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Controlling the release of hydrophobic compounds by a supramolecular amphiphilic assembly†

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Here, we report a novel approach of using a supramolecular system based on calix[4]resorcinarene and surfactant to facilitate the release of hydrophobic compounds. This finding is an important step towards the development of controlled-release formulations for water-insoluble drugs.

Controlling the release is an essential technique developed in order to increase the effectiveness and decrease the side effects in long-term administration of therapeutic agents.[1] A controlled-release formulation or delivery system can allow drug delivery to the target organ at controlled rates over a specified period. One form of these systems is surfactant aggregates filled with the drug in a liquid state.[2] Amphiphilic molecules aggregate to form nanoscale carriers in particular micelles that can effectively encapsulate hydrophobic guest molecules in aqueous solution.[3] Moreover, the preferred use of surfactants over other dissolution media for *in vitro* dissolution testing of water-insoluble drugs has occurred in recent years because of the mechanistic similarities to *in vivo* dissolution.[4]

Drug-loaded micelles often suffer sluggish drug release at the tumor sites as well as in the cancer cells.[5] Drugs which are physically entrapped in micelles have low diffusion coefficients to qualify for a sustained release profile.[6] However, the rapid release of drug is the large requirement for prompt rise in drug concentration to reach the therapeutic level. To substantially increase drug release rate, external stimuli that can drive transitions between assemblies can be used.[7] Herein, we report the novel strategy that facilitates effective release of hydrophobic compounds from ionic surfactant micelles by oppositely charged calixarene stimulus. Accordingly, the novel calix[4]resorcinarene (CR) sulfonatoethylated at the lower rim and ethanolamine-methylated at the upper rim (Fig. 1) was used to stimulate the release of hydrophobic substrates, including antitumor drug 2,2′-bibenzimidazole (BBI, NCS-322921),[8] from cetyltrimethylammonium bromide (CTAB) micelles.

To better understand the underlying principles of universal release behaviour presented here, we first investigated the structural aspects of the interaction between CR and CTAB in aqueous solution without guest molecules by different independent techniques: surface tension, fluorescence anisotropy and TEM measurements, dynamic and electrophoretic light scattering.

The aggregation properties of the mixed CR–CTAB system with fixed CR concentration (1 mM) were analyzed over a wide CTAB concentration range up to 0.02 M by surface-tension measurements, which were performed by du Nouy ring detachment method. It turned out that at low bulk CTAB concentrations (below the CTAB critical micellar concentration) the surface tension of mixed system with constant CR concentration (1 mM) is lower than that of pure CTAB (Fig. 1). This implies that the CR molecules change the surface active

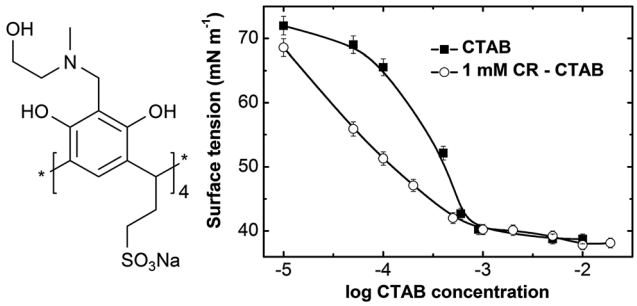

Fig. 1 Molecular structure of CR and tensiometry results for individual CTAB solution and CR–CTAB mixture with fixed CR concentration of 1 mM, H_2O, 25 °C.

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properties and bulk aggregate morphology from the CTAB micelles toward the mixed CTAB–CR aggregates.[9] In the presence of 1 mm CR the breakpoint in the surface tension data was observed at *ca.* 1 mM, and this was identified as the critical concentration for the onset of formation of aggregates from 1 : 1 stoichiometric ratio mixture of surfactant with CR. Based on the ability of sulfonated calixarenes to form host–guest complexes with organic cations[10] we propose that the onset of the plateau observed in the mixed system is owed to the formation of amphiphilic 1 : 1 host–guest complexes which form mixed assemblies. Therefore, despite the fact that CMC remained practically unchanged, the complexed CR acts as a new type of surfactant that demonstrates enhanced surface activity and promotes aggregate formation. This idea is reliably supported by data from other methods that are discussed below.

To complement the results obtained by surface-tension measurements, DLS measurements were taken under comparable conditions. The results are summarized in Fig. 2a. It can be seen that the mean size of the aggregates varies between 130 nm and 380 nm for 1 mM CR in the presence of CTAB. These particle sizes are characteristic of vesicular aggregates. The mean hydrodynamic diameter is highly dependent on the concentration of CTAB in the presence of CR (1 mM). This is a consequence of the variable vesicle composition as a function of added surfactant. As 5 mM CTAB is added to the 1 mM CR solution the vesicle grows as a consequence of charge neutralization, which leads to a decrease in the aggregate charge density[11] and allows the aggregates with lower curvature to occur. As the surfactant concentration is increased up to 19 mM, the vesicle becomes richer in CTAB and have reduced hydrodynamic diameter. Thereby, as the CTAB concentration increases above 5 mM the CR content starts to redistribute to all vesicles present in solution.

