Chemical Physics 441 (2014) 1–4

Contents lists available at ScienceDirect

Chemical Physics

journal homepage: www.elsevier.com/locate/chemphys

Bray–Liebhafsky oscillatory reaction in the radiofrequency electromagnetic field

Dragomir R. Stanisavljev [a,*], Zoran Velikić [b], Dragan S. Veselinović [a], Nevena V. Jacić [a], Maja C. Milenković [a]

[a] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, P.O. Box 473, 11001 Belgrade, Serbia
[b] Institute of Physics, University of Belgrade, Pregrevica 118, Zemun, Serbia

ARTICLE INFO

Article history:
Received 30 April 2014
In final form 27 June 2014
Available online 4 July 2014

Keywords:
Bray–Liebhafsky reaction
Radiofrequency field
Electromagnetic radiation
Oscillatory reaction
Cylindrical capacitor

ABSTRACT

Oscillatory Bray–Liebhafsky (BL) reaction is capacitively coupled with the electromagnetic radiation in the frequency range 60–110 MHz. Because of the specific reaction dynamics characterized by several characteristic parameters (induction period, period between chemical oscillations and their amplitude) it served as a good model system for the investigation of the effects of radiofrequent (RF) radiation. RF power of up to 0.2 W did not produce observable changes of the BL reaction parameters in the limit of the experiment reproductivity. Results indicate that, under the given experimental conditions, both dissipative and reactive properties of the solution are not considerably coupled with the RF electrical field.

1. Introduction

Due to the constant increase of the number electromagnetic emitters in the human environment a large effort is made in investigating their effects on biological systems [1–3]. Results are controversial and difficult to compare due to the inhomogeneity and multifunctionality of biological samples, different experimental conditions and chosen parameters for the description of the radiation effects. Chemical systems are easier to investigate, and the number of experiments with use of microwave-heating sources constantly increases [4]. The main effects of microwave (MW) radiation may be ascribed to thermal (ordinary, and specific thermal effects) [4,5], and tentative nonthermal effects, not connected with the temperature in the system [5,6]. Despite of the lower frequency of the radiofrequency (RF) radiation, their influences on systems are basically related with the same two effects.

For the investigation of electromagnetic influences on chemical processes, oscillatory reactions [7] are convenient systems. Although the actual mechanism is still under the investigations, Bray Liebhafsky (BL) oscillatory reaction [8–11] may serve as a model system for the mentioned investigations due to the specific reaction dynamics described by discernible parameters serving as indicators of external influences. The reaction belongs to the class of chemically oscillating systems characterized by periodic creation and decomposition of reaction intermediates. It may be formally described as periodic domination of two complex processes [8–11], reduction of iodate to iodine (1)

$$2IO_3^- + 2H^+ + 5H_2O_2 = I_2 + 5O_2 + 6H_2O, \quad (1)$$

and subsequent oxidation of formed iodine to iodate (2)

$$I_2 + 5H_2O_2 = 2IO_3^- + H^+ + 4H_2O. \quad (2)$$

Due to the specific reaction dynamics, the periodic disappearing and appearing of the iodine can be observed (chemical oscillations) on a time scale of minutes. Beside iodine, all intermediates, not showed explicitly in (1) and (2) exhibit periodic evolution and may serve for monitoring reaction dynamic. The whole reaction has characteristic induction regime (time before the first oscillation), period between oscillation and their amplitude. All these parameters are the "fingerprints" of the reaction and depend of the initial composition and temperature. If the initial reaction composition and temperature are kept constant, mentioned parameters may serve as indicators of the RF effects. In order to eliminate simple thermal effects, keeping constant reaction temperature is necessary. It can be achieved by thermostating the system with an external heat bath.

Microwave influence on the BL mixture provoked observable changes of the reaction dynamics, relative to the conventional heating, which cannot be ascribed to thermal effects only [12–14]. Microwave irradiation heats conductive water solutions through two mechanisms, orientation of molecular dipoles (mainly water) and translational movement of solvated ions [4]. In the MW frequency region this causes the phase lag of the polarization in the

* Corresponding author. Tel.: +381 11 3336769.
E-mail address: dragisa@ffh.bg.ac.rs (D.R. Stanisavljev).

http://dx.doi.org/10.1016/j.chemphys.2014.06.017
0301-0104/

sample relatively to the applied field and efficient dissipation of the MW energy as heat. From the microscopic point of view, lag of the polarization is caused by breaking the relatively weak hydrogen bonds between water molecules in the bulk [15] as well as between solvated water around ions and nearby water molecules. This enables dissipation of electromagnetic energy as heat through friction between dipoles and solvated ions.

In this work we examined possibility that lower frequency RF radiation can induce changes of the BL reaction dynamics.

2. Experimental

Bray–Liebhafsky reaction is conducted in the cylindrical glass vessel of the diameter $d = 2.2$ cm and height $h = 4.3$ cm. The volume of the solution was $V = 13.3$ cm^3. Reaction dynamics are followed by recording the potential of the Pt electrode relatively to the Hg/Hg_2SO_4 reference electrode (Schott electrode) connected to the reaction solution with the electrolyte bridge filled with $KClO_4$ (0.372 M). Each reaction solution was mixed with magnetic stirrer at 300 rpm to prevent formation of temperature and concentration gradients. Reaction mixtures were kept constant in all experiments at the temperature of 63 ± 0.2 °C.

