodically initiated on the membrane surface by using silver- and platinum-wire electrodes. When the area around the silver electrode is made marginally excitable by sufficiently shortening the period of perturbations, an unusual transition between circular fronts and spiral waves is observed.

1. Introduction

Spiral waves are ubiquitous in spatially distributed biological and chemical systems whose local kinetics are excitable.[1] As they play an important role in cardiac arrhythmias and in cellular ion transport mechanisms, formation of spiral waves has been actively studied for a long time.[2–7] Transition from a target pattern (a picture of concentric rings emanating from a pacemaker centre) to a spiral pattern is generally attributed to local inhomogeneities or anisotropies in the medium.[8,9] It has also been shown that transverse coupling of circular waves supported on the surfaces of semipermeable membranes may lead to spontaneous formation of rotating patterns.[10,11] Generation of spiral waves in the presence of obstacles in an otherwise homogeneous medium has been also predicted[12] and later observed experimentally.[13] The criteria for the appearance of spiral waves are: (i) the frequency of a wave train approaching an obstacle must exceed a critical value and (ii) the obstacle must have sharp corners.

The BZ reaction[14] has been widely used to investigate a number of spiral-wave phenomena. For a detailed account consult, for example, a recent review by Kapral.[7] To eliminate the disadvantages of liquid or gel systems applied in earlier experiments, Lázár *et al.*[15,16] have developed a novel technique to fix BZ catalysts on a polysulfone membrane. When a loaded membrane is placed in a batch reactor containing the other components of a BZ mixture, reaction takes place only on the membrane surface, consuming minute amounts of reagents. Thus, chemical waves can be observed under the same conditions for very long periods (8–10 h).

Lázár *et al.*[15] have also pointed out that excitable media of arbitrary geometries can be created with this technique by cutting and painting the membranes. Steinbock *et al.*[17] have utilized the method by loading the catalyst onto membranes with an ink jet printer. They reported the observation of some unusual wave forms (*i.e.* hexagonal, diamond-shaped and pentagonal) as well as the spontaneous formation of spiral waves in different patterned excitable media. As the loaded membrane can be easily cut, it is an ideal gadget for studying the formation of spirals around sharp corners in an otherwise uniform medium. However, before such experiments are performed, the following two critical parameters of wave behaviour supported by the membrane should be known: (i) the planar-wave velocity, c, which determines the critical radius, r_{crit}, for wave generation in a resting medium and (ii) the minimal period, T_{min}, by which a series of stimuli can be generated from a single source of excitations.

In this paper, we present results of experiments for determining the values of c and T_{min} in various BZ mixtures. Waves are initiated on the membrane by using silver- and platinum-wire electrodes. We also report on an unusual transition between circular fronts and spiral waves. This is observed when the area around the silver electrode is made marginally excitable by sufficiently shortening the period of perturbations. To check if microscale inhomogeneities were responsible for the observed behaviour, the membrane surface is studied by scanning electron microscopy (SEM).

2. Experimental

2.1 Preparation of the membrane

All reagent solutions were made with analytical grade chemicals (Reanal, except indicated otherwise). For the fixation of 'bathoferroin' catalyst (the complex of Fe^{2+} ion and bathophenantroline, analogous to ferroin) on the polysulfone membrane (Gelman, pore size: 0.45 μm, diameter: 47 mm) the procedure of Lázár *et al.*[15] has been slightly modified. The following two solutions were applied: A, 5.0 mg bathophenantroline (4,7-diphenyl-1,10-phenanthroline, Aldrich) in 5.0 cm^3 glacial acetic acid and B, a mixture of 20.0 cm^3 0.002 mol dm^{-3} $Fe(NH_4)_2(SO_4)_2$ in 0.20 mol dm^{-3} H_2SO_4 (Acidum) and 5.0 cm^3 ethanol. The dry polysulfone membrane was dipped into solution A for *ca.* 2 s, then placed into solution B for 2 min. The membrane was continuously moved around in solution B, with a wooden rod, to avoid inhomogeneity in the formation of the catalyst. The loaded membrane was washed in distilled water for *ca.* 20 min. The ready-to-use membranes were stored in the dark under distilled water.

