

ACOUSTIC EMISSION OF THE BRIGGS–RAUSCHER OSCILLATORY REACTION: EFFECT OF STIRRING

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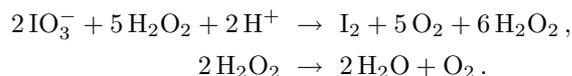
The acoustic emission method has been applied to the investigation of the dependence of the oxygen release in the Briggs-Rauscher oscillatory reaction on the rate of stirring. The oxygen distribution does not increase toward a limiting value but achieves a maximum and decreases afterwards. There exists a low stirring rate at which the release of oxygen from the solution proceeds in the form of “fountains”. This can be observed before the disappearance of the iodine oscillations. The results obtained by the acoustic emission method can be useful in the description of the unknown mechanism of the Briggs-Rauscher reaction.

1. Introduction

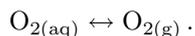
Regular periodic reactions and reactions showing a very complicated and chaotic progress occur first of all in systems being far away from the equilibrium state; irreversible physicochemical processes take place during those reactions. Until quite lately, only processes in that the reactants change monotonically towards equilibrium quantities in a closed system have been investigated. However already in 1921, Bray discovered the phenomenon of the periodic release of iodine and oxygen during the decomposition of hydrogen peroxide in the presence of iodate as catalytic agent [1]. These processes could not be described by the mechanisms accepted at that time in chemical kinetics. The oscillatory oxidation of organic acid by bromate in the presence of cerium ions, discovered by Belusov-Zhabotynski, has aroused a growing interest in oscillatory reactions and other non-linear phenomena of irreversible processes. The main stimulus for the development of chemical kinetics was the need to explain periodic biological processes caused by chemical reactions, e.g. the enzymatic catalysis of redox reactions occurring in living

organisms or the oscillatory course of the glycolysis (which is one of the most important metabolic processes).

The oscillatory Briggs-Rauscher process (BR), known also as the “iodine clock”, is a coupling of Bray-Liebhafsky oscillators (BH) and the well-known Belusov-Zhabotynski oscillator (BZh) [2–6]. The substrates of the BR reaction are potassium iodate, KIO_3 , hydrogen peroxide, H_2O_2 , a manganese (II) salt, MnSO_4 , malonic acid, $\text{CH}_2(\text{COO})_2$, and sulphuric acid, H_2SO_4 . The number of oscillations of the concentrations of iodine and iodide ions, and of the accompanying oscillations of oxygen release, depends on the initial concentrations of the reactants, the reactor type, temperature and on the rate of stirring of the reaction system. Both the oscillation processes are mutually phase shifted. [6]. The reaction mechanism is very complex and has been cleared only to a small extent. The main global reactions may be written:



The mechanism includes a large number of elementary reactions, among them being radical reactions (autocatalytic production of HJO_3) and non-radical ones (iodation of the malonic acid). From the viewpoint of the problems discussed in this paper, the most important process is the velocity of transfer of oxygen from the solution to the atmosphere:



This is why the kinetics of this reaction depends on stirring.

Stirring is a very complicated phenomenon occurring in the time and space scales. The space aspect of macroscopic stirring consists in the superimposing of flows of different initial reactant streams leading to a homogeneous system. In the micro-scale, imperfect mixing causes the formation of local swirls with small gradients of the reactant concentrations in the elementary flux. The initiation time and the spot of vortex peculiarities in the space are difficult to predict, however their occurrence is the source of extreme processes of different dynamic runs. Among other things, this is the reason why a standardization of the mixing process would be very much needed. It should be stressed that not homogeneity but heterogeneity is the normal phenomenon in biology and inanimate nature (geologic processes). The effect of mixing in non-linear reaction systems, particularly in the BZh reaction, is the subject of frequent studies. A decrease in stirring causes increasing in the heterogeneity of the reaction system and, because of the increasing non-linearity, the occurrence of new phenomena such as reaction clocks and homogeneous chaos. Thus, the mixing rate is an example of a parameter of bifurcation in non-linear reaction systems. In the BR reaction, the transport of the gas released in the solution to the atmosphere depends first of all on the stirring rate. For a given reaction system, there exists a rate at that the thin superficial liquid layer can be neglected; the transport of the gas from the solution occurs immediately and without any drag [9]. If, however, the mixing is very slow, the liquid flows are laminar and supersaturated gas solutions are likely to appear. Consequently, the nucleation of gas bubbles becomes spontaneous; the bubbles increase very quickly and are emitted to the atmosphere in an

explosive way. Those phenomena are visually attractive and because of their periodicity the name *fountain effect* is rather justified [10].

