A Detection Method for Oscillating Chemical Reactions by Resonance Light Scattering Technique

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In this contribution, a resonance light-scattering (RLS) detection method is proposed for the measurements of oscillating reaction with H_2O_2–KSCN–$CuSO_4$–NaOH close system as an example. The seasonal change of oscillating chemical reactions concerning the particle size is examined, and the qualitative analytical information could be obtained from this straightforward and expeditious approach.

Some far-from-equilibrium chemical systems exhibit oscillating behavior as a result of their complex mechanisms including autocatalytic step.[1] Such systems are usually referred to as oscillating reactions. Studies on the analytical applications of chemical oscillators have been developed,[2] since oscillating reactions were first used by Tichonova et al. in 1978.[3] The chemical oscillating systems most widely known and studied are the Belousov–Zhabotinskii[4] and the copper sulfate-catalyzed reaction of hydrogen peroxide with sodium thiocyanate system.[5] More recently, oscillating chemical systems involving amino acids have aroused increasing attention for they have close relevance to human metabolism,[6] and several nonlinear dynamical phenomena provide simpler analogues of behavior found in biological systems.

Oscillations are usually monitored potentiometrically with a platinum electrode. H_2O_2–KSCN–$CuSO_4$–NaOH system as an example of color oscillation, however, exhibits oscillations between yellow and white in the dissolved oxygen concentration and chemiluminescence in the presence of luminal.[7] Resonance light-scattering (RLS) technique is a newly developed one with a common spectrofluorometer to detect light-scattering signals by coupling and scanning simultaneously the excitation and emission monochromators and has been successfully exploited as a sensitive and selective tool to investigate the electronic and geometrical properties of aggregation species.[8] In this work, we propose a new method to monitor the oscillating reaction with the RLS technique.

Figure 1 shows the cycles of the H_2O_2–KSCN–$CuSO_4$–NaOH oscillating system. The $CuSO_4$-catalyzed reaction of hydrogen peroxide with thiocyanate ion occurs in a homogeneous, halogen-free liquid system,[7] and the oscillation is constructed from two non-autocatalytic mechanisms concerning the subsystems of alkaline H_2O_2–$CuSO_4$ and H_2O_2–KSCN.[7] The two subsystems are coupled through various intermediates to construct a feedback network, displaying oscillatory behavior in both batch and flow configurations. The $CuSO_4$-catalyzed alkaline H_2O_2 decomposition in the reaction provides two essential intermediates, HO_2–Cu^I and $Cu^+[SCN]_n^-$ for the core part of the oscillation. The sizes of Cu^{II} and HO_2–Cu^I which represents both HO_2–$Cu(OH)_2^-$ and O_2–$Cu(OH)_2^{2-}$ are different, so the oscillation system can be monitored by RLS technique.

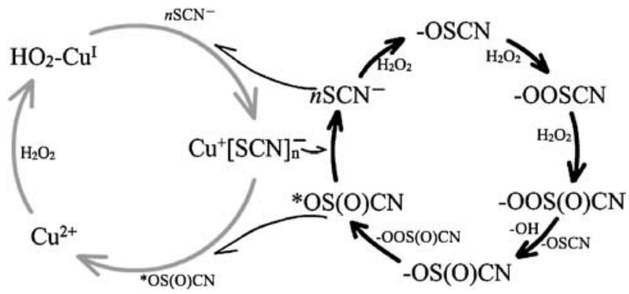

Figure 1. The main cycles of the H_2O_2–KSCN–$CuSO_4$–NaOH oscillating system.

Figure 2 displays the RLS and absorption measurements of the oscillatory system of H_2O_2–KSCN–$CuSO_4$–NaOH. As it can be seen, there are high similarities in the behavior of the oscillating period between the absorption and RLS detection. The centerpieces of the mechanism of this oscillating reaction are positive and negative feedback loops by which a yellow HO_2–Cu^I complex is formed and destroyed,[7] respectively, and on which the autocatalytic process relies. Thus, the positive feedback loop produces the yellow HO_2–Cu^I through the following reactions, and the produced HO_2 disappears in the negative feedback loop:

$$OS(O)CN^* + Cu^+[SCN]_n^- \rightarrow OS(O)CN^- + Cu^{2+} + nSCN^-,$$

$$H_2O_2 + Cu^{2+} + OH^- \rightarrow HO_2\text{–}Cu^I_{yellow} + H_2O,$$

$$HO_2\text{–}Cu^I_{yellow} + nSCN^- \rightarrow Cu^+[SCN]_n^- + HO_2^*.$$

It was found that the concentration of $Cu[SCN]_n^-$ species is crucial for this feedback network. The absorption involves in the color oscillation between yellow and white, while the RLS involves in oscillation between HO_2–Cu^I and Cu^{II}. In a word, HO_2–Cu^I, which is dependent on the rate of the process, is responsible for the color and size changes, and the oscillation period is T.