2.2 Amount of catalyst on the membrane

To check if the applied procedure resulted in membranes of constant properties, the amount of catalyst was determined as follows.

A weighed sample (10–12 mg) of a dried membrane containing the catalyst was first soaked in distilled water, and then dissolved in 3.0 cm^3 dimethyl sulfoxide (DMSO). We note that DMSO does not moisturize the polysulfone-based membrane, therefore, its wetting by water is a must. Absorbance of the clear, red-coloured solution was measured at $\lambda_{max} = 538$ nm. Bathoferroin cannot be prepared at sufficiently high concentration in DMSO. Therefore, its molar absorbance coefficient, $\varepsilon_{538} = 20\,730$ mol^{-1} dm^3 cm^{-1}, was determined by using 1–4 × 10^{-5} mol dm^{-3} solutions in an 18 : 1 : 1 (v/v) mixture of DMSO, glacial acetic acid and water. (This mixture, unfortunately, cannot be applied to dissolve the loaded membrane because of the formation of a white precipitate.) A stock solution of the catalyst was prepared in 1 : 1 (v/v) mixture of glacial acetic acid and water and diluted with the other mixture accordingly. The amount of catalyst formed on the membrane surfaces was found to be constant within experimental error (0.2 ± 0.01 μg cm^{-2}).

2.3 BZ solutions

BZ solutions were freshly prepared from stock solutions in a 50 cm^3 stoppered Erlenmeyer flask. 2.0 cm^3 malonic acid solution (2.0 mol dm^{-3}), 2.0 cm^3 $NaBrO_3$ solution (varied between 1–2 mol dm^{-3}), 2.0 cm^3 H_2SO_4 solution (4–6 mol dm^{-3}) and 4.0 cm^3 KBr solution (0.66 mol dm^{-3}) were mixed in this order. After the yellow colour of bromine disappeared, 8.0 cm^3 of $(NH_4)_2SO_4$ solution (2.0 mol dm^{-3}) was added as suggested by Lázár *et al.*[15] The above recipe produced BZ media that, in contact with the loaded membrane, were not self-oscillatory but of supported wave behaviour upon excitation.

2.4 Reactor

The simple reactor used for wave-train experiments is shown in Fig. 1. It consisted of a flat polycarbonate Petri dish (Nalgene, diameter: 85 mm) with a cover and a glass-fibre disc (Macherey-Nagel, Rundfilter GF-2, diameter: 55 mm). The cover was manufactured to hold a silver-wire electrode (0.5 mm) and a platinum-wire electrode (0.5 mm). A circular opening (diameter: 50 mm) in the centre of the cover allowed us to record better quality video images. Before a loaded membrane was placed on the glass-fibre disc, it was soaked in a freshly prepared BZ medium for 2 min. For simple wave experiments, a glass Petri dish (diameter: 70 mm) was applied without a cover because of technical reasons (see Section 2.5).

2.4 Wave generation

Experiments were carried out at room temperature without thermostatting. For single-wave experiments, a wave was initiated by touching the membrane with a silver wire. For wave-train experiments, series of waves were initiated electrochemically. The silver electrode (in contact with the membrane) was negatively biased at −1.3 V with respect to the platinum electrode (in contact with glass-fibre filter-disc) except for 2 s intervals when it was positively biased at +1.2 V. Pulses of excitations were triggered at preset intervals by using a programmable D/A converter (PAL-Multilab 711B) built into an IBM PC/AT (386/40MHz).

