

Supramolecular systems based on calix[4]resorcine with mono-, di-, and tetracationic surfactants: Synergetic structural and solubilization behavior

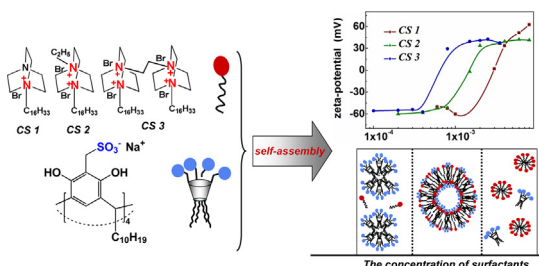
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HIGHLIGHTS

- Calixresorcine and cationic surfactants with bicyclic fragment form mixed aggregates.
- Mixed aggregation occurs at the lower concentrations as compared to single solutions.
- Mixed aggregation is favored by an increase in the number of cationic head groups.
- Aggregates formed can be used as nanocontainers for hydrophobic compounds.

GRAPHICAL ABSTRACT



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ABSTRACT

Formation of nanosized aggregates in aqueous solutions of amphiphilic calix[4]resorcine with sulfonate groups at upper rim (CR), cationic surfactants (CS) with bicyclic head group (mono-, di-, and tetracationic alkylated derivatives of 1,4-diazabicyclo[2.2.2]octane), and their mixtures has been shown by a variety of physicochemical methods (tensiometry, conductometry, dynamic light scattering, and dye solubilization). Critical association concentration of CR is shown to be of 6.2 mM (tensiometry). Beyond this concentration, CR forms aggregates of ca. 7–10 nm, which are capable of solubilizing hydrophobic dye Sudan. The formation of mixed structures of CR with cationic surfactants has been found to proceed at the lower concentrations as compared to single CR solutions. The characteristics of mixed aggregates (size, morphology, surface potential, and solubilizing properties) depend on the concentration of the surfactants. Aggregation in mixed solutions is favored by increase in the number of charged head groups of the surfactants.

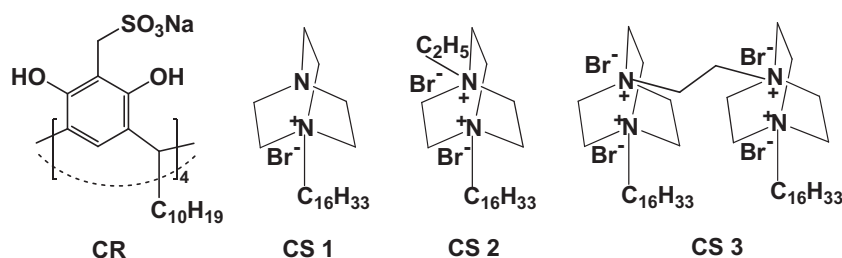
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1. Introduction

It is known that the use of the mixed systems based on surface-active substances leads to the optimization of the properties of the materials and diminishes their cost, which plays an important

role in modern industry. Nowadays, the interest in mixed compositions is due to the novel direction of supramolecular chemistry, that is, the formation of supramolecular amphiphiles [1–3]. Growing interest in supramolecular amphiphiles is determined by two aspects [4]: (i) facile design of supramolecular amphiphiles that can be formed through various non-covalent interactions (hydrogen bonds, metal–ligand coordination, electrostatic and π -stacking, as well as host–guest interactions) [5–7] and (ii) dynamic character of non-covalent associates that enable easy control of the

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Scheme 1. Structural formulae of amphiphilic calix[4]resorcine that contains sulfonate fragments at the upper rim (CR) and mono- (CS 1), di- (CS 2), and tetra- (CS 3) quaternized derivatives of 1,4-diazabicyclo[2.2.2]octane.

properties of formed structures [8]. The latter is essential for the design of smart supramolecular materials, which are responsive to various factors (pH, temperature, light, magnetic field, oxidation, and so on) [9–11]. The use of macrocyclic receptors (cyclodextrin [12–14], cucurbituril [15,16], calixarenes [17,18]) for the design of supramolecular amphiphiles is of particular interest. It is known that macrocycles can take part in guest–host interactions due to the presence of molecular cavity and preorganization of functional groups [19,20], which is important from the viewpoint of the design of biomimetics. Besides, specific geometry of calixarene molecules highlights them as potential drug delivery systems [21–23]. Among the vast number of various types of macrocycles published, sulfonate calix[*n*]arenes have several advantages [24]. It is known that calix[*n*]arenes with a sulfo group are attractive due to their high water solubility and selective binding ability toward biological [25–28] and pharmaceutical molecules [29–31] including compounds of bicyclic identity [32], as well as their catalytic properties, biocompatibility [33], and so on. In addition, some representatives of sulfonate calixarenes are known as surface-active substances, which are able of self-assembling in aqueous solution with the formation of nanostructures [34,35].

