

Oscillatory concentration pulses of some divalent metal ions induced by a redox oscillator

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Received 24th September 2009, Accepted 1st December 2009

First published as an Advance Article on the web 23rd December 2009

DOI: 10.1039/b919924a

Oscillations in the concentration of divalent ions Cd^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} are induced by adding these species to the BrO_3^- – SO_3^{2-} chemical oscillator in a flow reactor. Producing periodic pulses in the concentrations of these non-redox ions extends our earlier approach to generating forced periodic behavior. Instead of driving pH-dependent equilibrium reactions of the target ion by a pH oscillator backward and forward, we now couple a redox core oscillating reaction to two consecutive reactions taking place between the components of the oscillator and the target element. In the systems examined here, the oscillatory reductant SO_3^{2-} binds the free metal ion in a MSO_3 precipitate, reducing its level to a minimal value when $[\text{SO}_3^{2-}]$ is high, followed by release of the metal ion when the sulfite is oxidized by BrO_3^- .

1. Introduction

Until quite recently, oscillatory behavior in chemical systems was limited to elements possessing several oxidation states. In living organisms, however, non-redox species such as calcium ion can also undergo periodic oscillations. We have recently developed methods for constructing chemical oscillators in which non-redox species participate. We first implemented a systematic design algorithm to induce periodic changes in the concentrations of cations and anions that have a single non-zero oxidation state.¹ Our approach was to couple a pH-dependent equilibrium involving the target species to a pH oscillator. If the pH oscillator is capable of moving the equilibrium periodically back and forth, all participants in the equilibrium reaction are forced to oscillate. For successful coupling, several conditions must be fulfilled: a moderate equilibrium constant, a large change in pH, no interference between the components of the oscillator and those of the equilibrium.² Meeting all these requirements simultaneously turns out to be quite challenging. Therefore—contrary to our initial expectations—only a few such matches have met with experimental success. Thus far we have obtained oscillations in the concentrations of Ca^{2+} , Al^{3+} and F^- ions, when the BrO_3^- – SO_3^{2-} – $\text{Fe}(\text{CN})_6^{4-}$ or the BrO_3^- – SO_3^{2-} – Mn^{2+} pH oscillators were connected to strongly pH-dependent equilibria involving the target ions. In these experiments, the system oscillated between states in which Ca^{2+} , Al^{3+} and F^- were present as hydrated free ions at low pH but were bound in a stable complex or a sparingly soluble precipitate at high pH.^{2,3}

Here we report that a modification of our original design procedure allows us to extend the number of non-redox ions

capable of participating in oscillatory processes. Instead of coupling a pH oscillator to pH-dependent complex formation or precipitation equilibrium, we propose combining the primary oscillator with nearly *irreversible* chemical reactions between the input reagents of the core oscillator and the target non-redox ion. This modified method of coupling enables us to generate periodic changes in the concentrations of Cd^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} and Ni^{2+} ions.

Our working hypothesis starts from the observation that the majority of chemical oscillators function in an open system, where the reactants are continuously fed into the reactor and the products are removed from it. Under flow conditions the concentrations of all participants of the oscillator undergo periodic changes. In most cases, one of the input reagents—usually the reductant—is almost completely consumed and then replenished during each oscillatory cycle. Therefore, its concentration varies periodically between a value close to zero and one that exceeds the threshold for a new cycle to start.

This periodic increase and decrease in the concentration of the reductant may be used to induce oscillatory changes in the concentration of an ion that forms a precipitate with that reductant. When the reductant is present at high concentration, most of the metal ions are bound in the precipitate. During this stage of the oscillation, the quantity of free metal ion is determined by the solubility product of the precipitate. As the oscillatory cycle continues, the reductant—both in the bulk solution and in the precipitate—undergoes oxidation, and all the metal ions are released. Oscillations in the concentration of the free metal ion should occur if no precipitation takes place between the oxidized form of the reductant and the target ion.

2. Experimental

The following chemicals were used: NaBrO_3 (Reanal), Na_2SO_3 (Aldrich), $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (Reanal), $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Reanal), $\text{Zn}(\text{NO}_3)_2 \cdot 7\text{H}_2\text{O}$ (Reanal), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Reanal), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (Reanal).

