



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

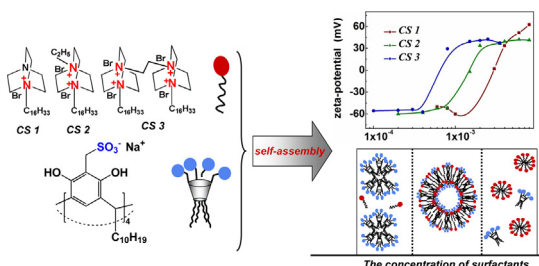
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## HIGHLIGHTS

- 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.

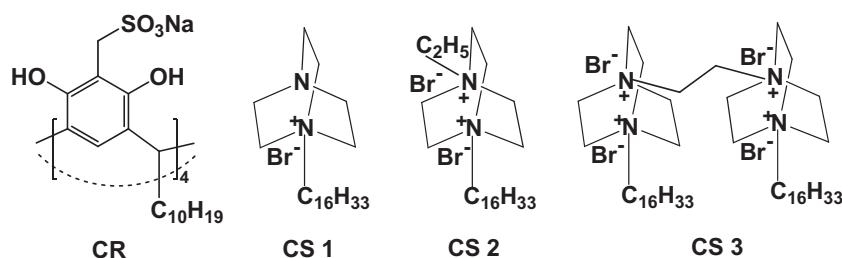
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## 1. Introduction

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  $\pi$ -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  $25 \pm 0.1$  °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  $\eta$  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

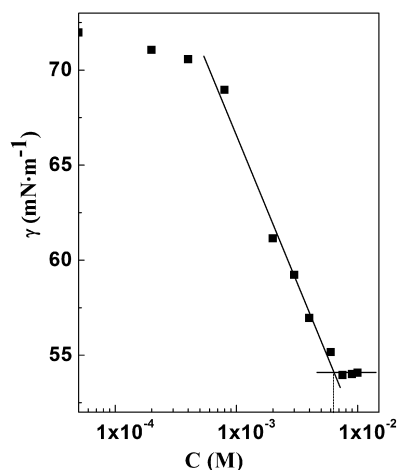


Fig. 1. Surface tension of aqueous solutions of CR vs. its concentration, 25 °C.

wavelength of 485 nm corresponds to a maximum in absorbance of Sudan I under the experimental conditions. Quartz cuvettes containing the sample were used, with a cell length of 0.1 cm.

### 3. Results and discussion

#### 3.1. Self-association of calix[4]resorcine

This work is a continuation of our investigations of new types of self-assembling systems based on superamphiphiles [3,39]. In single aqueous solutions of typical surfactants, direct micelles are known to be formed beyond critical micelle concentration (CMC) [49]. For mixed systems, for example, those based on two different types of amphiphilic molecules or surfactant–polymer mixtures, the term “critical aggregation concentration” (CAC) is often used [49]. This is because the more complicated morphological behavior occurs in such systems differing from the simple micelle formation. The same is true for amphiphilic macrocycles, that is, calixarenes that are capable of associating through different mechanisms including both the close and open models [50] owing to the specific packing parameter differing from that of typical surfactants [51]. Importantly, along with hydrophobic effect responsible for the micelle formation in surfactant solutions, a wider spectrum of interactions can contribute to the aggregation in mixed systems. Besides, structural rearrangements may be observed within the concentration range studied [3,39]. Therefore, in this article, the term “CMC” is used in the case of single surfactant solutions, while term “CAC” is related to CR solution and mixed systems.

Tensiometry data show that CR decreases the surface tension ( $\gamma$ ) at the air–water interface in analogy with conventional surfactants. Dependence of the surface tension of CR vs. its concentration in water has clear inflection point that confirms the formation of aggregates of CR at CAC of 6.2 mM (Fig. 1). In literature, CMC values of anionic amphiphiles with sulfate or sulfonate polar groups are available, for example, CMC of ca. 10 mM for typical anionic surfactant sodium dodecyl sulfate [49] and CAC of 12 mM for sulfonate calix[4]resorcine with pentyl radicals on the lower rim [51] are reported.