This work focuses on the design of supramolecular amphiphiles that are composed of new water-soluble calix[4]resorcine bearing sulfonate fragments at the upper rim and decyl tails at the lower rims (Scheme 1), and cationic surfactants (CS), which include one, two, and four charged nitrogen atoms. The choice of these compounds is caused by the fact that sulfonate calixarenes are widely recognized as the receptors for organic ammonium ions [3,36–40]. The presence of terminal sp^2 carbons may introduce additional disordering effect in the packing mode of molecules upon aggregation, thereby affecting the geometry of aggregates and their solubilization capacity. The aim of this work was to optimize the composition of binary systems based on CSs with variable number of cationic centers and calixresorcine that contains four anionic fragments in order to achieve the synergetic effect in the structural behavior. This makes it possible to design novel types of nanoassemblies with required properties and functionality. Amphiphilic mono- (CS 1), di- (CS 2), and tetra- (CS 3) quaternized derivatives of 1,4-diazabicyclo[2.2.2]octane (DABCO) were used (Scheme 1).

The presence of double bonds at the lower rim of CR implies that CR can be used for the creation of amphiphilic polymer systems. Preliminary results showed that the double bond of CR reacts with dimercaptanes (HSC_2H_4SH and $HSC_2H_4OC_2H_4SH$) in an aqueous media with the formation of monodisperse polymeric nanoparticles. The structure and properties of the polymer nanoparticles based on CR are studied at this moment.

Interest in CS 1–3 is caused by the fact that these compounds have improved properties (aggregation, catalytic, and biological activity) compared to known conventional cationic surfactants [41–44]. Besides, toxicities of the DABCO-based surfactants are usually lower than those for conventional CS–cetyltrimethylammonium bromide.

2. Material and methods

2.1. Materials

CS 1 was prepared by the reaction of DABCO with 1-bromohexadecane; and CS 2 by quaternization of CS-1 with ethyl bromide according to the procedure described earlier [41,43]. CR was prepared through protocol reported elsewhere [45]. 1-Phenylazo-2-naphthol (Sudan I, Acros Organics) was used as received. For details of the synthesis of 1.2-bis(4-hexadecyl-1,4-diazoniabicyclo[2.2.2]octane-1-yl)ethane tetrabromide (CS 3), see Supporting Information.

2.2. Tensiometry

Surface tension measurements were performed using the Du Nouy Ring detachment method (Kruss K6 tensiometer). The experimental details are described elsewhere [46].

2.3. Electrical conductivity

Electrical conductivities were measured using an InoLab Cond 720 precision conductivity meter. Reproducibility was checked for selected samples, and no significant differences were observed. All samples were studied at 25 ± 0.1 °C. Purified water ($18.2 M\Omega$ cm resistivity at 25 °C) from Direct-Q 5 UV equipment was used for all sample preparation.

2.4. Dynamic light scattering

Dynamic light scattering (DLS) measurements were performed by means of Malvern Instrument Zetasizer Nano. The measured autocorrelation functions were analyzed by Malvern DTS software, and the second-order cumulant expansion methods. The effective hydrodynamic radius (R_H) was calculated according to the Einstein–Stokes relation: $D = k_B T / 6\pi\eta R_H$, in which D is the diffusion coefficient, k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity. The diffusion coefficient was measured at least three times for each sample. The average error in these experiments was approximately 4%. The solutions were filtered with Millipore filters to remove dust particles from the scattering volume.

2.5. Dye solubilization study

The solubilization experiments were performed by adding an excess of crystalline dye Sudan I to solutions. These solutions were allowed to equilibrate for about 48 h at room temperature. They were filtered, and their absorbency was measured at 485 nm using SP-26 spectrophotometer. The absorbance of Sudan I is known to be sensitive to the microenvironmental conditions and may change under the variation in the polarity of solution, pH, etc. [47,48]. The

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