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Time-dependent effects of [apyr]BF_4 and key contributors to their mixture stimulation on *Vibrio qinghaiensis* sp.-Q67 at apical and biochemical levels

ZhenYang Yu[b], Jing Zhang[a,*]

[a] College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing, Zhejiang 314001, PR China
[b] Key Laboratory of Yangtze River Water Environment, Ministry of Education, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, PR China

HIGHLIGHTS

- Toxicities of individual [apyr]BF_4 on luminescence decreased over time.
- Biochemical effects of individual [apyr]BF_4 correlated with those on luminescence.
- Mixture stimulation was great on luminescence and greater on biochemical indices.
- The positive contributor was [bpyr]BF_4 at both apical and biochemical levels.
- The negative contributor was [hpyr]BF_4 at both apical and biochemical levels.

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ABSTRACT

Earlier reports studied the time-dependent effects of imidazolium-based ionic liquids ([amim]X) in the aspect of biochemical explanation and that of key contributor in mixture effects. Presently, the effects of *N*-alkylpyridinium-based ILs ([apyr]BF_4) were studied combining the above two aspects, *i.e.*, the time-dependent effects of [bpyr]BF_4, [hpyr]BF_4 and [opyr]BF_4 on luminescence and biochemical indicators in *Vibrio qinghaiensis* sp.-Q67, and those of the mixtures. In individual results, the inhibition on luminescence increased over concentrations and the side chain length, showing concentration- and side chain-dependence. Moreover, the inhibition of [apyr]BF_4 decreased from 0.25 to 24 h, showing a time-dependence. Notably, [hpyr]BF_4 stimulated the luminescence at 24 h. The biochemical effects, including inhibition and stimulation, were well correlated to those on luminescence. In mixture results, the inhibition on luminescence was lower than the predicted effects by concentration addition model which was based on individual results. Moreover, the mixture stimulation on luminescence was significantly higher than individual ones, and the mixture stimulation on biochemical indicators was even greater than that on luminescence. In mixture effects, [bpyr]BF_4 was the positive contributor, and [hpyr]BF_4 was the negative contributor. Similarities and differences between [amim]X and [apyr]BF_4 indicated underlying mechanisms of the commonly observed hormetic effects of ionic liquids.

1. Introduction

Ionic liquids (ILs) are applied as active pharmaceutical ingredients to facilitate the processes of extracting drug molecules from the biological carrier [1,2]. Such application is based on their characteristics of being non-volatile and thermally stable with high solvency. These characteristics also result in their increasing utilization in chemical industry [3] and biomass processing [4]. So far, ILs haven't been detected in environmental water bodies, but they will find their way eventually because of their high water solubility and inaccessible biodegradability [5,6].

Accordingly, the effects of ILs on aquatic organisms are widely studied. For example, imidazolium-based ILs ([amim]X) inhibited the cell density of freshwater algae [7], reduced immobilization of *D. magna* (crustacean), and caused morphological and mortality effects in *H. attenuate* (cnidarian) [8]. In zebrafish, [amim]X and pyridnium-based ILs ([apyr]X) caused acute lethality and histological damage [9]. Recently, it was reported that [amim]X provoked

* Corresponding author.
E-mail address: zhjshy@163.com (J. Zhang).

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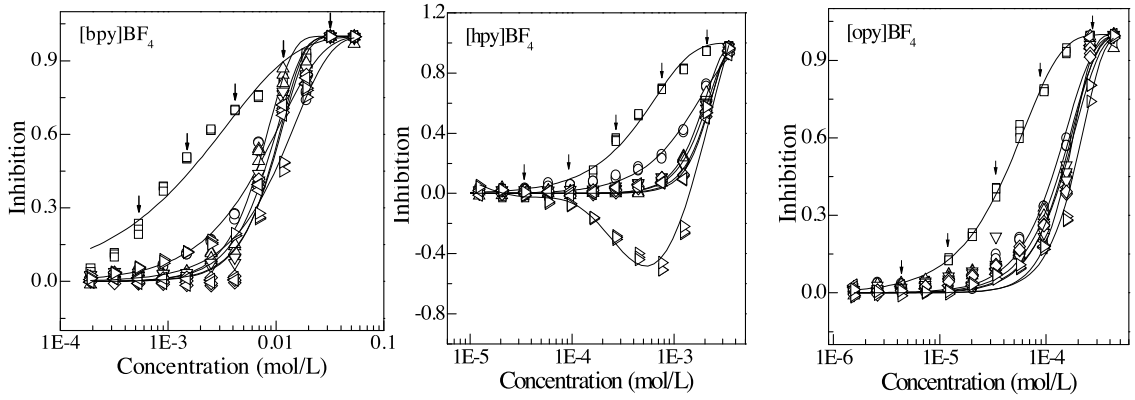

Fig. 1. The time-dependent effects of individual [apyr]BF_4 on luminescence of *Vibrio qinghaiensis* sp.-Q67. Solid line: concentration-response curves fitted by APTox program and SVR procedure; □: 0.25 h; ○: 4 h; △: 8 h; ▽: 12 h; ◊: 16 h; ◁: 20 h; ▷: 24 h. Concentrations with an arrow were employed in subsequent time-dependent exposure in conical flasks to test biochemical effects.