Using the tensiometry data, quantitative characteristics of the adsorption were determined, that is, the surface excess,  $\Gamma_{\max} = 0.45 \times 10^{-6} \text{ mol m}^{-2}$ ; minimum surface area per a molecule,  $A_{\min} = 3.69 \text{ nm}^2$ ; standard free energy of adsorption,  $\Delta G_{\text{ad}} = -49.30 \text{ kJ mol}^{-1}$ ; and free energy of micelle formation,  $\Delta G_{\text{m}} = -9.60 \text{ kJ mol}^{-1}$ . Conductometry data support the formation of associates of the macrocycle as well. Inflection point can be observed on the dependence of specific electric conductance of

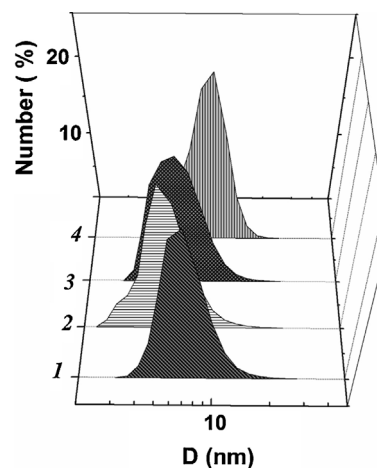


Fig. 2. The number-averaged size distribution for aqueous CR solution; C, mM: 2 (1); 3 (2); 4 (3); 6 (4); 25 °C.

aqueous solutions of CR vs. its concentration (Fig. S1, see Supplementary Data) at the concentrations of 6.1 mM which was treated as the onset of aggregate formation, CAC, which is in good agreement with tensiometry result.

Dynamic light scattering data also prove the formation of CR aggregates in water. As follows from Fig. S2, bimodal size distribution is observed, with particle sizes ranged from 7 to 10 nm and from 50 to 100 nm depending on the CR concentration. At the same time, the number-averaged size distribution (Fig. 2) testifies that the population with the sizes of 7–10 nm predominates in the solution. The primary size distribution obtained from DLS measurements is the intensity-weighted distribution that is highly sensitive to the presence of larger particles and tends to overestimate their contribution. Intensity distribution can further be transformed to the number-averaged distribution, which mainly highlights the smaller population of nanoparticles. While the small particles can be easily attributed to the micelle-like aggregates, the large aggregates may provide evidence for the non-micellar association mechanism probably contributed by inclusion head-to-tail packing mode [52] or hydrogen bonding.

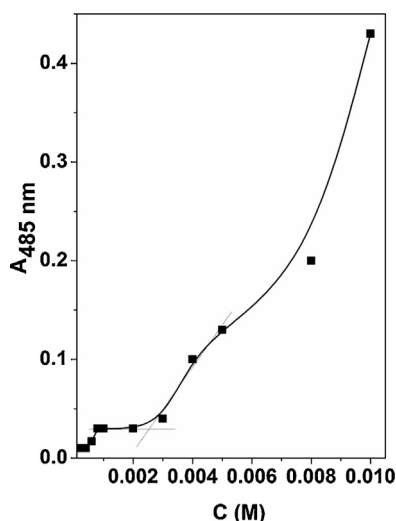
The data on solubilization of water-insoluble Sudan I dye are in line with the above tensiometry and conductometry data. It is known that aqueous solution of sulfonato-ethylated calix[4]resorcines without long-chain alkyl tails is unable to solubilize hydrophobic dyes. This is because unlike the associates of «closed» micellar type, calixresorcines form aggregates of «open» type («head-to-tail» mode) with no hydrocarbon core [3,39]. Study of the solubility of Sudan I in aqueous solution of CR by spectrophotometry showed that, starting from the concentration of ca. 3.0 mM, remarkable increase in optical density of the dye takes place (Fig. 3).

The latter proves the solubilization of water-insoluble probe, namely, its penetration to hydrophobic zone of CR associates, thereby testifying the occurrence of aggregates with non-polar domains.

#### 3.2. Aggregation of CS–CR mixed systems

CAC values of calixarene–CS mixed compositions obtained by the variety of physicochemical methods are given in Table 1.

Tensiometry data show that the addition of CR ( $C = 0.5 \text{ mM}$ ) to the CS solutions results in the increase in CAC in the case of CS 1 and decrease in the case of CS 2 and CS 3 compared to their individual solutions. The surface tension vs. concentration plot for calixarene–CS 2 mixed system is given in Fig. 4 as an example. Conductivity measurements exemplified by the CR–CS 2 mixed



**Fig. 3.** Optical density of Sudan I in CR solution vs. concentration of CR;  $\lambda = 485$  nm;  $25^\circ\text{C}$ ,  $L = 0.1$  cm.