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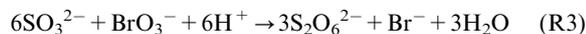
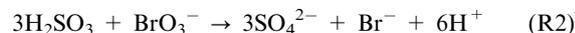
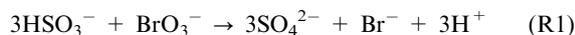
The NaBrO₃ stock solution can be stored indefinitely without changing its titer. Due to the slow oxidation of sulfite to sulfate by air oxygen, Na₂SO₃ solutions were prepared immediately before use. The SO₃²⁻ and metal ion content of the stock solutions, and of the reaction mixtures where needed, were determined by titration with standard iodine and EDTA solutions, respectively.

Coupling of the BrO₃⁻-SO₃²⁻ oscillator to Cd²⁺, Ca²⁺, Zn²⁺, Co²⁺ and Ni²⁺ (abbreviated as M²⁺) ions was carried out in a CSTR of volume 35.0 cm³, operated at 45 °C. Stock solutions of NaBrO₃, Na₂SO₃, H₂SO₄ and the M²⁺ ions were introduced into the reactor through four input tubes with a Gilson Minipuls peristaltic pump at a constant stirring rate of 600 rpm. The excess reaction mixture was removed by a second pump *via* an outlet tube. Changes in pH were monitored with a Radelkis OP-823P glass electrode connected to a Hanna pH-209 pH meter. Changes in the concentration of the free metal ions were followed visually by observing the periodic appearance and disappearance of the MSO₃ precipitate and by using Cd²⁺ and Ca²⁺ ion-selective electrodes (ISE, Thermo Orion 9648BNWP and 9700BNWP, respectively). Data were collected on a personal computer and recorded with a Kipp & Zonen BD41 flatbed recorder.

3. Results and discussion

For our primary oscillator, we chose the BrO₃⁻-SO₃²⁻ reaction, which was reported by Szántó and Rábai⁴ to oscillate between pH 3.5 and 7.3 in a flow reactor (CSTR) at 45 °C with a period of about 3 h. The pH oscillations were attributed by those authors to the existence of two pathways of sulfite oxidation by bromate. The total oxidation of S(IV) to S(VI) (SO₃²⁻ to SO₄²⁻) proceeds autocatalytically, producing H⁺ and resulting in a drop in pH, whereas the partial oxidation of S(IV) to S(V) (SO₃²⁻ to S₂O₆²⁻) consumes H⁺ and is accompanied by a pH increase.

The basic processes in the oscillatory cycle were described by the protonation equilibria of the SO₃²⁻ (eqn (E1) and (E2)) and the oxidation of SO₃²⁻ by BrO₃⁻ *via* eqn (R1)–(R3):



The BrO₃⁻-SO₃²⁻ oscillator is well-suited to our task of inducing periodic pulses in the concentrations of non-redox M²⁺ cations. The reductant, SO₃²⁻, forms precipitate with several divalent metal ions, and the precipitate is converted to a soluble product, the SO₄²⁻, when the reductant undergoes total oxidation. Additional advantages of selecting the BrO₃⁻-SO₃²⁻ oscillator as the core system are its simple composition, good reproducibility and known chemical background.

The inconveniently long period (~3 h) and high working temperature (45 °C) represent significant drawbacks. We were able to ameliorate these problems, particularly the first, by

modifying the original recipe described in ref. 4. We established a composition of [BrO₃⁻]₀ = 0.15 M, [Na₂SO₃]₀ = 0.175 M and [H₂SO₄]₀ = 0.012 M as initial concentrations in the CSTR (the values if no reaction occurs between the reactants)—which we refer to as the “optimal composition”—that results in a much shorter period (~45 min) and oscillates at lower temperatures (35–45 °C). This composition oscillates through a larger pH range, 2.65 to 7.98, and due to the higher input reagent concentrations, it is more resistant to perturbation by the added metal ions. The time the system spends in the high and low pH ranges can be tuned by varying the flow rate (*k*₀). At a residence time of $\tau = 1/k_0 = 8.3$ min, the high pH range (pH 6.0–7.5) is maintained for about 26 min (~3 τ), which is long enough for [SO₃²⁻] in the reactor to attain its maximum value and for completion of the precipitation reaction when the metal ions are present.

A number of divalent metal ions, including Cd²⁺, Ca²⁺, Sr²⁺, Ba²⁺, Zn²⁺, Co²⁺, Pb²⁺ and Ni²⁺, form MSO₃ or mixed sulfite–hydroxide precipitates of moderate solubility. With the exception of SrSO₃, BaSO₃ and PbSO₃, these precipitates dissolve when the SO₃²⁻ in the precipitate is oxidized to SO₄²⁻ by BrO₃⁻. The precipitation and dissolution processes are completed in a much shorter time than the system spends in either the low or the high pH state; therefore these processes only slightly affect the amplitude and frequency of the core oscillator. Any changes in these parameters can be restored by a small adjustment in the flow rate.