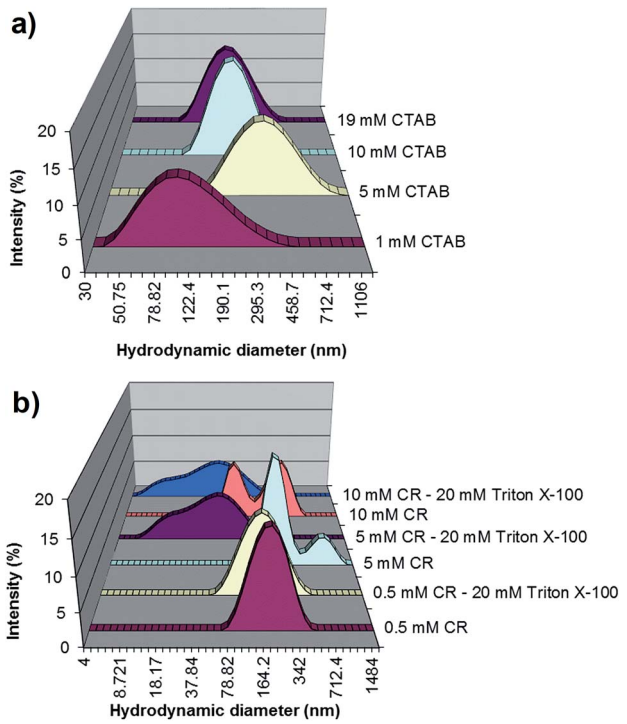

Fig. 2 DLS results obtained from (a) 1 mM CR–CTAB solutions and (b) 10 mM CTAB–CR solutions in absence and presence of 20 mM Triton X-100, H_2O, 25 °C.

Taking into account the ionic nature of the species involved, additional information can also be derived from zeta-potential measurements (Fig. S7, ESI†). As could be expected, single 1 mM CR solution exhibits a highly negative zeta potential (*ca.* −53 mV) contributing by sulfonate fragments. By addition of the cationic CTAB, an increase in the zeta potential (towards more positive values) is observed giving rise to neutral complexes, which exhibit charge reversal on further addition of surfactant. Furthermore, the zeta potential of single CTAB aggregate is significantly higher than that of CTAB–CR mixture. Therefore, the most probable mechanism of CR–CTAB complex formation is an electrostatic attraction of surfactant cations to sulfonate groups of CR, which binding degree is higher as compared to CTAB bromide counter-ion. The electrostatic attraction between sulfonate groups of CR and cationic head groups of CTAB combined with the hydrophobic interaction involving the CTAB alkyl tails contribute to the formation of vesicles.[12] In addition, the geometry of the hydrophobic moiety of surfactant building block is changed with sulfonate residues of CR switching from more conic structure with a higher curvature to the quasi-cylindrical shape with a lower curvature and an increased cross-sectional area of the hydrophobic chain volume. Such a conformational change triggers the collapse of the micelles into a vesicular structure.

It was noticed that samples became turbid when 1 mM of CR is mixed with CTAB at concentrations between 0.5 mM and 20 mM and precipitated near the charge neutrality point. This behavior is common in some catanionic systems.[13] It is well known that the associative phase separation is usually a physicochemical phenomenon caused by the strong electrostatic interaction between two oppositely charged species so that they form an insoluble solid in the vicinity of charge neutrality zone.[14] The DLS results of the dispersion containing 1 mM of CR and 5 mM of CTAB, where all four negative charges of CR sulfonate groups are completely neutralized by cationic CTAB, indicate a similar phenomenon, in which a monomodal size distribution with a hydrodynamic diameter around 382 nm is observed, suggesting vesicle formation (Fig. 2a). The presence of these large vesicles is the reason for the opaque appearance of the dispersion.

Interestingly, CR spontaneously self-assembles into vesicles of various sizes and shapes in water (Fig. S8, ESI†). These noncovalent self-assemblies probably consist of CR interacting laterally with π-stacking of the aromatic walls. Additional driving force of CR vesicles is considered to be the strong hydrogen bonding interaction among the ethanolamine-methylated and hydroxyl groups. Therefore, the presence of CR in surfactant system probably promotes the formation of multilamellar vesicles of different sizes through intermolecular hydrogen bonding between CR layers. An increase of CR fraction from 0.5 mM to 10 mM in micellar (10 mM) surfactant solution leads to an increase in polydispersity index (PdI) from

0.127 to 0.355. At 5 and 10 mM CR, the size distributions obtained from DLS are bimodal, and the larger-sized vesicles are formed (Fig. 2b).

