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Novel self-assembling systems based on amphiphilic phosphonium salt and polyethylene glycol. Kinetic arguments for synergetic aggregation behavior

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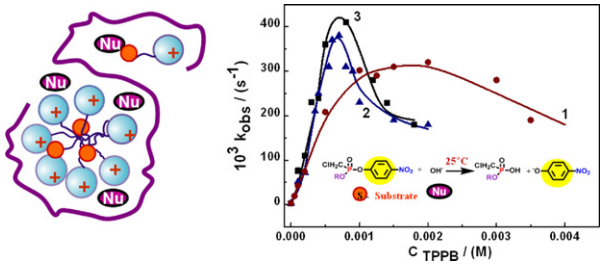
HIGHLIGHTS

- Synergetic behavior occurs in the phosphonium surfactant–PEG systems.
- Zeta-potential of cationic micelles decreases in the presence of PEG.
- The counterion binding of micelles decreases with the addition of PEG.
- An increase in the reactivity of phosphonates occurs in polymer-bound micelles.

GRAPHICAL ABSTRACT



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ABSTRACT

Structural behavior and catalytic activity toward basic hydrolysis of O-alkyl-O-p-nitrophenyl chloromethyl phosphonates (alkyl = ethyl (S1) and hexyl (S2)) of mixed cetyl triphenyl phosphonium bromide (TPPB)–polyethylene glycol (PEG) systems are studied. The interdependence of aggregates and substrates is revealed from symbate changes in their self-diffusion coefficients determined by NMR FT-PGSE method. Much lower zeta-potentials of mixed systems as compared to single TPPB micelles are found, although the counterion binding of aggregates decreases with the addition of PEG. A 1.5–2-fold increase in the reactivity of phosphonates is shown to occur in mixed TPPB–PEG systems versus single surfactant micelles. In addition, a polymer induced shift of the onset of the rate acceleration toward the lower concentrations is observed. These findings provide strong evidences for synergetic solution behavior in the TPPB–PEG systems. The quantitative treatment of kinetic data in terms of pseudophase model sheds light on the factors of catalytic action. In the case of hydrolysis of S1, the more favorable microenvironment is responsible for the higher catalytic effect of mixed systems as compared to single TPPB micelles, while the factor of concentration decreases. The opposite trend is observed for hydrolysis of phosphonate S2, for which an increase in the micellar rate effect with the PEG addition is mainly contributed by the growth of the factor of concentration.

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1. Introduction

The catalysis of reactions in organized media is of current interest [1–8]. Effects of single micellar solutions and microemulsions on reaction rates have been extensively studied [1–4]. In these systems, aggregates act as nano- or microreactors, compartmentalizing and concentrating or diluting reagents and thereby altering the observed rate of chemical reactions. The sphere of our interest is the design of supramolecular catalytic systems for reactions of nucleophilic substitution in phosphorus and carbon acids [9–12]. These reactions are of significance in organic chemistry and play a key role in biology [13]. Cationic micelles are known to accelerate these reactions due to effective

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