**Table 1**

CMC and CAC values of cationic CS 1–3 without and with CR ( $C = 0.5$  mM);  $25^\circ\text{C}$ .

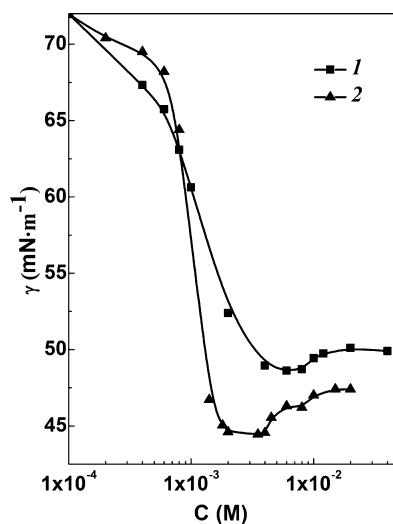
No.	System	CAC (CMC) $10^3$ (M)	
		Tensiometry	Conductometry
1	CS 1*	1	1; 11
2	CR–CS 1	2	0.1; 2
3	CS 2**	3	3.1; 10
4	CR–CS 2	1.5	1.5; 5
5	CS 3	1.5	0.1; 1
6	CR–CS 3	1	0.4; 2

\* Data from [41]

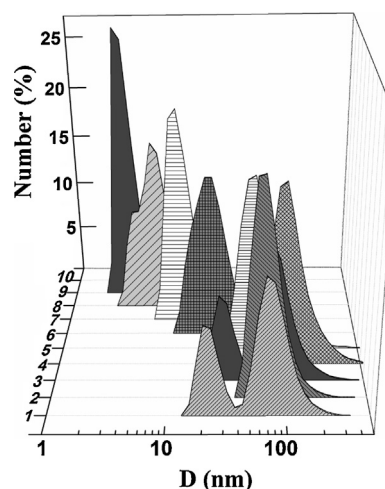
\*\* Data from [53].

system (Fig. S3) support tensiometry data. It is noteworthy that due to mainly electrostatic character of the CR–CS interactions conductivity measurements may provide additional information on the aggregation process. In particular, this technique revealed one more critical point at lower (CS 3) or higher (CS 2) surfactant concentrations as compared to tensiometry CACs (Table 1).

The DLS data (Fig. 5) provide additional information on the aggregation in mixed systems. Size distribution for all CR–CS mixed



**Fig. 4.** Surface tension of aqueous solutions of CS 2 vs. its concentration without (1) and with CR (2),  $C_{\text{CR}} = 0.5$  mM;  $25^\circ\text{C}$ .



**Fig. 5.** Size distribution for CR–CS 2 system vs. concentration of CS 2 averaged on number,  $C_{\text{CS}2} = 0.2$  (1); 0.4 (2); 0.6 (3); 0.8 (4); 1.5 (5); 2 (6); 3.5 (7); 4 (8); 6 (9); 10 (10) mM;  $C_{\text{CR}} = 0.5$  mM;  $25^\circ\text{C}$ .

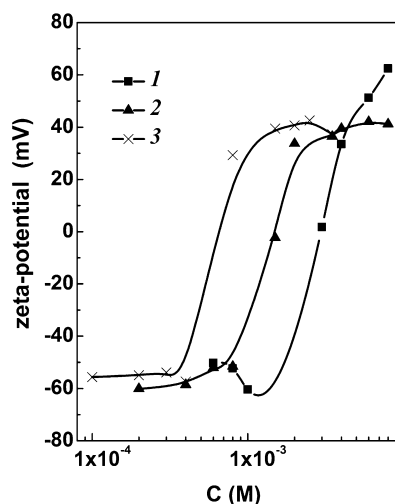
systems demonstrates the similar trends. The sizes distribution for CR–CS 2 mixed system is given as an example in Fig. 5. It is evident that within low concentration range of CS 2, bimodal size distribution occurs. Small aggregates of 7–20 nm and larger particles with the sizes of 40–70 nm are formed in the solution. Taking into account the data in Table 1, it is evident that bimodal size distribution is observed below the CAC of ca. 1 mM determined for this system. Therefore, it can be attributed to the calixarene associates, since CR is used at the concentration close to its aggregation threshold (Fig. 1). Importantly, unlike single CR solution (Fig. 2), the more pronounce contribution of large aggregates occurs in this case. Probably, the presence of even small surfactant molecules shifts association toward the formation of large CR particles.

