THE HYDRODYNAMIC OSCILLATOR AND ITS USE IN THE INVESTIGATION OF CHEMICAL OSCILLATORS

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Rules governing the hydrodynamic oscillator were studied with a view to using it in the examination of the coupling of two different chemical oscillators, in the periodical perturbation of the oscillatory system, or in the initiation of chemical oscillations by the self-regulating addition of one reactant to the other. The hydrodynamic oscillator can be employed in the study of the complex dynamic behaviour of chemical oscillators provided that the liquids used are not too viscous or that a vessel without a capillary is employed in order to maximally reduce the effect of viscosity.

In 1970, the geophysicist Martin[1] observed a strange phenomenon, viz. rhythmic oscillations of a water stream, which appeared if a vertically oriented syringe free of the plunger was filled with a salt solution and partly submerged in a reservoir with pure water. The oscillations began with the salt solution leaving the syringe. In a time, the flow direction reversed and water began to flow through the needle into the syringe. Yoshikawa and coworkers[2] monitored the flow oscillations by measuring the electric potential between the salt solution and the water using a pair of silver chloride electrodes. According to Noyes[3], the system oscillates between two positions of a hydrostatic equilibrium, which represent two steady states unstable to fluctuations. The salt oscillator exhibits various nonlinear states such as a limiting cycle, bifurcation of the oscillatory flow and entrainment between the oscillators[4]. Entrainment between oscillators was observed if in the common reservoir were placed two vessels whose openings were nearly identical in size and which contained NaCl solutions with different concentrations. Interactions between three nonlinear salt oscillators have also been studied[5]. The oscillations were synchronized spontaneously in a three-phase mode. The effects observed have been simulated mathematically using simple nonlinear differential equations.

Coupling of oscillatory chemical systems is very important from the chemical point of view as well as in the modelling of biochemical systems. Beck and Nagy[6] investigated the coupling of chemical oscillators of the Belousov–Zhabotinskii (BZ) type by means of a hydrodynamic oscillator.

In the first part of our work we studied the rules governing the hydrodynamic oscillator, which – despite its fascinating behaviour – has so far received rather little attention.

In the second part we investigated the feasibility of using the hydrodynamic oscillator in the examination of coupling of two different oscillators, in the periodical perturbation of the oscillatory system, and in a periodical mixing of reactants of an oscillatory system.

EXPERIMENTAL

All chemicals used were of reagent grade purity. Water was redistilled with an addition of $KMnO_4$. Hydrodynamic oscillations were measured in a system (Fig. 1) consisting of a reservoir B filled with water, a small glass vessel A containing a solution with a higher density and limiting the connection C between the two liquids; this connection is formed by a capillary or only by a small opening in the bottom of vessel A. The volumes of vessels A and B were 2 and 200 ml, respectively. The latter vessel was thermostatted. Two identical electrodes, e.g. Pt or calomel electrodes, were submerged in the two vessels, and the time behaviour of the change between their potential was monitored on an OH-105 polarograph (Radelkis, Hungary), which also served as a millivoltmeter. The viscosity of the solutions was measured with an Ubbelohde viscometer at 20 °C. For keeping the temperature constant, the viscometer was housed in a jacket interfaced to the thermostat.

The solution density was determined using a 25 ml pycnometer. Coupled chemical oscillators were studied in a plexiglass vessel whose shape and dimensions were as used by Beck and Nagy[6]. The solutions volumes in compartments A and B were 30 and 45 ml, respectively, and both were stirred. A magnetic stirrer was used for compartment B at a velocity of 100 r.p.m.; the stirrer radius was 0.4 cm, length 2.4 cm. The volume of transferred solution was 19.5 μl per period.

RESULTS

Hydrodynamic Oscillator

If vessel A (Fig. 1) contains initially, for instance, KCl at a concentration of 2 mol l^{-1} and vessel B contains distilled water, a rhythmical flow of the liquids establishes. For some time the higher-density liquid flows into the lower-density liquid, after which the lower-density liquid flows for some time into the higher-density liquid. The flow directions change periodically, the system is far from equilibrium. The oscillations can

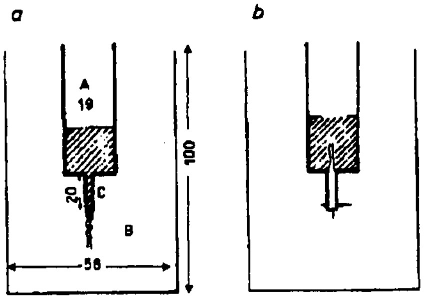

FIG. 1
A hydrodynamic oscillator. *a* outflow stage, *b* inflow stage. Dimensions in mm

be observed visually, or the time dependence of the difference of potentials of two identical electrodes submerged in vessels A and B can be measured (Fig. 2). The KCl–water system was measured in a vessel with a capillary as well as in a capillary-free vessel A having an opening 1 mm in diameter. The hydrodynamic oscillations were observed over KCl concentration regions of 0.2 – 2 mol l^{-1} or 0.1 – 2 mol l^{-1}. In either case the oscillation period decreases with KCl concentration. In the vessel with a capillary, the change in the KCl concentration only affects the time for which the salt solution flows out of the capillary but does not affect the time for which the lower-viscosity solution flows into the capillary.

