Non-Equilibrium Processes

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Belousov–Zhabotinsky Reaction in Protic Ionic Liquids**

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Rhythmic oscillation is one of the universal phenomena in living systems, and important rhythms that sustain a life, such as heart beating, breathing, and circadian rhythm, occur at all levels in physiological tissue. The Belousov–Zhabotinsky (BZ) reaction is an oscillating reaction accompanying a rhythmical oscillation of the redox potential of metal catalysts, such as ferroin and ruthenium bipyridine, $Ru(bpy)_3$. Typically, the BZ reaction is caused in a strong acidic aqueous solution using sulfuric acid or HNO_3 as proton source with an oxidant (for example, sodium bromate, $NaBrO_3$) and an organic acid acting as the reductant (for example, malonic acid, MA, or citric acid). The rhythmic self-oscillation of the BZ reaction is known to have many analogies to living systems and is important from the perspective of understanding nonlinear, non-equilibrium science.[1–3] Furthermore, as the first research group, which converted the chemical oscillation of a BZ reaction into a mechanical change in polymer gels, we have been systematically studying a "self-oscillating gel" that exhibits an autonomous swelling–deswelling oscillation under nonoscillatory outer conditions.[4–9] However, to apply this gel to functional materials, there are two problems that have to be solved: 1) the BZ reaction occurs only under strong acidic conditions (a typically pH value is below one) and 2) the duration of the operation is short.

Ionic liquids (ILs) are room-temperature molten salts and have attracted much attention because of their interesting properties, which render them useful for applications in materials science.[10–12] These properties are a high ion conductivity, non-flammability, (electro)chemical stability, and thermal stability.[13] ILs can be divided generally into two categories: ILs with an ion structure that includes active protons (protic ILs: PILs) and that does not include active protons (aprotic ILs: APILs).[14] Recently, many research groups have pointed out the affinity between living matter and (P)ILs. PILs are assumed to be a promising class of a preservation medium for biopolymers. Byrne and Angell reported that a hen egg protein recovered from a thermally denatured structure to a significant higher-order architecture by using a PILs/water mixture as the solvent.[15] Ohno and co-workers also found that cytochrome c retained 70% of its original activity for a long period of time (as long as 18 months) in a mixture of choline dihydrogen phosphate PIL and water,[16] known as a "hydrated IL". MacFarlane and co-workers reported long-term structural and chemical stabilities of DNA in hydrated PILs.[17] Excellent review articles are now available on (P)ILs for biopolymers.[18,19] Studies on the preparation of ILs from bioderivatives also received attention.[20,21]

On the other hand, for the development of energy conversion and storage materials, PILs are widely seen as a promising novel proton-conducting medium for fuel cell applications, instead of the traditional acidic aqueous solution.[22] For this purpose, Angell and co-workers proposed that the proton energy level diagram of PILs could be depicted using pK_a data of the constituent acids and bases.[23] Also, low-frequency vibrational FT-IR studies supported by DFT calculations for certain PILs confirmed that the ammonium hydrogen atoms could interact through hydrogen bonding with the oxygen atoms of the nitrate ion, thus leading to a three-dimensional network structure closely resembling the network structure of water.[24]

These facts strongly imply that certain kinds of PILs have a high proton activity comparable to acidic water, which encourages us to apply PILs as BZ reaction medium. Here, we report the BZ reaction for the first time using PILs as proton source instead of a conventional acid such as H_2SO_4 or HNO_3. We demonstrate that certain hydrated PILs can be an alternative medium for the BZ reaction and determine the chemical structure of this medium, which is necessary for acting as proton source. The self-oscillating behavior in this medium is compared with that of a conventional BZ reaction using HNO_3. Through analysis of the period of oscillation and the waveform, the characteristic behavior for the PIL system is revealed. These findings emphasize the advantages of using PILs for application in biomimetic functional materials.

