



Self-assembling systems based on amphiphilic alkyltriphenylphosphonium bromides: Elucidation of the role of head group

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ABSTRACT

A systematic study of the aggregation behavior of alkyltriphenylphosphonium bromides (TPPB-*n*; *n* = 8, 10, 12, 14, 16, 18; here *n* is the number of carbon atoms in alkyl groups) in aqueous solutions has been carried out and compared with trimethyl ammonium bromides (TMAB-*n*). Critical micelle concentrations (cmcs) of TPPB-*n* and TMAB-*n* decrease with the number of carbon atoms with the slope parameter of ca.0.3. The low cmcs and effective solubilization power toward Orange OT indicate high micellization capacity of phosphonium surfactants. The low counterion binding parameter β is revealed for TPPB-10 and TPPB-12, while high counterion binding of $\geq 80\%$ is observed for high TPPB-*n* homologs. Values of the surface potential ψ calculated on the basis of pK_a shifts of *p*-nitrophenols is similar for both series and monotonously increase with alkyl chain length. Several points indicate non-monotonic changes within TPPB-*n* series. There are peculiarities of the tensiometry and solubilization plots for high homologs and above mentioned increases in counterion binding on transiting from low to high molecular weight surfactants. Differences in aggregation behavior between TPPB and TMAB series and between low and high homologs can be due to the specific structural character of the TPP⁺ cation, which is supported by X-ray data.

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1. Introduction

Self-assembling systems are widely used in various areas of practice including catalysis, gene and drug delivery, design of nanocapsules and nanoreactors, synthesis of nanoparticles, mesoporous materials [1–8], etc. A majority of modern strategies involving self-assembling amphiphilic solutions are underlain by their capacity to form nanosized aggregates in solutions, when exceeding a certain concentration. These aggregates are capable of binding (solubilizing, compartmentalizing) the guests molecules, thereby controlling the thermodynamic stability and physical and chemical properties of the included compounds. The morphology of the aggregates formed due to non-covalent interactions, their binding capacity, and hence functional activity (catalytic, sensory, etc.) depends to a great extent on the chemical structure of amphiphiles. The role of structural factors in self-organization and properties of systems based on amphiphilic compounds are in the focus of our recent investigations [9–12]. One of the key factors is the nature of charged fragments, i.e., head

groups and counterions. There are a lot of publications focused on the influence of the nature of head groups on the aggregation behavior and catalytic activity of cationic surfactants [13–27]. On the contrary, few studies deal with the association of cationic surfactants with highly hindered head groups, such as triphenylphosphonium (TPP), in aqueous solutions [28–36]. Meanwhile, the TPP⁺ cation is widely explored as a tool in mitochondrial bioenergetics, in particular in the strategy to target bioactive molecules to mitochondria by their attachment to the lipophilic triphenylphosphonium cation through an alkyl linker [37–42]. The delocalized positive charge of these lipophilic cations enables them to easily permeate lipid bilayers and to accumulate several hundredfold within mitochondria, because of the large membrane potential, negative inside. The above considerations focus attention on the aggregation behavior of alkyltriphenylphosphonium bromides of varied hydrophobicity (TPPB-*n*; here *n* is the number of carbon atoms in alkyl groups) (Fig. 1).

The aggregation in the TPPB-series is studied in works [28–36], which are mainly focused on the mixed systems based on TPPB-*n*. The results obtained are of importance, though there exist some contradictory points. The comparison of two cationic surfactant series, i.e., alkyl trimethylammonium bromides (TMAB-*n*) and

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