Based on the linear dependence of the oscillation position t, in seconds, on the oscillation order x, a simple rule of the oscillation positioning can be formulated in the form of

$$t = 44 + bx, \qquad (1)$$

the slope b decreasing with increasing concentration of KCl (Fig. 3).

The oscillation period is markedly affected by the length of the vessel A capillary (Fig. 4). Glass capillaries with capillaries 2, 4.3 and 7 cm long were used keeping the remaining parameters constant. The oscillation period extended from 45 s at l = 2 cm to 970 s at l = 7 cm. The oscillation period changes linearly with the capillary length. Temperature across the 10 – 40 °C range has no effect on the oscillation parameters of the KCl–water hydrodynamic system.

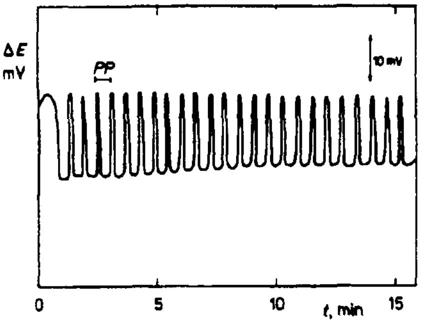

FIG. 2

Hydrodynamic oscillations. Starting conditions: vessel A: 2 ml of KCl solution (2 mol l^{-1}); vessel B: 200 ml of distilled water. Temperature 20°C

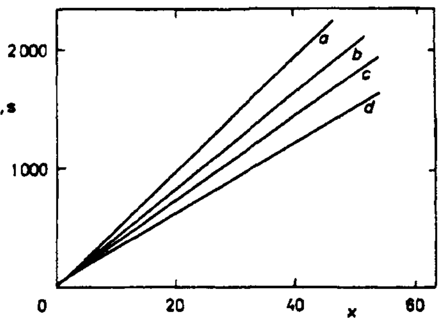

FIG. 3

Dependence of oscillation positioning on their order in the KCl–water system. Vessel A: KCl solution; vessel B: distilled water; c(KCl), mol l^{-1}: *a* 0.3, *b* 0.5, *c* 1.0, *d* 2.0. Temperature 20 °C

We also investigated the effect of stirring on the oscillation parameters of the hydrodynamic oscillator, with a particular view to employing the oscillator for the study of coupled chemical BZ oscillators where reaction mixture stirring must be allowed for. A favourable finding was that the oscillation period was independent of the stirring velocity over the 50 – 400 r.p.m. range, only the oscillation amplitude changed. We also found that the electrode in the stirred vessel B is best positioned just above the vessel bottom, where the oscillations are regular. If the electrode is positioned just below the solution level, the observed oscillations are irregular due to turbulence of the electrolyte. In addition to the KCl–water system, the KBr–water, KI–water, $MgSO_4$–water, Na_2SO_4–water, NaSCN–water, NaN_3–water, $NaClO_4$–water and $K_3[Fe(CN)_6]$–water systems were also examined. Table I demonstrates that no major changes occurred in the oscillation periods for the different electrolytes. Higher oscillation periods were only measured for Na_2SO_4, $MgSO_4$ and NaSCN in either case, if the oscillation period was expressed as a function of equally concentrated electrolytes (1 mol l^{-1}) or as a

TABLE I

Oscillation periods of hydrodynamic oscillators containing various salts

Salt	*PP1*[a]	*PP2*[b]	Salt	*PP1*[a]	*PP2*[b]
KCl	16.5	12.0	NaSCN	18	16.5
KBr	16	12	NaN_3	18	13.5
KI	14.5	10.5	$NaClO_4$	15.5	13.5
$MgSO_4$	19.5	16.5	$K_3[FeCN_6]$	16.5	13.5
Na_2SO_4	20.5	18.0			

[a] Oscillation period for salts at the same concentrations (1 mol l^{-1}); [b] oscillation period for solutions obtained by adding 10 g of salt to 100 ml of water.