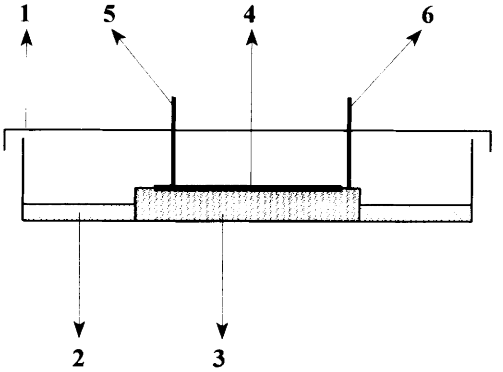

Fig. 1 Simple reactor to study chemical waves on a membrane surface. 1, Petri dish with cover; 2, BZ medium without catalyst; 3, glass-fibre filter-disc; 4, polysulfone membrane loaded with bathoferroin; 5, silver-wire electrode and 6, platinum-wire electrode.

2.5 Imaging system

For single-wave experiments, the wave behaviour was monitored by using a home-built two-dimensional spectrophotometer[18] including an SDT 4500 CCD video camera with a variable set of Eternic objectives. The membrane was illuminated from below by parallel beams of diffuse light passing through a broad band filter (*ca.* 520 nm peak transmittance). The images were stored on a video tape and later analysed by using a frame-grabber (LFS-AT, Leutron Vision AG). Standard techniques of image processing[18] were applied to achieve a high-resolution tracking of the wave-front position. For wave-train experiments, the membrane was illuminated from above (no filter was applied), and the images were recorded on a video tape without further processing.

3. Results and Discussion

3.1 Single-wave experiments

Advantages of the membrane system developed by Lázár *et al.*[15,16] over the earlier applied liquid or gel systems are the following: (i) as the catalyst is fixed on the membrane, its diffusion need not be taken into account; (ii) disturbing hydrodynamic effects are eliminated; (iii) waves can be observed in bubble- and convection-free media for long periods. Therefore, it is of prime importance to characterize the wave behaviour on the membrane quantitatively, and to compare the results with earlier measurements in other media. Such quantities are, for example, the planar-wave velocity, *c*, and its dependence on the composition of BZ mixtures.

Planar waves, however, cannot be produced by the wave-generation method described earlier. By touching the membrane with a silver wire, only circular waves can be initiated. To eliminate this problem, a small strip (1 cm × 4 cm) was cut out from a loaded membrane, and a wave was initiated at the centre of one of its shorter edges. Under these conditions, the expanding circular wave is soon transformed into a planar wave.

The dependence of planar-wave velocity, *c* (mm min^{-1}), on bromate and sulfuric acid concentrations in various BZ mixtures has been found to have the following form:

$$c = A + B([H_2SO_4][BrO_3^-])^{1/2} \qquad (1)$$

The coefficients $A = -3.9$ mm min^{-1} and $B = 20.8$ mm min^{-1} mol^{-1} dm^3 in eqn. (1) were determined from measurements of wave position as a function of time in a series of 24 BZ mixtures (Fig. 2), with bromate and sulfuric acid concentrations varying over the ranges 0.13–0.22 and 0.47–0.67 mol dm^{-3}, respectively. The values of coefficients *A* and *B* are in good agreement with the measurements of previous studies.[19]

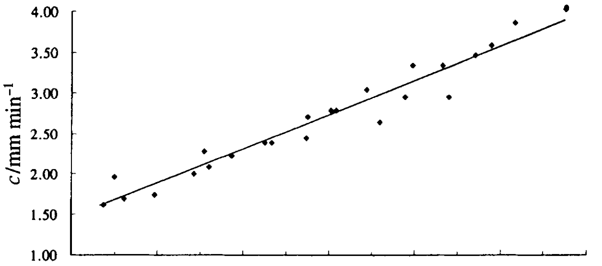

Fig. 2 Planar-wave velocity, *c*, as a function of bromate and sulfuric acid concentrations in various BZ mixtures at fixed concentration of malonic acid (0.22 mol dm^{-1})

It is a clear indication that the mechanism of wave behaviour on the membrane surface is the same as has been established earlier for gel or liquid systems.