In order to induce periodic pulses in the concentrations of Cd²⁺, Ca²⁺, Zn²⁺, Co²⁺ and Ni²⁺, 10⁻² M solutions of these ions were mixed with the “optimal composition” in the CSTR. During the oscillatory cycle, monitored by following the pH in time, dramatic visual changes were seen in the reactor: the reaction mixture was crystal clear in the acidic pH range (2.5–6); turbidity started to appear at pH 6–7; precipitate was gradually formed to its maximum amount during the time (~25 min) the system spent in the high pH range, but it abruptly disappeared when the pH dropped below 5. The largest amount of precipitate was formed with Cd²⁺ and Ca²⁺; somewhat less precipitate was seen with Zn²⁺; and a smaller, but still easily observable amount appeared when M²⁺ = Co²⁺ or Ni²⁺. All precipitates were white, with the exception of the Co²⁺ experiments, where both the precipitate formed at high pH and the clear solution at low pH were pale pink. In addition to visual observation of the oscillatory changes in the cloudy and clear states in the CSTR, we recorded the responses of the glass electrode, the CdISE and the CaISE. These results are shown in Fig. 1.

We performed measurements and collected literature data to establish the composition and the solubility products (*K*_{sp}) of the precipitates. For preparation of the metal ion–sulfite precipitates, equal volumes of solutions of 0.02 M M²⁺ salt and 0.08 M Na₂SO₃ (this [M²⁺] : [SO₃²⁻] ratio approximates that present in the CSTR at the highest pH) were mixed (*V*_{total} = 100 cm³), and the pH was adjusted with H₂SO₄ to 7.6. After about 20 min, the product was separated by centrifugation, washed with water, dried in air and analyzed. The composition of the sulfite precipitates was taken from *Gmelins Handbuch*⁵ and was also checked by titration of a