Beyond the CAC of mixed CR–CS 2 system around of ca. 1 mM, the transition from bimodal to monomodal size distribution occurs, thereby indicating the formation of mixed aggregates enriched by CR. As the surfactant concentration increases, one more morphological rearrangement is probably observed, which is reflected in the second CAC value (Table 1). Indeed, as can be seen in Fig. 5, a sharp decrease in aggregate size is observed above the CS 2 concentration of 5 mM, which may be due to the saturation effect, when all the calixarene units are bound with surfactant molecules and surfactant micelles become prevail in solution.

Fig. 6 shows data on zeta-potential for CR–CS mixed systems that are in line with the above tensiometry and DLS results. For low surfactant concentration, zeta-potential values of the aggregates correspond to  $\sim -60$  mV. As can be seen in Table 1 and Fig. 5, these data cover the concentration range before CAC value and can be attributed to aggregated calixarene molecules, with lower rim negatively charged. High negative value of zeta-potential in CR–CS 2 system confirms this fact. The zeta-potential compensation with the increase in the surfactant concentration (Fig. 6) confirms the above information on the mixed CR–CS aggregation, with the onset of the charge compensation roughly coinciding with the CAC values.

Increase in the concentration of CS 2 leads to the increase in aggregate size and the recharging of aggregate surface from negative to positive value. Within this concentration range, the adsorption of CS 2 molecules presumably takes place on the surface of CR aggregates due to electrostatic interactions of positively charged ammonium groups of CS and negatively charged sulfonate groups of calixarene. Around the concentration of CS  $\sim 1$  mM, maximum size of  $\sim 100$  nm is observed, with electrokinetic potential being close to 0 mV (Figs. 5 and 6). This low value of zeta-potential probably indicates that the system is instable and tends to



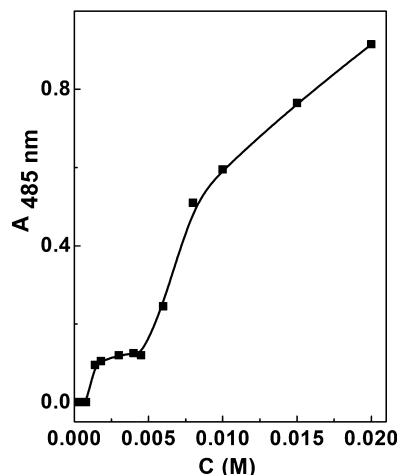


**Fig. 6.** Change of zeta-potential values of CR–CS 1 (1), CR–CS 2 (2), and CR–CS 3 (3) systems in water depending on the concentration of CS,  $C_{CR} = 0.5$  mM; 25 °C.

rearrange. One can conclude that the growing relative content of CS probably induces the formation of vesicles, which are known to occur in mixtures of cationic and anionic surfactants [36,54–56].

Meanwhile, subsequent increase in the concentration of CS 2 in CR–CS 2 system provides the decrease in aggregate size and increase in electrokinetic potential of system. In the range of the highest concentrations of CS 2 that exceed substantially the concentration of calixarene, zeta-potential does not change and takes the value of  $\sim 40$  mV. It should be noted that, for CR–CS 3 mixed system (Fig. 6), zero zeta-potential is achieved at the concentration by two times lower than that for CR–CS 2 system and by four times lower compared to CR–CS 1 system. This indicates that the rearrangement of supramolecular structure CR–CS is facilitated with an increase in charge character of CS, that is, electrostatic interactions contribute highly to association in the system.

The data on solubilization of Sudan I in CR–CS mixed solutions provide evidences for the structural transitions in system. In Fig. 7, dependence of optical density of dye in CR–CS 2 solutions vs. CS concentration is given. In the range of low concentrations of CS 2 (below 1 mM), that is in the range of expected existence of aggregates with predominant calixarene content, no absorbance of the dye is observed. This may be because very small amount of aggregates occurs at this CR concentration, and aggregates formed show



**Fig. 7.** Optical density of Sudan I in aqueous solutions of CS 2 vs. concentration of CS 2 at fixed CR concentration of 0.5 mM;  $\lambda = 485$  nm;  $L = 0.1$  cm; 25 °C.

low solubilization capacity. In the concentration range from 1 to 5 mM, an increase in optical density occurs with the tendency to plateau.