In this work, the time of gas release in the BR reaction was studied at different stirring rates. Oscillatory processes in chemical systems are measured mainly by potentiometric methods. In our opinion, the acoustic emission method seems to be reliable for the study of the gas release in chemical reactions [11, 12]. In the literature, there exists only one paper dealing with the application of acoustic emission, namely for the study of the oscillatory Bray reaction [13].

2. Experiment

Reactants: analytically pure potassium iodate (V), KIO_3 , malonic acid, $\text{CH}_2(\text{COOH})_2$, manganese sulphate (II), MnSO_4 , sulphuric acid, H_2SO_4 and hydrogen peroxide, H_2O_2 have been used without further purification. The stock solutions have been prepared using redistilled water. The amounts of solutions poured in a cylindrical vessel have been chosen so as to obtain the following concentrations: $[\text{KIO}_3]_o = 0.067$; $[\text{CH}_2(\text{COOH})_2]_o = 0.050$; $[\text{MnSO}_4]_o = 6.7 \times 10^{-3}$; $[\text{H}_2\text{SO}_4]_o = 0.026$; $[\text{H}_2\text{O}_2]_o = 1.200 \text{ mol/l}$. The final volume of the solutions studied was 50 ml. The MnSO_4 solution was added at the end. The solutions were stirred using a mechanical stirrer with $20 \times 10 \text{ mm}$ paddles. The minimum and maximum mixing rates were 50 and 2500 r.p.m., respectively.

The parameters of the acoustic emission (rate of counting, RMS values) were registered by a measuring set shown in Fig. 1.

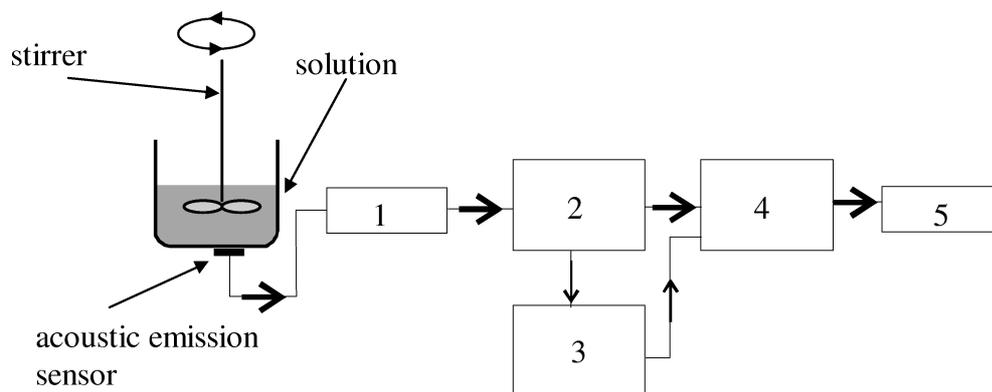


Fig. 1. Diagram of the measuring set: 1 — pre-amplifier, 2 — AE analyser of DEMA type, 3 — oscilloscope with memory of IWATSU OS-6612C type, 4 — computer, 5 — printer.

The counting rate and RMS values were registered at a time base of 0.1 s with the exception of the stirring process for which the values were collected in 1-second intervals. The single signals for the frequency analysis were registered by a digital oscilloscope of IWATSU OS-6612C type. The Fourier analysis of those signals was performed in the frequency range $0 \div 500 \text{ kHz}$.