The chemical structures and the abbreviations of ions used in this study are available in Scheme 1. The chemical structure of the ions forming PILs was varied systematically. The cations were selected from quaternized aliphatic ammonium ions with different (saturated or unsaturated) alkyl chains or from superstrong organic bases ([DBN] and [DBU]). The anions were taken from common oxo- or amide acids with different pK_a values. Figure 1 shows the pH of a 0.5 M aqueous solution with 14 different kinds of PILs to study the effect of the chemical structure of a PIL on the pH value. Since PILs of

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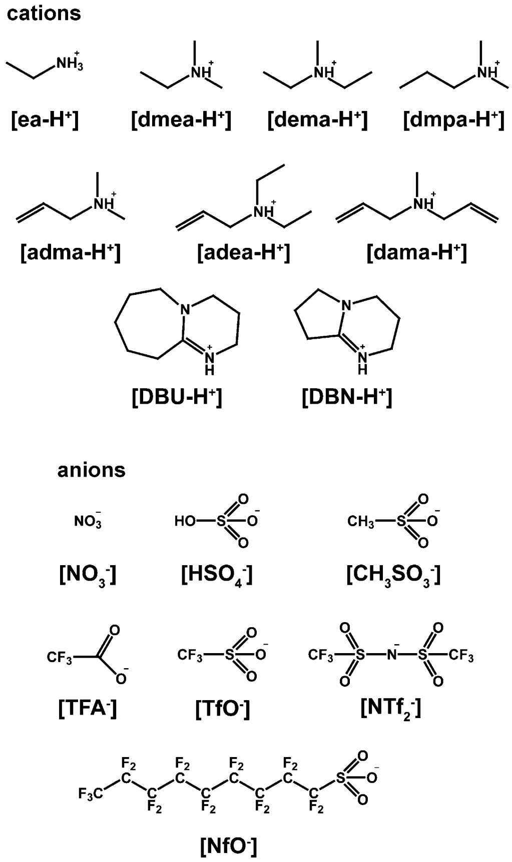

Scheme 1. Structure and abbreviations of ions used in this study.

the $[NTf_2^-]$ anion used in this study ($[dema\text{-}H^+][NTf_2^-]$, $[dmpa\text{-}H^+][NTf_2^-]$, $[adma\text{-}H^+][NTf_2^-]$, and $[DBN\text{-}H^+][NTf_2^-]$) did not affect the pH of water because of their water immiscibility, pH data for the mixtures were not included in Figure 1. The pH of an aqueous PIL solution depends strongly on the structure of the anion rather than that on the structure of the cation. PILs indicated by red bars in Figure 1, that is, $[dema\text{-}H^+][HSO_4^-]$, $[DBN\text{-}H^+][HSO_4^-]$, and $[dmea\text{-}H^+][CH_3SO_3^-]$, were found to release protons when mixed with water, which led to the initiation of the BZ reaction. Hence, $[DBN\text{-}H^+][HSO_4^-]$ can work as proton source for the BZ reaction, the basicity of the precursor cation does not seem to be of importance for the proton source.

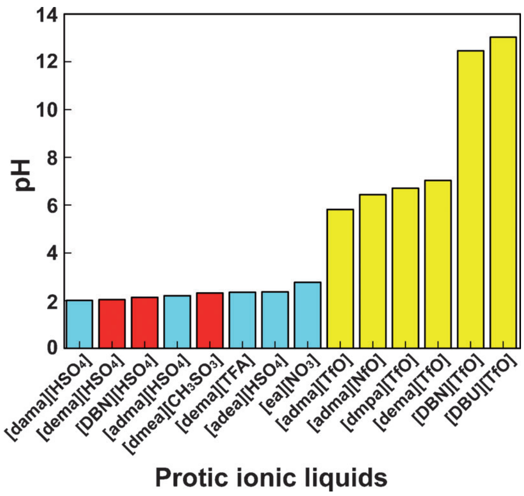

Figure 1. Relationship between the chemical structure of the PILs and the pH value of the aqueous PIL solution (0.5 M). PILs indicated by red bars induce the BZ reaction when the BZ components are mixed with water. Blue bars indicate a reduction reaction from $Ru(bpy)_3^{2+}$ to $Ru(bpy)_3^{3+}$ which occurs when $NaBrO_3$ (oxidant), PILs, and $Ru(bpy)_3^{2+}$ are mixed with water. Yellow bars represent PILs that cannot decrease the pH and do not act as proton source for the BZ reaction.