At the concentration of CS above 5 mM; that is, in the range of existence of small and stable nanoparticles, drastic increase in optical density of CR–CS 2 solutions is observed which is in line with the occurrence of aggregates of closed type, that is, micelles. Thus, the dye solubilization study supports the validity of critical points and structural transitions in the systems revealed by other techniques.

#### 4. Conclusions

Thus, it was shown by a variety of physicochemical methods that sulfonate calix[4]resorcine forms mixed aggregates with mono-, di-, and tetracationic alkyl derivatives of DABCO in aqueous solutions. The packing mode, morphology, and size of assemblies and their solubilizing properties depend on the structure of cationic surfactants, in particular, their charge character and the ratio of the components in mixed system. The key role of electrostatic interactions in the formation and rearrangement of mixed supramolecular structures was revealed. It was shown that the systems with either the minor or predominant CS content exhibit the lowest and the highest solubilizing capacity, respectively, toward hydrophobic organic guest. This is essential from the viewpoint of the design of nanocarriers with controlled and reversible binding capacity toward therapeutic agents or biomolecules.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2014.02.012>.

#### References

- [1] T. Sun, J. Shen, H. Yan, J. Hao, A. Hao, Stable vesicles assembled by “supramolecular amphiphiles” with double hydrophobic chains, *Colloid. Surf. A* 414 (2012) 41–49.
- [2] L. Zhu, Y. Han, M. Tian, Y. Wang, Complex formation and aggregate transitions of sodium dodecyl sulfate with an oligomeric connecting molecule in aqueous solution, *Langmuir* 29 (2013) 12084–12092.
- [3] S.V. Kharlamov, R.R. Kashapov, T.N. Pashirova, E.P. Zhiltsova, S.S. Lukashenko, A.Yu. Ziganshina, A.T. Gubaidullin, L.Ya. Zakharova, M. Gruner, W.D. Habicher, A.I. Kononov, Supramolecular amphiphile based on calix[4]resorcinarane and cationic surfactant for controlled self-assembly, *J. Phys. Chem. C* 117 (2013) 20280–20288.
- [4] X. Zhang, C. Wang, Supramolecular amphiphiles, *Chem. Soc. Rev.* 40 (2011) 94–101.
- [5] S. Haldar, S.K. Maji, Role of non-covalent interactions in the molecular organization of N-n-hexadecanoyl amino acid amphiphiles with hydrophobic  $C_{\alpha}$ -side chains in Tris buffer (pH 9.3), *Colloid. Surf. A* 420 (2013) 10–21.
- [6] J. Li, H. Jiang, W. Hu, G. Zou, Q. Zhang, Morphology modulation in an azobenzene based supramolecular amphiphiles system, *J. Photochem. Photobiol. A* 245 (2012) 28–32.
- [7] C. Wang, S. Yin, S. Chen, H. Xu, Z. Wang, X. Zhang, Controlled self-assembly manipulated by charge-transfer interactions: from tubes to vesicles, *Angew. Chem. Int. Ed.* 47 (2008) 9049–9052.
- [8] K. Wang, D. Guo, Y. Liu, Temperature-controlled supramolecular vesicles modulated by p-sulfonatocalix[5]arene with pyrene, *Chem. Eur. J.* 16 (2010) 8006–8011.
- [9] Q. Li, X. Chen, X. Yue, D. Huang, X. Wang, Construction and transformation of stimuli-responsive vesicles from the ferrocene derivative supramolecular amphiphiles, *Colloid. Surf. A* 409 (2012) 98–104.
- [10] Y. Wang, N. Ma, Z. Wang, X. Zhang, Photocontrolled reversible supramolecular assemblies of an azobenzene-containing surfactant with alpha-cyclodextrin, *Angew. Chem. Int. Ed.* 46 (2007) 2823–2826.