The initial composition of the mixture was: $[KJO_3]_o = 0.072$ M, $[H_2SO_4]_o = 0.048$ M and $[H_2O_2]_o = 0.304$ M. Chemical composition in all experiments were the same. All chemicals: sulfuric acid, potassium iodate and hydrogen peroxide was of P.A. grade Merck. For the preparation of stock solutions deionized water of resistivity 18 MΩ cm is used throughout.

The system for the application of the radiofrequency electromagnetic radiation consisted of RF generator GW Instek GRG-450B and homemade amplifier LZY-23 able to deliver 3 W of electromagnetic energy. Due to a non ideal coupling with the load, part of the radiation is reflected to the amplifier, a small part is emitted in the space and part is transferred to the load. The actual power transmitted to the reaction cell is practically impossible to measure. It can be calculated only in the case of the coupling with purely thermal resistance load of 50 Ω by measuring the voltage at the load with oscilloscope. The power of 0.2 W emitted to the load was calculated. Due to the less efficient coupling, the actual power transmitted to the reaction cell may be only smaller than this value.

The reaction solution was capacitively coupled with the amplifier by filling the space between electrodes of the cylindrical capacitor. It is formed of a central copper wire electrode housed in the glassy tube and cylindrical copper electrode placed at the outer side of the reaction vessel. In this way, both electrodes of the capacitor are chemically isolated from the solution. The experimental setup is shown in Fig. 1. Conductive reaction solution between capacitor electrodes configures a "lossy" capacitor.

The experimental procedure begins with thermostating the mixture of potassium iodate and sulfuric acid till the desired temperature after which the reaction is initiated with the addition of small volume of hydrogen peroxide. The RF field is applied after the initiation of the reaction during the induction period (time between the addition of hydrogen-peroxide and the first oscillation) and the first five oscillations. After this, the field is turned off and the next five oscillations (without field) are monitored as well. Oscillations with the applied RF field are compared with the oscillatory evolution without the field. Only three frequencies (60, 80, and 110 MHz) are randomly chosen for the investigations.

3. Results and discussion

In Fig. 2, an oscillogram without the RF field and oscillograms with the application of 60, 80, and 110 MHz radiation are

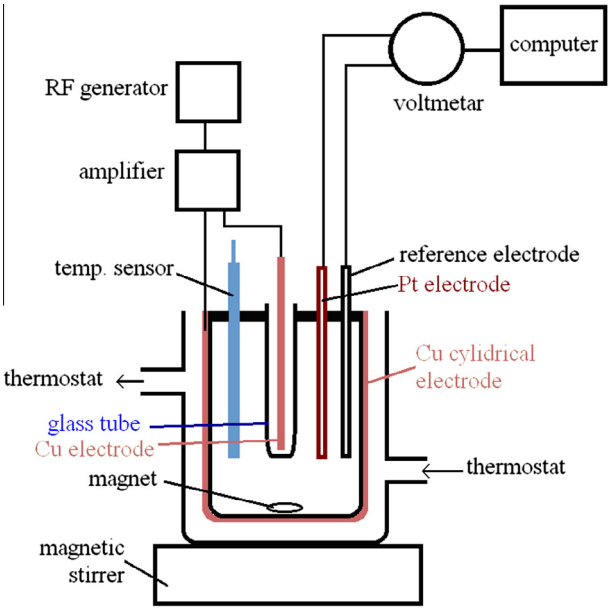

Fig. 1. Experimental setup.

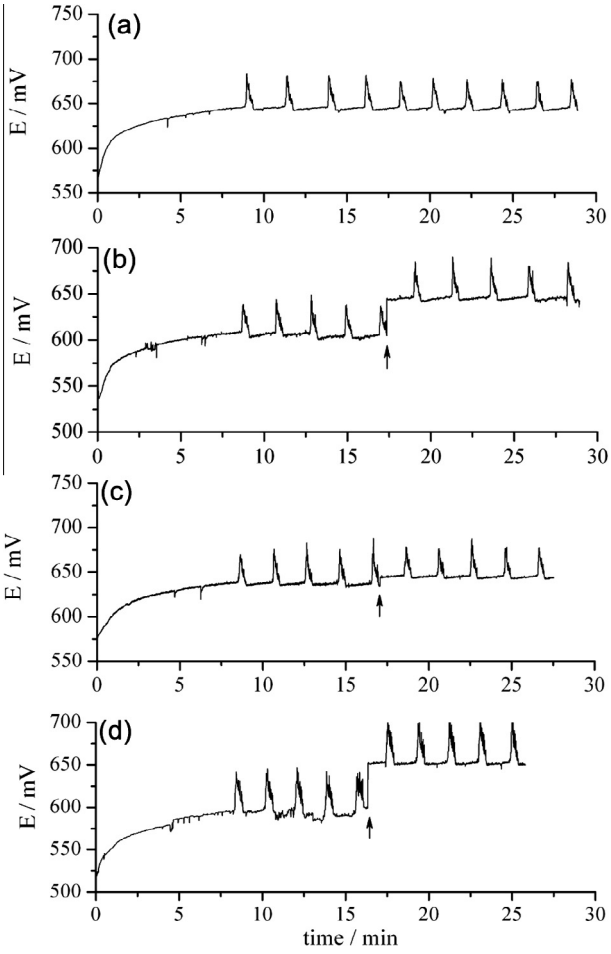

Fig. 2. BL oscillograms obtained by recording the potential E of the platinum electrode: (a) without RF field (b) with RF field of frequency 60 MHz, (c) 80 MHz and (d) 110 MHz, respectively. The arrows indicate when the RF field was turned off.