Certain PILs indicated by blue bars in Figure 1, such as $[dema\text{-}H^+][TFA^-]$, $[adea\text{-}H^+][HSO_4^-]$, and $[ea\text{-}H^+][NO_3^-]$, can decrease the pH value when they are mixed with water. However, the BZ reaction is not observed under these experimental conditions. When $NaBrO_3$ and $Ru(bpy)_3$ complexes were mixed in these hydrated PILs, the orange color of the mixture derived from reduced $Ru(bpy)_3^{2+}$ immediately changed to a light green because of the oxidation reaction of the metal complex. This is also evidence by protons that are released from the PILs in water, but the pH of these mixtures may not be low enough to initiate the BZ reaction. Interestingly, in the case of aqueous $[dama\text{-}H^+][HSO_4^-]$ and $[adma\text{-}H^+][HSO_4^-]$ solutions, the BZ reaction does not occur although the solutions exhibit a sufficiently low pH value. The allyl group attached to the cation structure may have some effect, which prevents the cation from acting as proton source for the BZ reaction. We assume that there are other structural effects of the constituting ions which are different from a pH effect.

PILs which do not effectively release protons to oxidize $Ru(bpy)_3^{2+}$ in the presence of water and $NaBrO_3$ are indicated by yellow bars in Figure 1. When the pK_a value of the acid anion precursor is as low as -7 (e.g., as for HTfO and HNfO; see Scheme 1), the pH value of the resulting hydrated PIL is higher than 5. From these results we can conclude that not all PILs have an effectively decreaced pH value to be used as proton source and solvent for the BZ oscillating reaction. Water-miscible PILs with an anion from a relatively weak acid as precursor have a decreased pH value, which leads to the redox oscillation of $Ru(bpy)_3$. Although the reason is still unclear, it is also found that PILs used as medium for the BZ reaction should not have allyl groups in the cation structure.

We then compared the self-oscillating behavior of the BZ reaction in a $[dema\text{-}H^+][HSO_4^-]$ aqueous solution with that in a typical HNO_3 solution. Figure 2 shows the self-oscillation profiles for a) $[dema\text{-}H^+][HSO_4^-]$ (1.6 M) as proton source and b) HNO_3 (0.3 M), respectively. An almost 7 h lasting $Ru(bpy)_3$ redox oscillation with a large amplitude was achieved when hydrated $[dema\text{-}H^+][HSO_4^-]$ was used as BZ reaction medium. In a conventional HNO_3 aqueous solution, the duration of an oscillation was as short as 5000 s. The BZ reaction was confirmed to occur when the concentration of $[dema\text{-}H^+][HSO_4^-]$ was within a range between 0.3 and 4 M. In particular, extremely stable self-oscillation was realized when the $[dema\text{-}H^+][HSO_4^-]$ concentration was approximately 1.5 M with concentrations for $Ru(bpy)_3$, $NaBrO_3$, and MA of 17, 84, and 62.5 mM, respectively (see Figure S1 in the Supporting Information).

We further investigated the relationship between the initial concentrations of the BZ medium (that is, [dema-

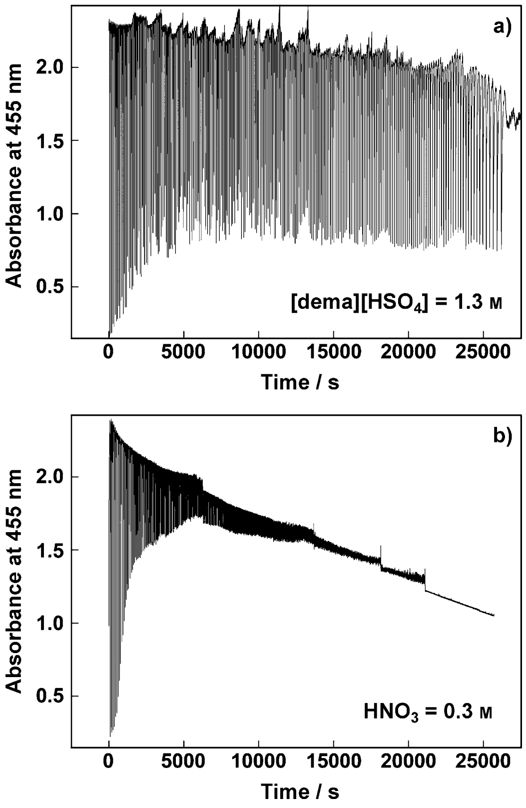

Figure 2. Self-oscillation profile of the BZ reaction in a) [dema-H$^+$][HSO$_4^-$] (1.3 M) and b) aqueous HNO_3 solution (0.3 M), respectively. The concentration of the other BZ compounds are as follows; [Ru(bpy)$_3$] = 17 mM, [$NaBrO_3$] = 84 mM, and [MA] = 62.5 mM.