Knowing the planar-wave velocities in different BZ mixtures, one can calculate values of r_{crit}, the radius of a circular region corresponding to the critical nucleation size for wave initiation. The critical radius can be estimated by the eikonal equation,[20] $r_{crit} = D/c$, where $D = 2 \times 10^{-5}$ cm^2 s^{-1} is the diffusion coefficient of $HBrO_2$. Depending on the composition of BZ mixtures, the critical radius for the polysulfone membrane system varies between 30 and 80 μm, in good agreement with values reported in previous studies.[19] The importance of knowing the critical radius as a function of the composition of the BZ medium is discussed in the concluding section.

3.2 Wave-train experiments

Wave-train experiments have been carried out by using the reactor shown in Fig. 1. Waves were initiated electrochemically as described in the experimental section. The original aim of these experiments was to determine the values of T_{min} (the minimal period by which series of waves can be initiated from a single source of excitations) as a function of the composition of the BZ media. The value of T_{min} also defines the length of recovery period characterizing the membrane system.

Shown in Fig. 3 are the results of experiments when trains of stimuli are applied at different periods. Changes in behaviour are shown as a function of bromate concentration at two different concentrations of sulfuric acid. When the period of perturbations is large enough, every excitation generates a wave. We characterize the pattern in terms of the firing number n_f. It is defined by the number of circular waves emitted from the centre of initiations divided by the number of stimuli applied. For these regular patterns (Fig. 4), which are observed in the regions above curves (a) in Fig. 3A and B, the value of n_f is 1/1.

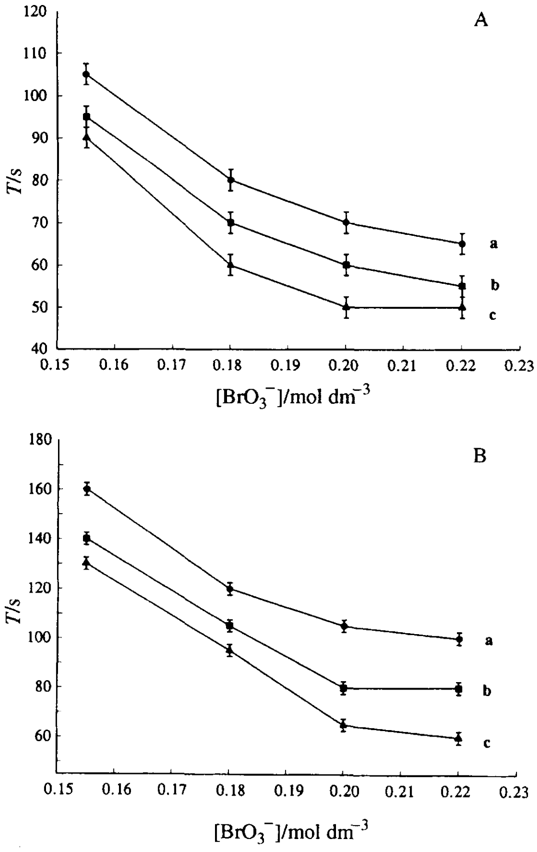

Fig. 3 Regions of different wave patterns observed in wave-train experiments as a function of period T of stimuli and the concentration of bromate at different concentrations of sulfuric acid: (A) 0.64 and (B) 0.55 mol dm^{-3}. The concentration of malonic acid (0.22 mol dm^{-3}) has been kept constant. The following wave patterns were observed: (i) regular target pattern with firing number 1/1 in the region above curve (a); (ii) broken wave fronts between curves (a) and (b); (iii) spiral waves between curves (b) and (c) and (iv) target patterns with firing number 1/2 in the region below curve (c) (Error bars indicate experimental error in determining T values by using membranes that were prepared in one batch.)