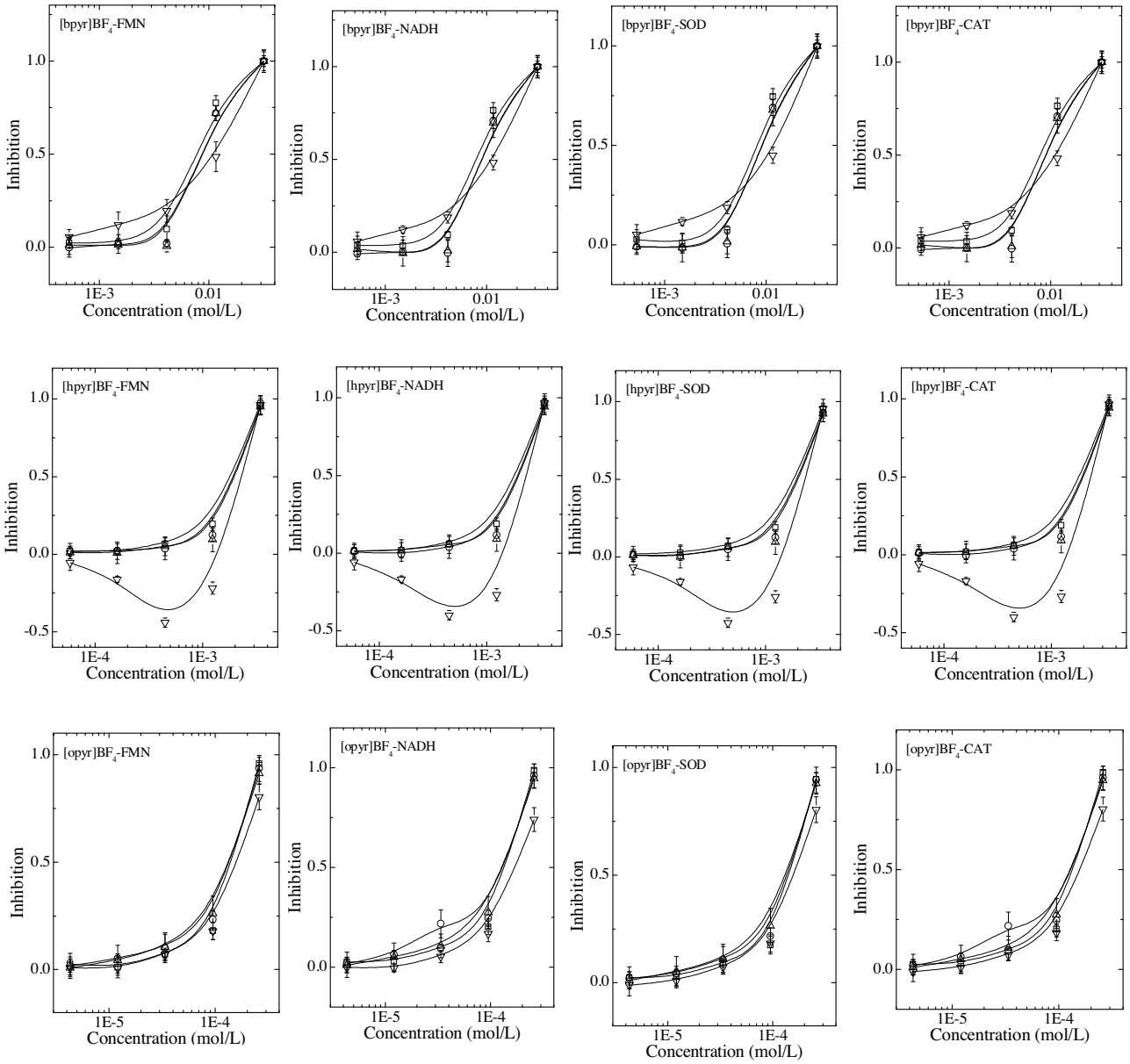

Fig. 2. The time-dependent effects of [apyr]BF_4 on flavin mononucleotide (FMN), nicotinamide adenine dinucleotide (NADH), superoxide dismutase (SOD) and catalase (CAT) in *Vibrio qinghaiensis* sp.-Q67. Solid line: concentration-response curves fitted by APTox program and SVR procedure; □: 0.25 h; ○: 8 h; △: 16 h; ▽: 24 h. The data were represented as mean ± standard deviation.