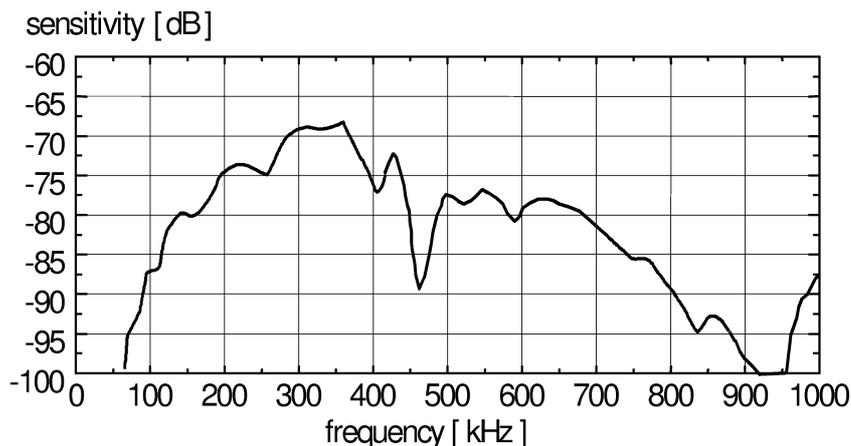


Fig. 2. Frequency characteristic of the broad-band transducer, type NANO-30, produced by PAC.

Mean spectra of a few or a few dozen of acoustic emission signals taken from selected time intervals of the BR reaction at room temperature have been put to the tests. The broad-band PZT transducer from the PAC company (Fig. 2) was attached to the outside of vessel bottom. The amplification and the discrimination threshold of the AE analyser and oscilloscope were the same for all the specimens.

3. Results and discussion

The periodic variations of the iodine concentration, observed by change of the color of the solution, start immediately after the addition of KMnO_4 . The colorless solution becomes yellow-tawny and then again colorless. The color change cycle was repeated sixteen times and lasted for about 200 s. At the same time gases have been liberated, mainly oxygen. The oxygen release has become most intensive after the termination of the iodine oscillations. The complete characteristics of the acoustic emission are different depending on the stirring rate (Fig. 3). In a very narrow range of the stirring rates, oxygen is released in the form of periodic fountain-like explosions (Fig. 3B).

The rate of the AE countings in a range selected from the course shown in Fig. 3B, in that a fountain-like oxygen emission occurs, is shown in Fig. 4. Beside the five oscillating explosions lasting for about 54 s, a distinct splitting of the maxima is observed. The latter is probably due to the fact that the counting rate base is 0.1 s and the liberation of unit volumes of oxygen from the solution is not synchronised with the stirring rate (ca. 1 r.p.m.).

This result shows that the AE method is suitable for the monitoring of the dynamics of the gas release from solutions.

The dynamics of the gas release during the iodine oscillations, i.e. during the first 200 s, characterised by the RMS values, shows a monotonic AE energy increase and the rate of the energy increase depends on the stirring rate (Fig. 5). Furrow and Noyes, measuring the oxygen volume by a thermostatic burette joined to the reaction solution [14],