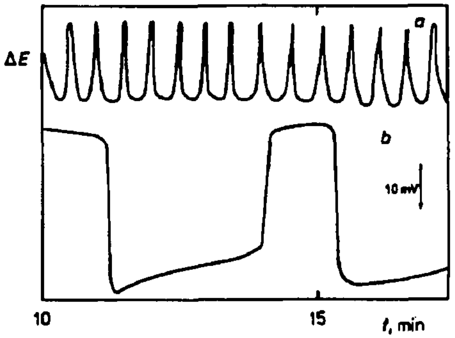

FIG. 4

Effect of capillary length on the oscillations. Capillary length: *a* 2cm, *b* 4.3 cm. Starting conditions: vessel A: KCl (0.5 mol l^{-1}), vessel B: distilled water. Temperature 20 °C function of the same weights of the salts added to the same volume of water (10 g of salt dissolved in 100 ml of water). The period lengthening can be explained in terms of a higher viscosity of the above electrolytes.

If the water in the system is replaced with a substance possessing a higher viscosity, such as aqueous glycerine, more differences are observed. Among them is a nonlinear dependence of the positioning of oscillations on their order (Fig. 5), which precludes the use of such a hydrodynamic oscillator in the study of chemical oscillators. In fact, the oscillation period changes markedly during one cycle. As the viscosity of the solution increases, so does the oscillation period, obeying the relation (average of the first 2 to 3 periods)

$$PP = 29.9 + 7.17 \,.\, 10^3 \eta \,, \tag{2}$$

where PP is in seconds and η in Pa s units.

The effect of temperature was investigated in a system where vessel A contained a glycerol–water 70 : 30 mixture and vessel B contained distilled water. The dependence of the logarithm of the oscillation period on inverse temperature was linear. The viscosity vs temperature dependence is usually expressed as $\eta = C \exp (E / RT)$, where E is the molar activation energy of the viscous flow. Expressing analogously the temperature dependence of the oscillation period as $PP = C' \exp (E / RT)$, a value of E = 38 kJ mol^{-1} is obtained for the activation energy of the viscous flow. This value is between the published molar activation energies for pure water, $E(H_2O)$ = 18.7 kJ mol^{-1}, and for pure glycerol, $E(G)$ = 47.2 kJ mol^{-1}, which indicates that viscous damping predominates in the oscillations.

In conclusion of this part it can be stated that the hydrodynamic oscillator, if formed by not very viscous liquids, can be used to study the coupling and perturbation of chemical oscillators; a capillary-free vessel can be employed to suppress the effect of viscosity.

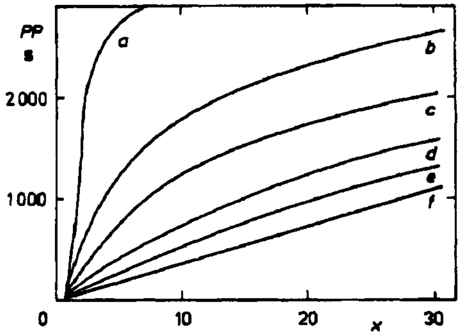

FIG. 5

Dependence of oscillation positioning on their order in the aqueous glycerol–water system. Vessel A: aqueous glycerol, vessel B: distilled water, temperature 20°C. Glycerol volume fraction: *a* 0.9, *b* 0.8, *c* 0.7, *d* 0.6, *e* 0.4, *f* 0

The Use of the Hydrodynamic Oscillator in the Study of Chemical Oscillators

A hydrodynamic oscillator, which has the ability to periodically transport matter, was used to join two different BZ type chemical oscillators: one contained malonic acid as the substrate[7] (accommodated in compartment B of the vessel) whereas the other

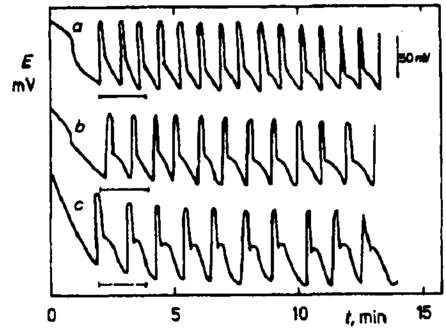

FIG. 6

Coupling of chemical oscillators with different substrates by means of a hydrodynamic oscillator. Starting conditions: compartment A: H_2SO_4 (3 mol l^{-1}), $MnSO_4$ (3 . 10^{-4} mol l^{-1}), $NaBrO_3$ (0.019 mol l^{-1}), oxalic acid: *a* 0.06, *b* 0.08, *c* 0.1 mol l^{-1}; compartment B: H_2SO_4 (1 mol l^{-1}), $MnSO_4$ (3 . 10^{-4} mol l^{-1}), $NaBrO_3$ (0.019 mol l^{-1}), oxalic acid (0.06 mol l^{-1}). Potential was measured in compartment B, stirring velocity 100 r.p.m. Horizontal line shows the period of hydrodynamic oscillations