H$^+$][HSO$_4^-$], $NaBrO_3$, and MA) and the oscillation period at a fixed Ru(bpy)$_3^{2+}$ concentration. Figure 3 shows the oscillation period (logarithmic scale) as a function of the initial concentration of the components of the BZ medium. In all cases, the oscillation period decreases when the concentration of the BZ component increases (Figure S2 in the Supporting Information). We obtained the following empirical relation between the period T and the initial molar concentration of the component [Eq. (1) and Figure 3].

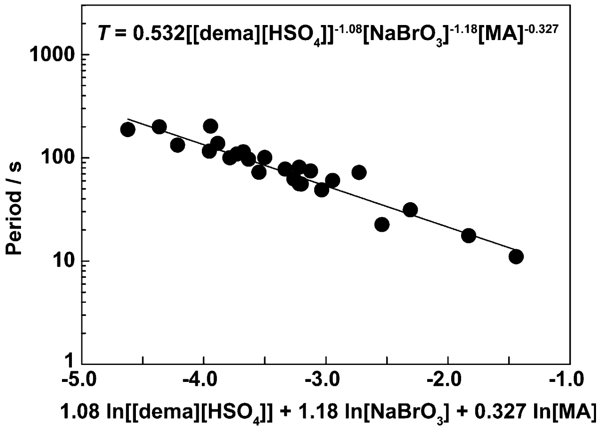

Figure 3. Plots of the period against the concentration of a BZ component under fixed initial concentrations of the other components of the BZ solution.

$$T = 0.532[[\mathrm{dema}][\mathrm{HSO_4}]]^{-1.08}[\mathrm{NaBrO_3}]^{-1.18}[\mathrm{MA}]^{-0.327} \qquad (1)$$

This result indicates that the oscillation period strongly depends on the concentration of [dema-H$^+$][HSO$_4^-$] and $NaBrO_3$ relative to the previously reported self-oscillation using HNO_3 as proton source (the exponents of [HNO_3], [$NaBrO_3$], and [MA] were 0.743, 0.796, and 0.414, respectively.)[25] Furthermore, it was confirmed that a shorter period results from rapid kinetics of the BZ chemical reaction. For hydrated [dema-H$^+$][HSO$_4^-$] pH measurements revealed that the pK_a value of [dema-H$^+$][HSO$_4^-$] could be estimated to be 0.31, indicating a weak acid comparable to trichloro acetic acid (pK_a = 0.7), which is higher than the values of strong acids such as HNO_3 (pK_a = −1.8), H_2SO_4 (pK_{a1} = −3), and $HClO_4$ (pK_a = −8.6 ≈ −9.9), which are typical proton sources for the BZ reaction (Figure S3). Previous reports on the BZ reaction using strong acidic aqueous solutions confirmed that a pH below 1 is required for a stable self-oscillation.[26] These results indicate that [dema-H$^+$][HSO$_4^-$] is a proton source for the BZ reaction under conditions milder than under conventional strong acid conditions.

To understand the effect of [dema-H$^+$][HSO$_4^-$] in detail, we compared the oscillation waveform of a PIL system with that of a typical HNO_3 system. In Figure 4 the representative waveforms of self-oscillation observed in [dema-H$^+$][HSO$_4^-$] and HNO_3 solution are compared. The Field–Kôrös–Neyes (FKN) mechanism is well-known as a reaction scheme which describes the process of the BZ reaction.[2] According to this scheme, the overall BZ reaction can be divided into the following three subprocesses: the consumption of the bromide ion (process A), the autocatalytic reaction of bromous acid with the oxidation of Ru(bpy)$_3^{2+}$ (process B), and the production of bromo malonic acid and the proton accompanying re-reduction of Ru(bpy)$_3^{3+}$ to Ru(bpy)$_3^{2+}$ (process C; see the Supporting Information).

Following the FKN mechanism, the waveform can be divided into three processes (Figure 4). When HNO_3 is used, the duration of each of the three processes found within one period is as follows; process A [Eqs. (S1)–(S3)]: 25.4 %, process B [Eqs. (S4)–(S6)]: 16.7 %, and process C [Eqs. (S7)–(S10)]: 57.9 %. The duration of process C is the longest and about two times longer than that of process A. In contrast, in the [dema-H$^+$][HSO$_4^-$] system the duration of the three processes are as follows; process A: 41.7 %, process B: 18.3 %, and process C: 40.0 %. Thus, the duration of process A increases but the duration of process C decreases when HNO_3 is replaced by [dema-H$^+$][HSO$_4^-$]. Since the pH value in aqueous [dema-H$^+$][HSO$_4^-$] solution is higher than in HNO_3 solution (Figure S3), it is reasonable that the reactions rates of process A [Eq. (S1)–(S3)], in which protons participate as a reactant, are slower. As a result, the duration of process A becomes longer in the [dema-H$^+$][HSO$_4^-$] system.