As has been expected, below a critical value (T_{min}), only every second perturbation initiates a circular wave. These patterns with $n_f = 1/2$ are observed in the regions below curves (c) in Fig. 3. Surprisingly, at slightly larger T values (in the region between curves (b) and (c), not circular but rotating wave patterns evolve. At still slightly larger T values [in the region between curves (a) and (b)] another unusual wave behaviour is observed. Circular waves emanating from the centre of excitations may break-up into smaller pieces. Frequently, only part of a circular wavefront develops. These 'broken' wave fronts may or may not transform into small rotors, which then annihilate each other, resulting in turbulent wave patterns.

The above described transition from circular fronts to spirals has been reported neither in gel- nor in liquid-based BZ systems. It is, in fact, quite unusual that spiral waves emerge from only one centre of excitation. Since the formation of spirals by this mechanism has been observed over a large range of bromate and sulfuric acid concentrations, it appears to be a general phenomenon in the membrane system. It seems always to occur when the medium around the silver electrode is made marginally excitable by shortening the period sufficiently.

Shown in Fig. 5 are images of a spontaneously formed spiral wave rotating, seemingly, around the silver electrode. However, a closer look at the images reveals the existence of a small circle (about twice the size of the silver electrode) that appears to be the core of the spiral wave. That this small circle is slightly brighter than the background indicates its more active state compared with other parts of the membrane, especially the region close to the silver electrode. The picture is very similar to that reported by Lázár *et al.*,[16] where spirals were observed to rotate around a central hole cut out of the membrane.

The mechanism of the observed behaviour is not yet clear. Some important factors, however, can be observed by watching the video tape of the whole event. When the first stimulus is applied to a membrane in a 'resting' state, a nice circular wave develops. Upon the second excitation, however, only part of a circular wave is generated. This behaviour is similar to that observed in the region between curves (a) and (b) in Fig. 3. When the third stimulus is applied, activity can be observed only on a very small section of the circle around the silver electrode. A small piece of wavefront is formed, which then starts to travel around the circle (in this case, counterclockwise). It first evolves into a double-rotor with one arm touching the circle (first image in Fig. 5). Then, it changes into a regular spiral arm (last image in Fig. 5) that looks more like the involute of the small circle. It is important to note that the period of 'rotation' is approximately twice the period of excitation, which may explain why the fourth excitation is inactive. Surprisingly, the spiral arm does not circle around the 'dead' zone forever. Just before completing a full turn, it suddenly 'leaves' the centre circle, resulting in a curved wave front that now travels outward 'freely'. However, when the fifth stimulus is applied, a new spiral is formed, as described earlier, and the whole process is repeated again, and again at every second excitation.

It is clear that the observed behaviour is closely related to the appearance of the small 'dead' zone around the silver electrode. When a stimulus is applied, the reaction is locally switched to the autocatalytic production of $HBrO_2$ by