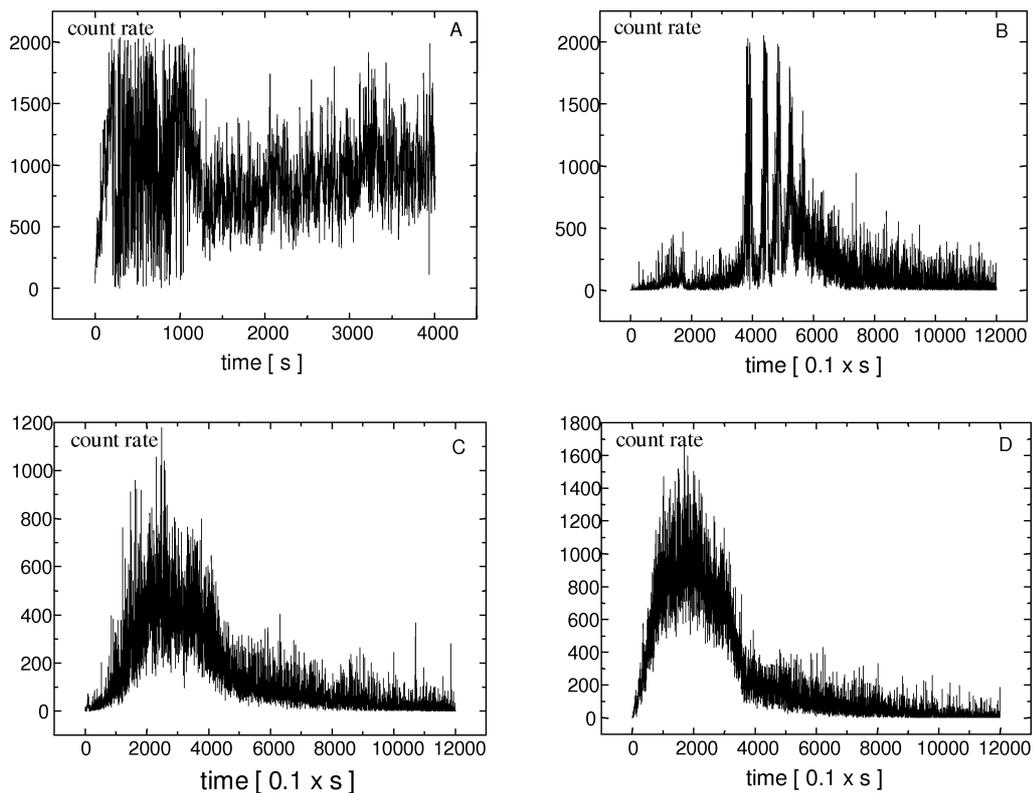


Fig. 3. Dynamic of the oxygen release in the BR reaction for different stirring rates: A — without stirring, B — 50 r.p.m., C — 800 r.p.m., D — 1500 r.p.m.

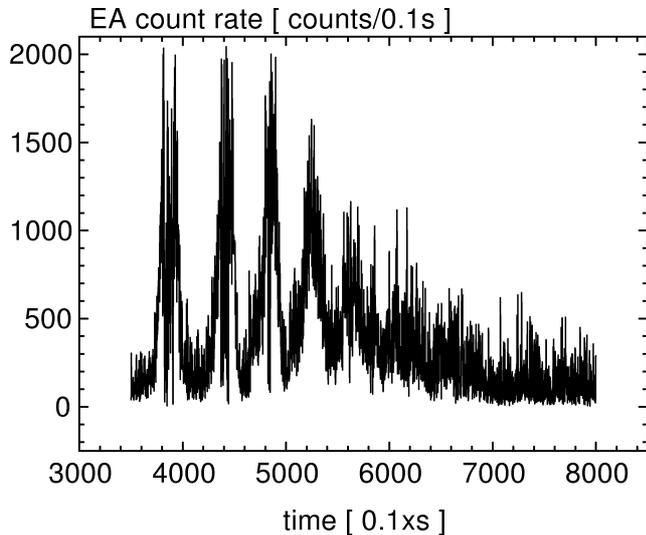


Fig. 4. Rate of AE countings during the fountain-like release of oxygen (as in Fig. 3B).