- [11] Y. Xing, C. Wang, P. Han, Z. Wang, X. Zhang, Acetylcholinesterase responsive polymeric supra-amphiphiles for controlled self-assembly and disassembly, *Langmuir* 28 (2012) 6032–6036.
- [12] T. Sun, M. Ma, H. Yan, J. Shen, J. Su, A. Hao, Vesicular particles directly assembled from the cyclodextrin/UR-144 supramolecular amphiphiles, *Colloid. Surf. A* 424 (2013) 105–112.
- [13] J. Zhang, P.X. Ma, Cyclodextrin-based supramolecular systems for drug delivery, *Adv. Drug Deliver. Rev.* 65 (2013) 1215–1233.
- [14] R. Sharma, S. Mahajan, R.K. Mahajan, Physicochemical studies of morpholinium based ionic liquid crystals and their interaction with cyclodextrins, *Fluid Phase Equilib.* 361 (2014) 104–115.
- [15] V.D. Uzunova, C. Cullinane, K. Brix, W.M. Nau, A.I. Day, Toxicity of cucurbit[7]uril and cucurbit[8]uril: an exploratory in vitro and in vivo study, *Org. Biomol. Chem.* 8 (2010) 2037–2042.
- [16] Y.H. Ko, E. Kim, I. Hwang, K. Kim, Supramolecular assemblies built with host-stabilized charge-transfer interactions, *Chem. Commun.* (2007) 1305–1315.
- [17] K. Wang, D. Guo, X. Wang, Y. Liu, Multistimuli responsive supramolecular vesicles based on the recognition of p-sulfonatocalixarene and its controllable release of doxorubicin, *ASC Nano* 5 (2011) 2880–2894.
- [18] C. Bize, J. Garrigues, M. Blanzat, I. Rico-Lattes, O. Bistri, B. Colasson, O. Reinaud, Spontaneous vesicles formation of a cationic association involving a head and tail functionalized amino-calix[6]arene, *Chem. Commun.* 46 (2010) 586–588.
- [19] T. Oshima, K. Oishi, K. Ohto, K. Inoue, Extraction of catecholamines by calixarene carboxylic acid derivatives, *J. Inclusion Phenom. Macrocyclic Chem.* 55 (2006) 79–85.
- [20] D.A. Uhlenheuer, K. Petkau, L. Brunsveld, Combining supramolecular chemistry with biology, *Chem. Soc. Rev.* 39 (2010) 2817–2826.
- [21] L.M. Arantes, C. Scarelli, A.J. Marsaioli, E. Paula, S.A. Fernandes, Proparacaine complexation with  $\beta$ -cyclodextrin and p-sulfonic acid calix[6]arene, as evaluated by varied <sup>1</sup>H-NMR approaches, *Magn. Reson. Chem.* 47 (2009) 757–763.
- [22] L.K. Tsou, G.E. Dutschman, E.A. Gullen, M. Telpoukhovskaia, Y. Cheng, A.D. Hamilton, Discovery of a synthetic dual inhibitor of HIV and HCV infection based on a tetrabutoxy-calix[4]arene scaffold, *Bioorg. Med. Chem. Lett.* 20 (2010) 2137–2139.
- [23] M. Mourer, N. Psychogios, G. Laumond, A. Aubertin, J. Regnouf-de-Vains, Synthesis and anti-HIV evaluation of water-soluble calixarene-based bithiazolyl podands, *Bioorg. Med. Chem.* 18 (2010) 36–45.
- [24] F. Perret, A.N. Lazar, A.W. Coleman, Biochemistry of anionic calix[n]arenes, *Chem. Commun.* 47 (2011) 7303–7319.
- [25] C.S. Beshara, C.E. Jones, K.D. Daze, B.J. Lilgert, F. Hof, A simple calixarene recognizes post-translationally methylated lysine, *Chembiochem* 11 (2010) 63–66.
- [26] A. Specht, S. Ludwig, L. Peng, M. Goeldner, Complexing photolabile cholinergic ligands with synthetic and biological receptors: a dynamic survey, *J. Inclusion Phenom. Macrocyclic Chem.* 65 (2009) 157–163.
- [27] K. Wang, D. Guo, H. Zhang, D. Li, X. Zheng, Y. Liu, Highly effective binding of viologens by p-sulfonatocalixarenes for the treatment of viologen poisoning, *J. Med. Chem.* 52 (2009) 6402–6412.