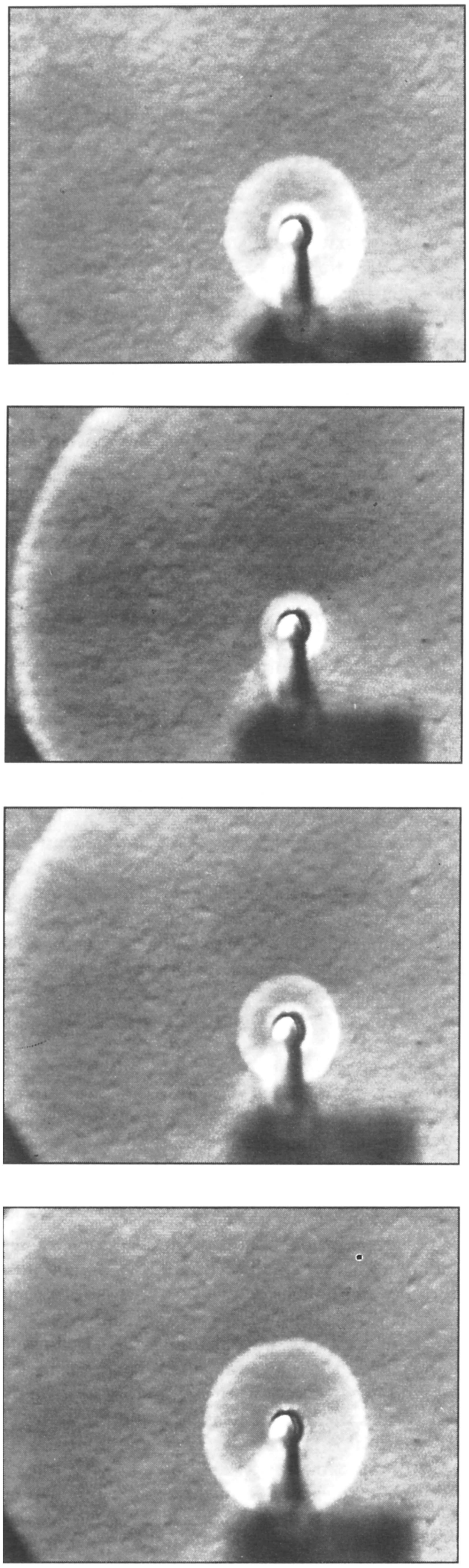

Fig. 4 Successive images of circular waves around the silver electrode when the period of stimuli is large enough. Every excitation generates a wave, thus the value of n_f is 1/1. The period of stimuli (2 s each) is 120 s. The images (in the order from top to bottom) show wave positions at 10, 140, 150 and 160 s after the first initiation has been applied. The field of view in each panel is 11.7 mm × 9.1 mm. Concentrations in the BZ mixture are: $[BrO_3^-] = 0.22$ mol dm^{-3}, $[H_2SO_4] = 0.55$ mol dm^{-3}, [malonic acid] $= 0.22$ mol dm^{-3}

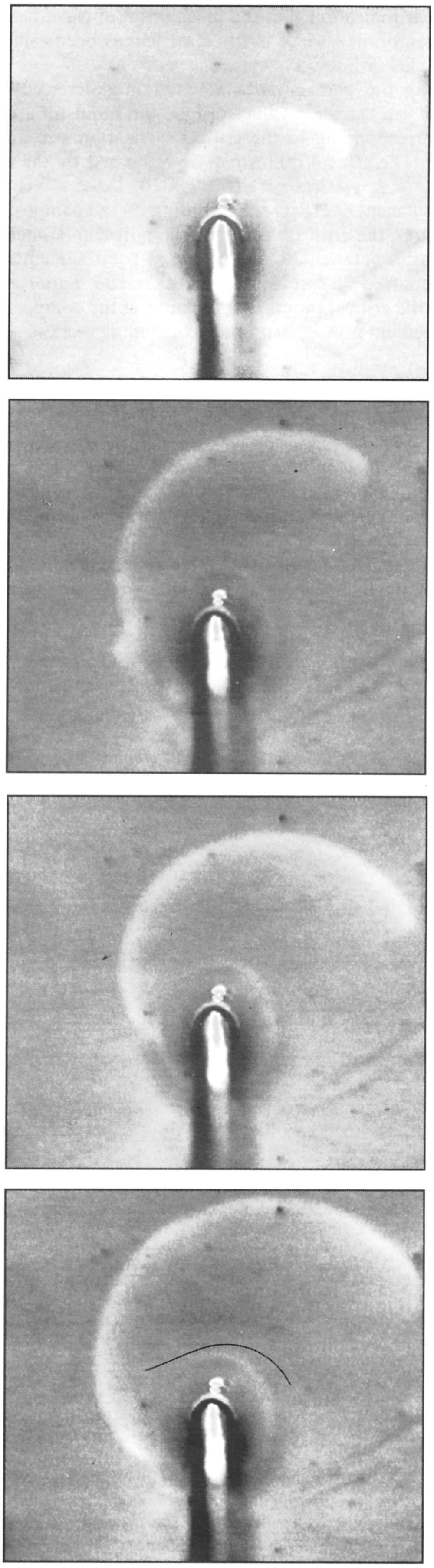

Fig. 5 Successive images showing a spiral wave rotating, seemingly, around the silver electrode. The period of stimuli (2 s each) is 50 s. The images (in the order from top to bottom) show a spiral wave at 50, 80, 90 and 100 s after the first spiral has appeared on the membrane. The field of view in each panel is 12.4 mm × 13.3 mm. Concentrations are the same as in Fig. 4.