It was found that T is dependent on the concentration of Cu^{II}. The Cu^{II} concentration over the range of 2.0×10^{-5} to 1.0×10^{-4} mol L^{-1} had a significant effect on the behavior of the oscillating system. The oscillation period was found to be decreased with increasing Cu^{II} concentration (Figure 3). The magnitude of the reciprocal of oscillation period was proportional to the injected concentration, which can be used to determine Cu^{II} with a linear function of $T^{-1} = 1.86 \times 10^{-3} + 1.14 \times 10^{-3}c$ ($r = 0.992$, $n = 8$).

In conclusion RLS technique can be successfully used to monitor the oscillatory H_2O_2–KSCN–$CuSO_4$–NaOH system. It provides a new method to describe the metabolism of the oscillating reaction, and it will be able to determine species in real samples. We believe that the method will be applicable preponderantly to the other oscillating chemical reactions.

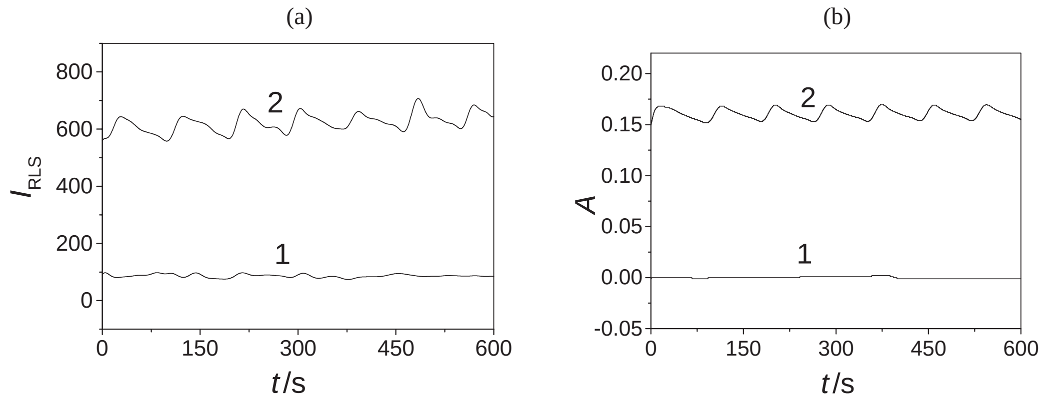

Figure 2. RLS (a) and absorption measurements (b) of H_2O_2–KSCN–$CuSO_4$–NaOH oscillatory system. Concentrations (mol L^{-1}): KSCN, 1.2×10^{-2}; H_2O_2, 0.18; NaOH, 6.0×10^{-3}; $CuSO_4$, 6.0×10^{-5}. Curve 1 shows the signal of oscillating reaction without copper, while curve 2 shows the signal of oscillating reaction in the copper work solution.

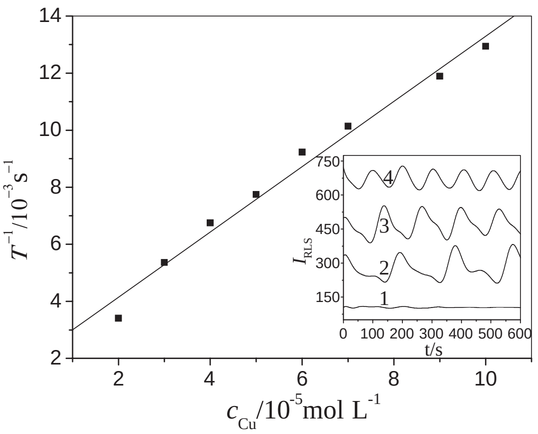

Figure 3. The relation between T^{-1} and concentration of Cu^{II}. Concentrations (mol L^{-1}): KSCN, 1.2×10^{-2}; H_2O_2, 0.18; NaOH, 6.0×10^{-3}. Insert plots show RLS spectra of oscillating reactions in different concentration of Cu^{II}. Concentrations (10^{-5} mol L^{-1}): $CuSO_4$, 1 → 4, 0; 3.0; 5.0; 8.0.

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