Furthermore, the rapid chemical reaction in process C [Eqs. (S7)–(S10)] must contribute to the shorter self-oscillation period when [dema-H$^+$][HSO$_4^-$] is used as proton source. It is expected that the proton transfer reaction between [dema-H$^+$][HSO$_4^-$] and a water molecule occurs during the following dissociation reaction of an acid given in Equation (2),

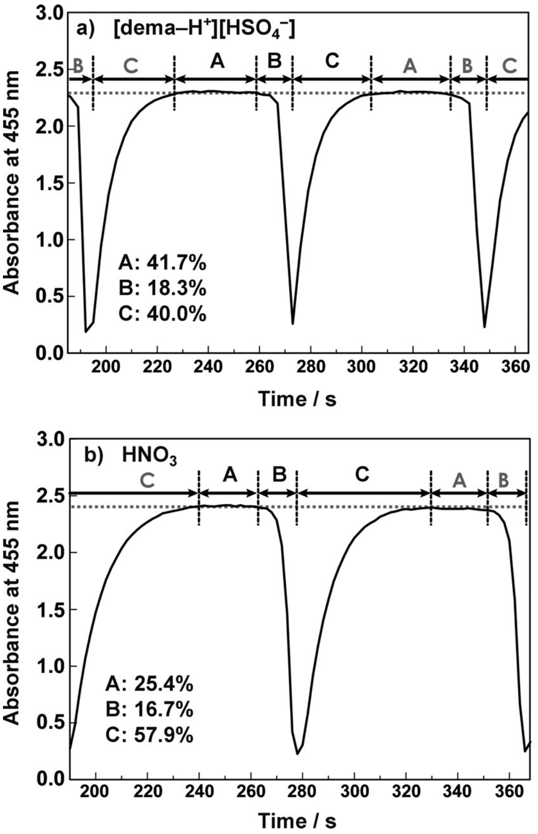

Figure 4. Waveform analysis of the BZ self-oscillation for systems using a) [dema-H$^+$][HSO$_4^-$] and b) HNO$_3$ as proton source.

$$[\text{dema-H}^+] + [\text{HSO}_4^-] + [\text{H}_2\text{O}] \rightarrow [\text{dema}] + [\text{H}_2\text{SO}_4] + [\text{H}_2\text{O}] \rightarrow [\text{dema}] + [\text{HSO}_4^-] + [\text{H}_3\text{O}^+] \qquad (2)$$

where [dema] denotes the deprotonated neutral amine. The equilibrium of Equation (2) tends toward the right-hand side rather than the left because [dema-H$^+$][HSO$_4^-$] clearly releases protons when water is added to decrease the pH (Figure S3). Therefore, a certain amount of neutral amine ([dema]) exists in the reaction system when [dema-H$^+$]-[HSO$_4^-$] is mixed with water. Since the free neutral [dema] behaves as a proton acceptor, the proton produced in process C is eliminated rapidly. As a result, the reactions rates of process C become faster. This is one possible explanation for the long-lasting oscillation with a short period.

Since (P)ILs offer great flexibility in designing cationic and anionic structures and their combinations, one can in principle manipulate their properties as required; they have been termed the "designer solvent". We will prepare PILs that have a much more optimized ion structure for a stable and long-lasting BZ reaction under mild conditions in the future. A long-lasting oscillation reaction with a large amplitude under mild conditions achieved by a PIL will be useful for development of biomimetic materials that can undergo self-oscillation without external stimuli.[5–9] A more systematic study is currently in progress to elucidate the correlation between chemical structure of PILs and the characteristics of the BZ reaction. Also, polymer networks including a PIL-type structure will be promising material for constructing novel soft materials that can work autonomously for a long term under mild conditions. In addition, if a BZ reaction in "pure PILs" was realized, self-oscillating polymers (gels) could be established that function under atmospheric conditions for a long term without taking care of solvent evaporation as the PILs are nonvolatile. We finally aim at realizing the BZ reaction in pure PILs for this purpose. Furthermore, the results presented here may imply the affinity between PILs and living matter and their significance for fundamental IL chemistry.

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