- [28] M. Megyesi, L. Biczok, Considerable change of fluorescence properties upon multiple binding of coralyne to 4-sulfonatocalixarenes, *J. Phys. Chem. B* 114 (2010) 2814–2819.
- [29] G. Arena, A. Casnati, A. Contino, A. Magri, F. Sansone, D. Sciotto, R. Ungaro, Inclusion of naturally occurring amino acids in water soluble calix[4]arenes: a microcalorimetric and <sup>1</sup>H NMR investigation supported by molecular modeling, *Org. Biomol. Chem.* 4 (2006) 243–249.
- [30] Q. Lu, J. Gu, H. Yu, C. Liu, L. Wang, Y. Zhou, Study on the inclusion interaction of p-sulfonated calix[n]arenes with vitamin K3 using methylene blue as a spectral probe, *Spectrochim. Acta A* 68 (2007) 15–20.
- [31] G. Wang, H. Zhang, F. Ding, Y. Liu, Preparation and characterization of inclusion complexes of topotecan with sulfonatocalixarene, *J. Inclusion Phenom. Macrocyclic Chem.* 69 (2011) 85–89.
- [32] H. Bakirci, A.L. Koner, M.H. Dickman, U. Kortz, W.M. Nau, Dynamically self-assembling metalloenzyme models based on calixarenes, *Angew. Chem. Int. Ed.* 45 (2006) 7400–7404.
- [33] M. Paclat, C.F. Rousseau, C. Yannick, F. Morel, A.W. Coleman, An absence of non-specific immune response towards para-sulphonato-calix[n]arenes, *J. Inclusion Phenom. Macrocyclic Chem.* 55 (2006) 353–357.
- [34] S. Shinkai, T. Arimura, K. Araki, H. Kawabata, Syntheses and aggregation properties of new water-soluble calixarenes, *J. Chem. Soc. Perk. T. 1* (1989) 2039–2045.
- [35] N. Basilio, V. Francisco, L. Garcia-Rio, Aggregation of p-sulfonatocalixarene-based amphiphiles and supra-amphiphiles, *Int. J. Mol. Sci.* 14 (2013) 3140–3157.
- [36] V. Francisco, N. Basilio, L. Garcia-Rio, J.R. Leis, E.F. Maques, C. Vazquez-Vazquez, Novel cationic vesicles from calixarene and single-chain surfactant, *Chem. Commun.* 46 (2010) 6551–6553.
- [37] G. Gattuso, A. Notti, A. Pappalardo, S. Pappalardo, M.F. Parisi, F. Puntoriero, A supramolecular amphiphile from a new water-soluble calix[5]arene and n-dodecylammonium chloride, *Tetrahedron Lett.* 54 (2013) 188–191.
- [38] H. Zhao, D. Guo, Y. Liu, Binding behaviors of p-sulfonatocalix[4]arene with gemini guests, *J. Phys. Chem. B* 117 (2013) 1978–1987.
- [39] R.R. Kashapov, T.N. Pashirova, S.V. Kharlamov, A.Yu. Ziganshina, E.P. Ziltsova, S.S. Lukashenko, L.Ya. Zakharova, W.D. Habicher, Sh.K. Latypov, A.I. Konovalov, Novel self-assembling system based on resorcinarene and cationic surfactant, *Phys. Chem. Chem. Phys.* 13 (2011) 15891–15898.
- [40] V. Wintgens, C.L. Coeur, C. Amiel, J. Guigner, J.G. Harangozo', M. Zsombor, L. Biczok, 4-Sulfonatocalix[6]arene-induced aggregation of ionic liquids, *Langmuir* 29 (2013) 7682–7688.
- [41] T.N. Pashirova, E.P. Ziltsova, R.R. Kashapov, S.S. Lukashenko, A.I. Litvinov, M.K. Kadirova, L.A. Zakharova, A.I. Konovalov, Supramolecular systems based on 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromides, *Russ. Chem. Bull.* 59 (2010) 1745–1752.
- [42] N.K. Gaisin, O.I. Gnezdilov, T.N. Pashirova, E.P. Ziltsova, S.S. Lukashenko, L.Ya. Zakharova, V.V. Osipova, V.I. Dzhabarov, *Kolloid. Zh.* 6 (2010) 755–761.
- [43] E.P. Ziltsova, T.N. Pashirova, R.R. Kashapov, N.K. Gaisin, O.I. Gnezdilov, S.S. Lukashenko, A.D. Voloshina, N.V. Kulik, V.V. Zobov, L.Ya. Zakharova, A.I. Konovalov, Alkylated 1,4-diazabicyclo[2.2.2]octanes: Self-association, catalytic properties, and biological activity, *Russ. Chem. Bull.* 61 (2012) 113–120.