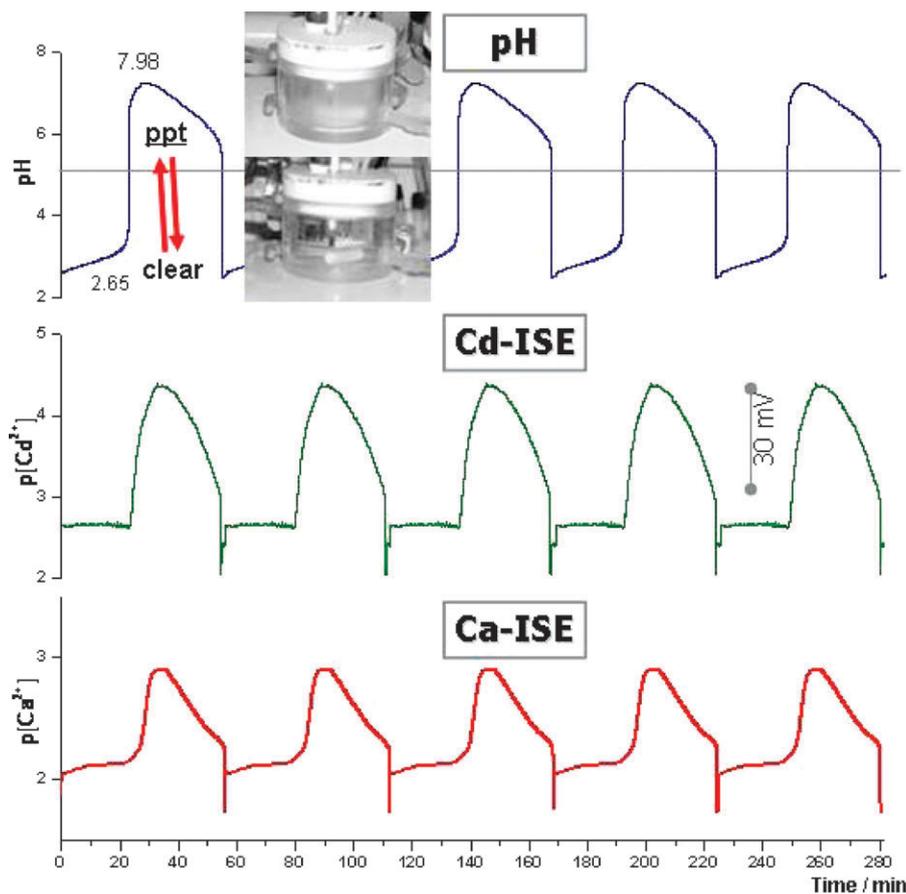


Fig. 1 Oscillatory changes in pH and in the responses of CdISE and CaISE recorded in a CSTR. Input concentrations: $[\text{BrO}_3^-]_0 = 0.15 \text{ M}$, $[\text{Na}_2\text{SO}_3]_0 = 0.175 \text{ M}$, $[\text{H}_2\text{SO}_4]_0 = 0.012 \text{ M}$, $[\text{CaCl}_2] = 0.01 \text{ M}$, $[\text{Cd}(\text{NO}_3)_2] = 0.01 \text{ M}$, $T = 45 \text{ }^\circ\text{C}$, $k_0 = 0.002 \text{ s}^{-1}$.

known amount of precipitate with EDTA in an appropriate buffer for the metal ion content and with iodine solution to measure the sulfite.

The analysis was carried out for the calcium, cadmium and zinc precipitates. The measurements showed a strict 1 : 1 stoichiometry for Ca^{2+} and Cd^{2+} to SO_3^{2-} ; both precipitates contain 2 mol water of hydration, in accordance with ref. 5. We were not able to establish the precise composition of the jelly-like Zn-precipitate (the molar ratio of Zn^{2+} to SO_3^{2-} in the precipitate was measured to be 1.3 ± 0.1), which appears to be a mixture of composition $2\text{ZnSO}_3 \cdot \text{ZnO} \cdot 3\text{H}_2\text{O}$.⁵ We had difficulty in preparing the ruby red cobaltous sulfite due to its facile oxidation by air to the Co(III) species. Ref. 5 gives the composition as $\text{CoSO}_3 \cdot 6\text{H}_2\text{O}$. No literature data were found, and no measurements were made for the nickel precipitate. In summary, results for the compositions of the precipitates are as follows: $\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{CdSO}_3 \cdot 2\text{H}_2\text{O}$, $\text{CoSO}_3 \cdot 6\text{H}_2\text{O}$, $2\text{ZnSO}_3 \cdot \text{ZnO} \cdot 3\text{H}_2\text{O}$ (estimated), NiSO_3 (no information).

We also needed to know the solubility of the precipitates at the temperature where the experiments were carried out ($45 \text{ }^\circ\text{C}$). No K_{sp} values were available for CdSO_3 , CoSO_3 , NiSO_3 and $2\text{ZnSO}_3 \cdot \text{ZnO} \cdot 3\text{H}_2\text{O}$. For CaSO_3 a range of K_{sp} values from 6.8×10^{-8} to 3.2×10^{-7} , depending on ionic strength and temperature, was found in the literature.⁶ The K_{sp} values for CaSO_3 and CdSO_3 at 25 and $45 \text{ }^\circ\text{C}$ were determined using the same technique employed to establish their composition.

Interestingly, there was no significant difference in the values measured at the two temperatures. The K_{sp} values found were 6.0×10^{-7} and 6.4×10^{-7} for CaSO_3 and CdSO_3 , respectively.

Only a single datum was found in the literature for the existence and stability of $\text{M}(\text{SO}_3)_2^{2-}$ complexes. For the Cd-complex $\log \beta_2 = 4.19$.⁶ If, in addition to the precipitate, complex ions can be formed, the amount of precipitate will be lower, and there may even be no visible oscillations despite the periodic binding of the metal ion. In order to estimate the extent of formation of $\text{M}(\text{SO}_3)_2^{2-}$ complex that may be present in the CSTR during the high pH stage of the oscillations, we mixed 0.01 M Cd^{2+} , Ca^{2+} and Zn^{2+} with SO_3^{2-} at molar ratios of 1 : 1, 1 : 2, 1 : 10 and 1 : 20 at pH 7.9. After shaking for 20 min, we separated the sulfite precipitate from the liquid phase in a centrifuge tube and measured the metal ion concentration in the supernatant by titration with EDTA. No complex formation was observed for Ca^{2+} . For Cd^{2+} , moderate complex formation was measured: at $[\text{Cd}^{2+}] : [\text{SO}_3^{2-}] = 1 : 1, 1 : 2, 1 : 10$ and $1 : 20, 5, 17, 22$ and 34%, respectively, of the Cd^{2+} was complexed. The most pronounced complex formation was found for Zn^{2+} , where 9, 15, 32 and 100%, respectively, of the metal ion was incorporated as complex.

