

## ORIGINAL PAPER

## Preparation of a new metallomicelle catalyst for the hydrolysis of bis(4-nitrophenyl) phosphate

<sup>a</sup>Jia-Qing Xie, <sup>b</sup>Ci Li, <sup>a</sup>Min Wang, <sup>a</sup>Bing-Ying Jiang\*<sup>a</sup>College of Chemistry and Chemical Engineering, <sup>b</sup>Academic Affairs Division, Chongqing University of Technology, Chongqing 400054, China

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A new metallomicellar system containing cerium(III), a macrocyclic polyamine ligand, and the non-ionic surfactant Brij35(polyoxyethylene(23) lauryl ether) was prepared and used as a catalyst in the hydrolysis of bis(4-nitrophenyl) phosphate (BNPP). Catalytic rate of the BNPP hydrolysis was measured kinetically using the UV-VIS spectrophotometric method. The results indicate that the metallomicellar system has relatively high stability and excellent catalytic function in the BNPP hydrolysis; also, the reaction rate of the BNPP catalytic hydrolysis increased by a factor of ca.  $1 \times 10^{10}$  compared to the BNPP spontaneous hydrolysis due to the catalytic effect of the active species and the local concentration effect of the micelles in the metallomicellar system. Experimental results also showed that the mono-hydroxy complex containing the macrocyclic polyamine ligand and cerium(III) is the real active species in the BNPP catalytic hydrolysis, and that the micelles provide a useful catalytic environment for the reaction. On basis of the research results, the reaction mechanism of BNPP catalytic hydrolysis has been proposed.

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**Keywords:** metallomicelles, construction, catalysis, hydrolysis, mechanism**Introduction**

Organophosphorus compounds are ubiquitous in nature. To fully understand their behavior it is very important to establish mechanisms of their transformation in biological systems. Many researchers have worked hard to develop biomimetic models for the metalloenzyme with high efficiency and selectivity in order to achieve friendly environment and economically favorable processes (Rossi et al., 2002; Iranzo et al., 2003; Tonde et al., 2006; Ferreira et al., 2008). In this research field, hydrolysis of phosphodiester is of paramount importance in biological and industrial processes (Westheimer, 1987). In recent decades, some metal complexes, such as Mn(III), Cu(II), Zn(II), Ni(II), and lanthanide (Ln(III)) complexes (Luedtke & Schepartz, 2005; Lombardo et al., 2010; Rossi et al., 2002; Patel et al., 2011; Gunnlaugsson et al., 2002; Anbu et al., 2010), have been used as catalysts for the

hydrolysis of phosphoric acid esters and as potential catalysts for the detoxification of anticholinesterase agents in chemical warfare. Among these model compounds, the lanthanide ion and its complexes have attracted much attention as catalysts for the hydrolysis of the phosphoric acid ester (Katada et al., 2008; Kuchma et al., 2010) because of their extremely strong Lewis acidity, higher oxidation state and charge density, coordination number, and high ligand exchange rates (Maldonado & Yatsimirsky, 2005; Jurek et al., 2000). These characteristics make the lanthanide ions well-suited to be catalytic centers in the development of artificial enzymes (Franklin, 2001). Cerium is unique among the lanthanides and it has been found to be particularly effective in promoting phosphodiester hydrolysis and DNA hydrolysis (Rammo et al., 1996; Komiyama et al., 1999; Tjoet et al., 2012).

In a many biomimetic models of hydrolytic metalloenzymes, macrocyclic polyamine metal complexes

\*Corresponding author, e-mail: xjq8686@163.com