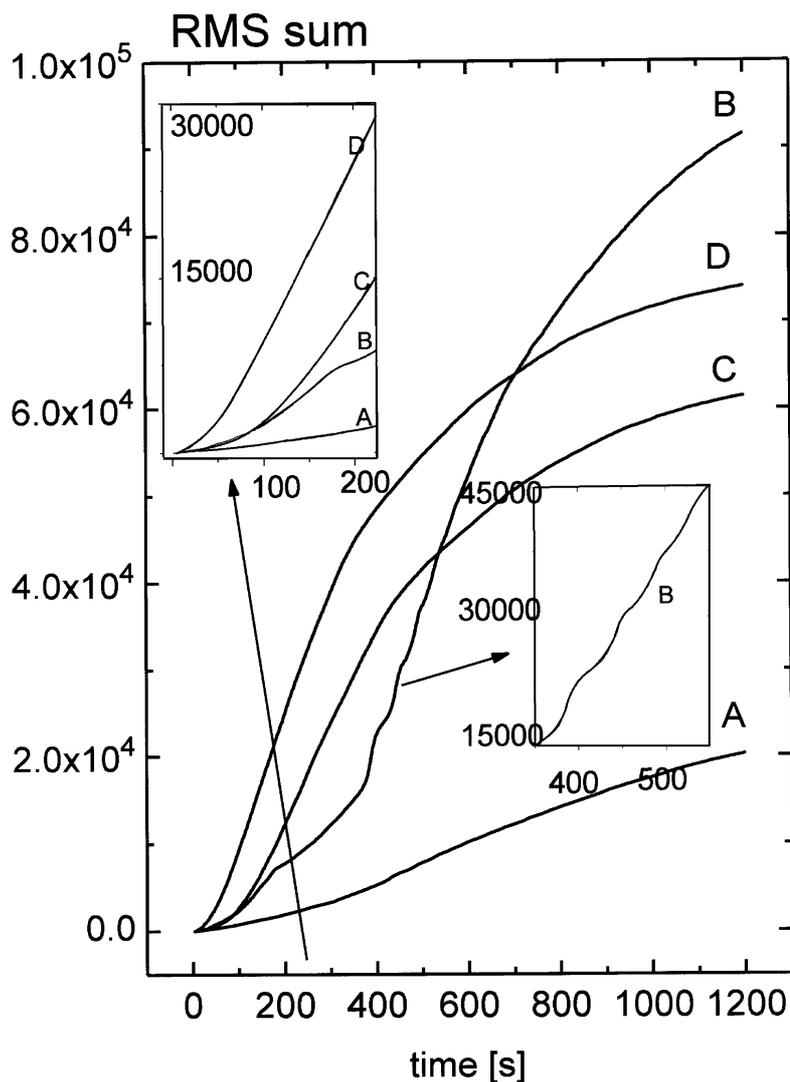


Fig. 5. Dependence of the AE energy on time during the BR reaction at different mixing rates.

observed a non-oscillating oxygen release in the BR reaction. Assuming the hypothesis of a monotonic increase in the oxygen release, the values due to the monotonic increase have been separated from the real RMS values; in this way the AE course, probably characterising the dynamics of the process of iodine oscillations, have been obtained (Fig. 6).

The averaged spectra of a dozen of single AE signals collected from different time intervals of the BR reaction were similar. In all the studied reactions, there appears a 100 kHz wide band in the frequency range $200 \div 350$ kHz (Fig. 7). The spectra are probably connected with perturbations of the solution surface caused by the gas emission.