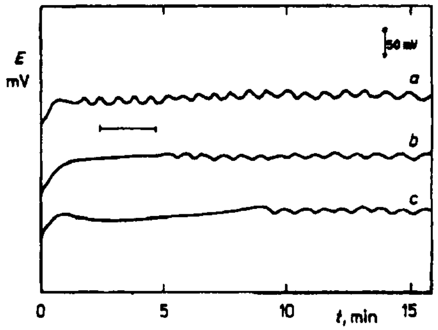

FIG. 7

Time dependence of Pt electrode potential in the NaH_2PO_2, $NaBrO_3$, $MnSO_4$, H_2SO_4 system to which acetone was added periodically by means of the hydrodynamic oscillator. Starting conditions: compartment A: acetone (2.05 mol l^{-1}), H_2SO_4 (3 mol l^{-1}), Na_2SO_4 (0.675 mol l^{-1}); compartment B: H_2SO_4 (3 mol l^{-1}), NaH_2PO_2 (0.04 mol l^{-1}), $MnSO_4$ (0.005 mol l^{-1}), $NaBrO_3$: *a* 0.02, *b* 0.03, *c* 0.04 mol l^{-1}. Potential was measured in compartment B stirred at 100 r.p.m. Horizontal line shows the hydrodynamic oscillation period

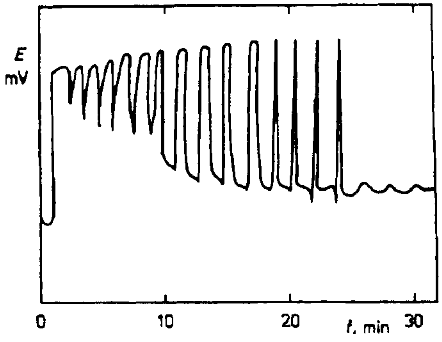

FIG. 8

Dependence of Pt electrode potential on time during reactant mixing by means of hydrodynamic oscillator. Starting conditions: compartment A: NaSCN (2 mol l^{-1}); compartment B: $NaBrO_3$ (0.08 mol l^{-1}), $HClO_4$ (0.1 mol l^{-1}). Potential measured in compartment B contained oxalic acid (in compartment A). The result of the coupling can be seen in Fig. 6. The double oscillations are analogous to those obtained by chemical coupling via mixed substrates[8]. The period of the hydrodynamic oscillator, which exceeds that of the chemical oscillator, is shown in a horizontal line.

By using a hydrodynamic oscillator it is possible to periodically disturb the oscillatory system with a substance affecting the oscillation kinetics. Oxidation of hypophosphate ions with bromate in the presence of a catalyst in batch conditions is no oscillation reaction. Periodical changes in the redox potential were observed only if bromine was removed from the system physically[9] or chemically by adding acetone to the reaction mixture[10]. Periodical self-regulatory feeding of acetone into the $NaBrO_3$, NaH_2PO_2, Mn(II), H_2SO_4 reaction system gives rise to chemical oscillations (Fig. 7). An induction period is first observed, followed by oscillations of the system. The oscillations were found over the NaH_2PO_2 concentration region of 0.025 to 0.04 mol l^{-1} and over the very narrow bromate concentration region of 0.02 to 0.04 mol l^{-1}. Changes in the bromate and hypophosphate concentrations have an effect on the induction period whereas the oscillation period is little affected.

Of interest is the appearance of oscillations if thiocyanate is added in the self-regulating manner, by the hydrodynamic oscillator, to sodium bromate in perchloric acid solution (Fig. 8). The measurement commenced with the solution flowing from compartment B into compartment A; the potential was roughly constant. After the flow direction reversed, the potential dropped abruptly by 315 mV but later returned slowly to the initial value. At the beginning, the hydrodynamic oscillator period was roughly the same as the period of oscillations of the chemical oscillator, the latter, however, extended with time. Oxidation of thiocyanate by bromate in perchloric acid is no oscillation reaction in a closed system. In the presence of excess bromate[11] the system exhibits nonmonotonous behaviour. Two abrupt changes in the Pt electrode potential are due to bromate being reduced by thiocyanate to bromide which combines with bromate to give bromine. Bromine reacts rapidly with thiocyanate ions. The cycle repeats on self-regulatory addition of thiocyanate ions to the solution of bromate.

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