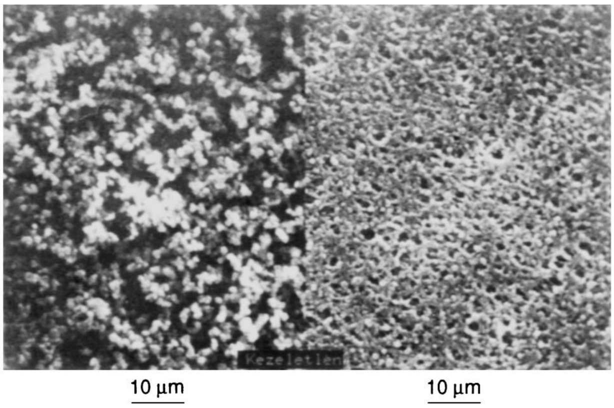

Fig. 6 SEM images (1000 × magnification) of two sides of a polysulfone membrane before loading with the catalyst

momentarily depleting bromide at the positively biased silver electrode. During this process, silver bromide precipitate is formed in a small layer around the silver electrode. Repeated generation of silver bromide and its accumulation on the membrane surface may account for the build-up of the 'dead' zone around the electrode.

Since the observed behaviour has been reported neither in gel nor in liquid systems, the role of the membrane itself should be also emphasized. For example, local inhomogeneities on the membrane surface could result in small differences in threshold values for an excitation to occur which, in turn, may account for the formation of a small wave front at only one part of the small circle around the silver electrode.

3.3 Morphology of the membrane

The morphology of loaded and unloaded polysulfone-membrane surfaces has been studied by SEM (JEOL, JEM-2000FX). The membranes were gold-plated using a standard technique. Fig. 6 shows SEM images of the unloaded-membrane surfaces at 1000 times magnification. The two sides of the same membrane are quite different: one side is bubbly, while the other is threaded. Loaded membranes resulted in the same images, indicating that these structures are not altered by loading the catalyst onto the membrane. Note that no long-range inhomogeneities could be detected in the range of critical nucleation size (30–100 μm) for wave initiation in the applied BZ media.

4. Conclusions

The velocity of planar waves on the surface of polysulfone membranes loaded with catalyst has been determined as a function of the composition of the BZ media. The mechanism of wave behaviour on the membrane surface was found to be the same as has been established earlier for gel or liquid systems. With the ability now at hand to estimate the critical nucleation size in different BZ mixtures, we plan to create patterned membranes[15–17] with walls and openings of different sizes resulting in different effects on the wave behaviour. Experiments with such membranes will be carried out in the near future to test the numerical predictions of Pertsov *et al.*,[12] and also to extend earlier studies on signal transmission in chemical systems.[19,21]

An unusual transition from target pattern to spiral waves has been observed in marginally excitable BZ systems. The phenomenon always occur when the period of excitation is close to the length of the recovery period of the given medium. In this respect, our observation is strongly related to the so-called 'vulnerability' of the BZ system as described by Gómez-Gesteira *et al.*[22] However, a direct comparison with their results is not easy because of differences in experimental conditions, in our case, the position of a stimulus with respect to a conditioning wave is not varied.

We think that formation of a 'dead' zone around the centre of excitations and local inhomogeneities of the membrane might play an essential role in the observed behaviour. Nevertheless, no long-range inhomogeneities, in the range of critical nucleation size (30–100 μm), could be detected by SEM. Another possibility is that the break-up of waves and the spiral formation are due to electric-field effects.[23–26] Experiments and modelling studies to understand the spontaneous formation of spiral waves in marginally excitable media are in progress.

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