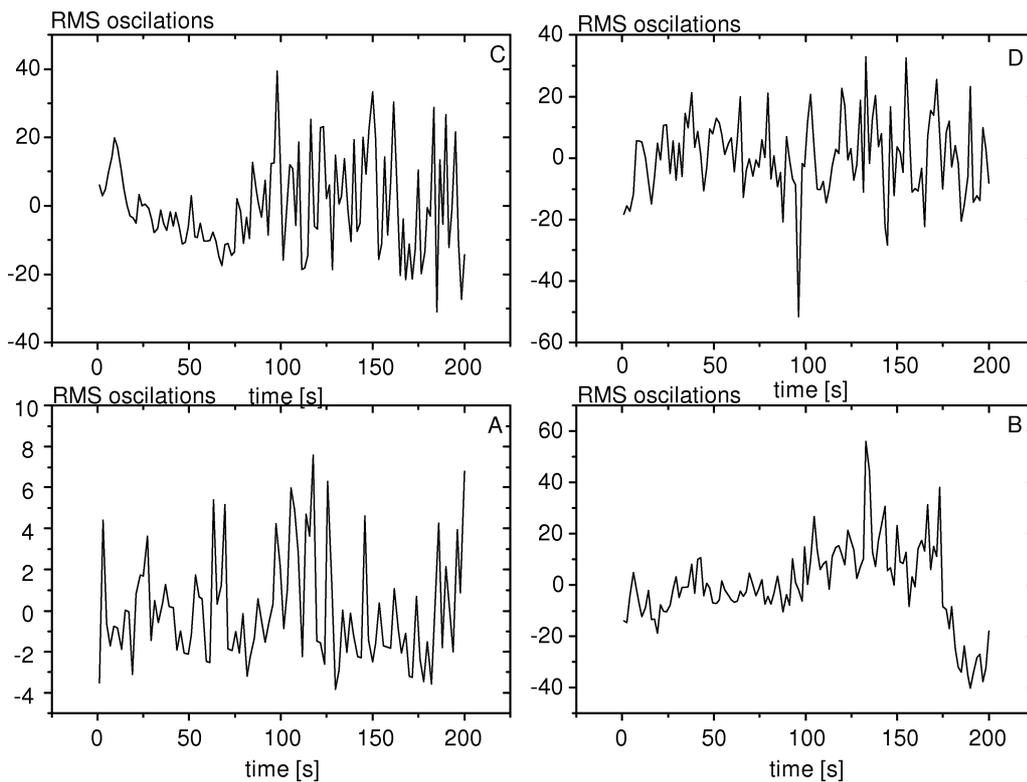


Fig. 6. Dynamics of the BR reaction during the $[I_2]/[I^-]$ oscillations (details are given in the text).

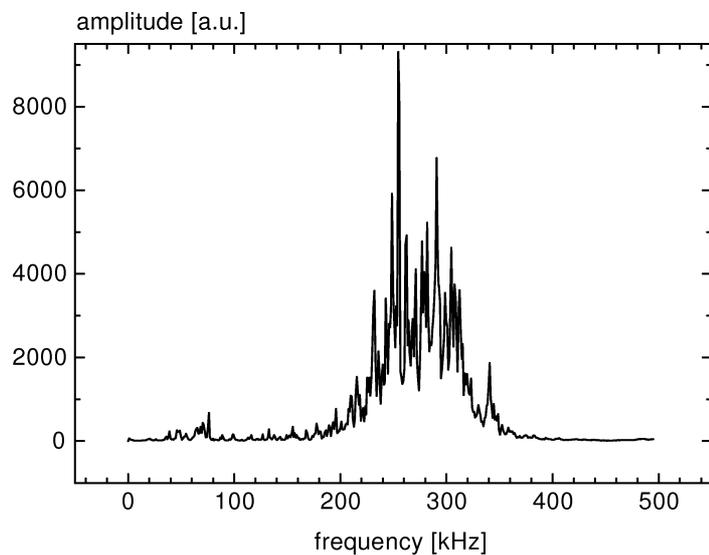


Fig. 7. Averaged spectra of 30 AE signals from the second maximum of the fountain effect (Fig. 4).

4. Conclusions

- In the BR reaction, the stirring affects the dynamics of oxygen release significantly in both the qualitative and quantitative senses. The dependencies of the RMS oscillations and AE counting rates increase with time and achieve maximum values the sooner the more intensive is the stirring (Fig. 3C and 3D). Stirring rates up to 50 r.p.m. cause a very intensive fountain effect in the oxygen emission.

- During the oscillations of the iodine concentration, the AE energy increases monotonically with time. It should be stressed that at this reaction stage, beside oxygen, also iodine is evolved and the mixing rate does not affect the quantity of the observed $[I_2]/[I^-]$ oscillations. However, the analysis of the RMS courses after the subtraction of the monotonic component of the increase, shows a dependence of the RMS amplitude on the stirring rate (Fig. 6).

- The investigations of the effect of stirring on the reaction dynamics seem to be helpful in the determination of the mechanism of the BR reaction and in the modelling of the influence of hydrodynamic effects on the kinetics of complex chemical reactions. The attempts at the connection of the hydrodynamic and chemical models in non-linear chemical reaction systems were initiated by DUTTA and MENZINGER [15]; they observed an effect of the manner and rate of stirring on the bistability of the hysteresis of the $BrO_3^-/Br^-/Ce^{+3}$ system. According to Epstein, if the stirring in autocatalytic biological and chemical systems is non-ideal in time and space, the consequences are extreme variations in the dynamics of those systems [16].

- The authors of this paper have for the first time observed that gas evolution oscillators involve nucleation, growth and escape of bubbles from the supersaturated solution in the Briggs-Rauscher reaction.

Acknowledgement

This paper is devoted to Professor Jerzy Ranachowski, the main originator of the Polish school of acoustic emission, on the occasion of the fiftieth anniversary of His scientific activity.

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