The mechanism of the $\text{BrO}_3^- \text{--} \text{SO}_3^{2-}$ oscillatory system⁴ suggests that the reaction between bromate and sulfite proceeds with different stoichiometries and with a very different rate in

the low and the high pH stages of the oscillation. The oxidation of SO_3^{2-} to SO_4^{2-} (eqn (R1) and (R2)) is autocatalytic in H^+ , becoming nearly instantaneous at low pH, and all the SO_3^{2-} is consumed, independently of whether it is present as the free anion or is incorporated in the precipitate. Iodine titration of SO_3^{2-} and BrO_3^- mixtures and of the samples taken from the CSTR showed that essentially no SO_3^{2-} is present below pH 4. Low pHs initiate the oxidation of SO_3^{2-} to $\text{S}_2\text{O}_6^{2-}$ (eqn (R3)). This reaction requires H^+ , therefore the pH starts to increase as SO_3^{2-} gradually builds up as a result of the flow. The system spends about 3τ in the high pH stage, where $[\text{SO}_3^{2-}]$ (measured by iodine titration of the mixture after quenching the reaction with solid NaHCO_3) reaches a maximum concentration of 0.04 M. From these experiments we can conclude that in the BrO_3^- - SO_3^{2-} oscillator, using the “optimal composition”, in parallel with the changes in pH, the $[\text{SO}_3^{2-}]$ also oscillates between 0 and 0.04 M. From our measurements of the $[\text{SO}_3^{2-}]$ present at the low and high pHs we constructed the oscillatory variation in $[\text{SO}_3^{2-}]$ during the operation of the core system as shown in Fig. 2. In this figure, the maximum and minimum values of $[\text{SO}_3^{2-}]$ were experimentally measured, but the curves between them have been interpolated by assuming that replenishment of SO_3^{2-} by the flow occurs according to a saturation-type behavior and that its oxidation occurs extremely rapidly.

In the BrO_3^- - SO_3^{2-} system the variation in $[\text{SO}_3^{2-}]$ is accompanied by pH changes between 7.98 and 2.65. In order to clarify the effect of pH on the dissolution of the MSO_3 precipitate, mixtures of Na_2SO_3 and $\text{Cd}(\text{NO}_3)_2$ (with the same concentrations as the oscillatory composition) were titrated with dilute HClO_4 . The initial basic pH of the mixture was gradually decreased to 2.5, and visual observations were made. At $\text{pH} \geq 8.7$ the cadmium was present as $\text{Cd}(\text{OH})_2$ precipitate ($K_{\text{sp}} = 2.5 \times 10^{-14}$). Between pH 8.7 and 7.9 the solution became clear due to the formation of a $\text{Cd}(\text{SO}_3)_2^{2-}$ complex. CdSO_3 began to precipitate at pH 7.7, and the mixture remained quite cloudy until the pH reached a value of 4,

where all precipitate dissolved. We calculated the distribution of species ($[\text{Cd}^{2+}]$, $[\text{SO}_3^{2-}]$, $[\text{HSO}_3^-]$, $[\text{H}_2\text{SO}_3]$, $[\text{Cd}(\text{OH})_2]$, $[\text{CdSO}_3]$, $[\text{Cd}(\text{SO}_3)_2^{2-}]$) in the same Na_2SO_3 - $\text{Cd}(\text{NO}_3)_2$ system as a function of pH with the Medusa⁷ software package. The results were in good agreement with our visual observations.

These experiments and calculations show that a drop in pH below 4 is sufficient to shift the precipitation equilibrium backward, releasing the metal ion from its sulfite precipitate due to the protonation of SO_3^{2-} to HSO_3^- and H_2SO_3 . However, the drop in pH in the BrO_3^- - SO_3^{2-} - $\text{Cd}(\text{NO}_3)_2$ (and other metal-containing) oscillatory system is necessarily accompanied by the fast and quantitative oxidation of the protonated sulfite species by BrO_3^- , which is present in high stoichiometric excess (2.5-fold excess at pH_{max} and much higher excess at low pHs) during all phases of the oscillatory cycle. The dissolution of the MSO_3 precipitate and the protonation and oxidation of SO_3^{2-} according to eqn (E1), (E2) and (R1)–(R3) together ensure that in the acidic regime of the oscillation the concentration of free metal ions is equal to its feed value.