- [44] A.A. Fedorova, E.P. Goncharova, M.P. Kovpak, V.V. Vlassov, M.A. Zenkova, Influenza virus inactivated by artificial ribonucleases as a prospective killed virus vaccine, *Vaccine* 30 (2012) 2973–2980.
- [45] E.Kh. Kazakova, N.A. Makarova, A.Y. Ziganshina, L.A. Muslinkina, A.A. Muslinkin, W.D. Habicher, Novel water-soluble tetrasulfonatometethyl-calix[4]resorcinarenes, *Tetrahedron Lett.* 41 (2000) 10111–10115.
- [46] L. Zakharova, F. Valeeva, A. Zakharov, A. Ibragimova, L. Kudryavtseva, H. Harlampidi, Micellization and catalytic activity of the cetyltrimethylammonium bromide–Brij 97–water mixed micellar system, *J. Colloid. Interf. Sci.* 263 (2003) 597–605.
- [47] A.R. Tehrani-Bagha, R.G. Singh, K. Holmberg, Solubilization of two organic dyes by anionic, cationic and nonionic surfactants, *Colloid. Surf. A* 417 (2013) 133–139.
- [48] A.R. Tehrani-Bagha, R.G. Singh, K. Holmberg, Solubilization of two organic dyes by cationic ester-containing gemini surfactants, *J. Colloid. Interf. Sci.* 376 (2012) 112–118.
- [49] K. Holmberg, B. Jonsson, B. Kronberg, B. Lindman, *Surfactants and Polymers in Aqueous Solution*, J. Wiley and Sons, Ltd, Chichester, 2002, pp. 562 pp.
- [50] L.Ya. Zakharova, Yu.R. Kudryashova, N.M. Selivanova, M.A. Voronin, A.I. Ibragimova, S.E. Solovieva, A.T. Gubaidullin, A.I. Litvinov, I.R. Nizameev, M.K. Kadirov, Yu.G. Galyametdinov, I.S. Antipin, A.I. Konovalov, Novel membrane mimetic systems based on amphiphilic oxyethylated calix[4]arene: Aggregative and liquid crystalline behavior, *J. Membrane Sci.* 364 (2010) 90–101.
- [51] L.Ya. Zakharova, V.V. Syakaev, M.A. Voronin, F.V. Valeeva, A.R. Ibragimova, Y.R. Ablakova, E.Kh. Kazakova, Sh.K. Latypov, A.I. Konovalov, NMR and spectrophotometry study of the supramolecular catalytic system based on polyethyleneimine and amphiphilic sulfonatometethylated calix[4]resorcinarene, *J. Phys. Chem. C* 113 (2009) 6182–6190.
- [52] V.V. Syakaev, A.R. Mustafina, Ju.G. Elistratova, Sh.K. Latypov, A.I. Konovalov, Head-to-tail aggregates of sulfonatometethylated calix[4]resorcinarene in aqueous solutions, *Supramol. Chem.* 20 (2008) 453–460.
- [53] T.N. Pashirova, E.P. Ziltsova, S.S. Lukashenko, L.Ya. Zakharova, A.I. Konovalov, Micelle formation and catalytic activity hydrophobic mono- and dicationic derivatives of 1,4-diazabicyclo[2.2.2]octane, *Liq. Cryst. Appl.* 1 (2009) 51–61.
- [54] J. Yu, D. Sun, H. Ai, X. Wang, L. Zhai, Novel mechanism for nanotube formation from vesicle: A transition induced by the rearrangement of molecular pairs, *Colloid. Surf. A* 422 (2013) 148–154.
- [55] S. Ghosh, C. Ghatak, C. Banerjee, S. Mandal, J. Kuchlyan, N. Sarkar, Spontaneous transition of micelle–vesicle–micelle in a mixture of cationic surfactant and anionic surfactant-like ionic liquid: a pure nonlipid small unilamellar vesicular template used for solvent and rotational relaxation study, *Langmuir* 29 (2013) 10066–10076.
- [56] J. Chen, J. Hao, Molecular dynamics simulation of cetyltrimethylammonium bromide and sodium octyl sulfate mixtures: aggregate shape and local surfactant distribution, *Phys. Chem. Chem. Phys.* 15 (2013) 5563–5571.