4. Conclusions

In the examples described here, the two component BrO_3^- - SO_3^{2-} oscillator serves as the core system, in which, besides the periodic changes in $[\text{H}^+]$, both the oxidant and the reductant directly participate in bringing about induced oscillations in the level of a target ion. In the combined system consisting of BrO_3^- , SO_3^{2-} and a divalent ion— Cd^{2+} , Ca^{2+} , Zn^{2+} , Co^{2+} or Ni^{2+} —the periodic appearance and dissolution of the precipitate observed visually (and the ISE signals recorded in the presence of Cd^{2+} and Ca^{2+}) clearly demonstrate the existence of periodic pulses in the concentrations of the chosen metal ions, four of which had not previously been shown to undergo chemical oscillations.

The time sequence of the reactions taking place in the CSTR is determined by the high and low pH segments of the

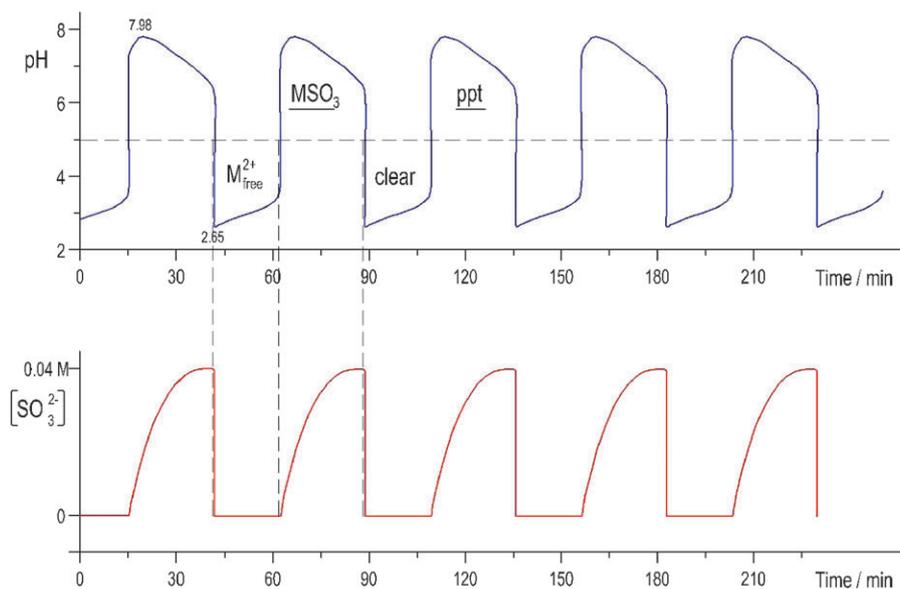


Fig. 2 The changes in $[\text{SO}_3^{2-}]$ vs. time in the BrO_3^- - SO_3^{2-} core oscillator. Experimental conditions as in Fig. 1.

oscillatory cycle of the core system. When $[\text{SO}_3^{2-}]$ is high (at high pH), the free metal ion (M^{2+}) forms a MSO_3 precipitate, and its concentration decreases to a minimum, but the original level is restored in the low pH period when the precipitate dissolves during the protonation of SO_3^{2-} to HSO_3^- , which is followed by its oxidation to SO_4^{2-} by bromate. This sequence of composite reactions in the overall process causes the free metal ion, which is introduced continuously at a constant rate into the CSTR, to undergo periodic changes in concentration.

The amplitude of the oscillations in the free $[\text{M}^{2+}]$ is largely determined by the completeness of the precipitation. This depends in turn on factors like the solubility product of the precipitate, the concentration of the input metal ion and the concentration of the reductant SO_3^{2-} at high pH. Higher values of these parameters lead to larger amplitude oscillations. The amplitude of the oscillation falls approximately between the input $[\text{M}^{2+}]$ as a maximum and the value calculated from the K_{sp} and the $[\text{SO}_3^{2-}]$ at high pH as a minimum. Under our experimental conditions, the calculated amplitude is about two orders of magnitude. The traces recorded with the CdISE and CaISE support our predictions.

Inducing oscillations in the concentration of chemical species by coupling them to a core oscillator through *irreversible* chemical reactions represents a new approach to bringing about oscillations in the concentrations of species that cannot be directly involved in a redox based oscillatory mechanism.

Acknowledgements

This work was supported by grants from the Hungarian Academy of Sciences (HAS, OTKA K67701 and K62029), the U.S. National Science Foundation (NSF, CHE-0615507), a U.S.–Hungarian cooperative grant from NFS–HAS and ESF Funcdyn programme.

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