Since the lipid composition of the vesicles is easily disrupted by Triton X-100,[15] we investigated effect of this surfactant on stability of vesicles obtained in 10 mM CTAB–CR solutions. As seen from the Fig. 2b, the addition of Triton X-100 in solution with a low CR content (0.5 mM) does not significantly affect the size and polydispersity of the vesicles, which may be associated with Triton X-100 integration into the vesicle bilayer without disassembling the latter. At higher CR content (5 and 10 mM), however, hydrodynamic diameter decreases by approximately an order of magnitude, indicating the vesicle-to-micelle transition.[16] Such different Triton X-100 effects are probably due to the fact that the stability of the vesicles depends on the CR content. When 0.5 mM CR is added to 10 mM CTAB solution, the vesicles formed are stabilized by electrostatic interactions between the headgroups of CTAB through the mediation of all four CR sulfonate-ions. As the CR concentration increases, so that surfactant content becomes by more than 4-fold lower, the vesicles formed acquire free negatively charged sulfonate-ions from CR, thereby slightly weakening van der Waals forces among surfactant molecules, which is reflected in PdI increase (Fig. S9, ESI†). Thus, Triton X-100 addition to vesicular solutions with a high CR content, where the number of CR molecules per four surfactant molecules is greater than one, leads to the destruction of the vesicles.

To characterize the aggregate morphology of the mixed system, the method of the steady-state fluorescence anisotropy probing was used. The probe 1,6-diphenyl-1,3,5-hexatriene (DPH) is mostly used in such measurements.[17] Being hydrophobic, DPH should prefer the hydrophobic environment of the aggregates. Therefore, its rotational diffusion and hence the fluorescence anisotropy will be influenced by the fluidity of the hydrophobic microenvironment of the aggregates. It is known[18] that fluorescence anisotropy values of DPH embedded in spherical and rod-like micelles are lower than 0.1; bilayers or vesicles show anisotropy around 0.1 or higher. For single CR solutions with concentration range of 0.5–10 mM, the DPH anisotropy is nearly constant (0.10–0.11) (Fig. S10, ESI†), consistent with the CR vesicular structures that were confirmed to be in reasonable agreement with DLS results (Fig. S8, ESI†). In the absence of CR, 10 mM CTAB micelles showed anisotropy value 0.01, this was well below 0.1. Addition of amounts of CR from 0.5 mM to 0.9 mM made significant increase in the anisotropy. In the presence of these CR amounts, anisotropy largely increased, starting from 0.125 it went up to 0.209. The micelle-to-vesicle transition was thus, supported from the anisotropy data. Further increasing CR content up to 10 mM results in a decrease in anisotropy, as expected for lipids in a disordered phase, which is also in line with an increase in PdI from DLS data. In other words, these vesicles with a higher CR concentration were more fluid than those with up to 1 mM CR as judged by the decrease of anisotropy. As in the case of DLS data, Triton X-100 induced a different effect on DPH anisotropy depending on CR content. It caused leakage of fluorescent dye only from lipid vesicles with 5 and 10 mM CR content, and not for 0.5 mM to 0.9 mM, and consequently, caused greater increases in the fluidity of lipid vesicles with higher CR content (Fig. S10, ESI†).

TEM measurements also directly supported vesicle formation of the CTAB–CR combinations. The micrographs of the single 10 mM CTAB and mixed 10 mM CTAB–0.5 mM CR species are depicted in Fig. S11 (ESI†). In the absence of CR CTAB micelles at 10 mM look spheroidal with diameters of 2 nm (Fig. S11a, ESI†). The average size of the CTAB–CR particles was in the range of 20–60 nm, indicating convincingly the vesicular structure (Fig. S11b, ESI†). The solvent removed (or dried) samples in the TEM produced lower sizes than those found from the DLS measurements in the CTAB–CR solution.

To elucidate the nature of aggregates formed at the different CR–CTAB ratio, the solubilization capacity for hydrophobic model drug was further evaluated by studying the solubilization of Sudan I as a function of the CTAB concentration (Fig. 3a). Sudan I is solubilized by nonpolar interior of the aggregates that is reflected by the absorbance value in the UV spectrum centered at 486 nm. The experiments performed with Sudan I confirmed that morphology of mixed aggregates differs from that of aggregates formed from the individual CTAB. At the presence of CR the absorbance of Sudan I is dramatically lower than for individual solutions of surfactant (Fig. S12, ESI†). This can be caused by aforementioned reassembly of CTAB micelles, resulting in disruption of the hydrophobic core and release of the Sudan I.

To verify this assumption, the binary systems with fixed CTAB (10 mM) and varied CR were also examined by the dye solubilization method (Fig. 3b). The dye absorbance in pure CTAB solution (10 mM) is *ca.* 0.98, indicating that rather high amount of dye is solubilized into the surfactant micelles. The amount of solubilized Sudan I decreases upon addition of CR, which once again confirms the interaction between CR molecules and CTAB micelles. The presence of CR likely destroys micelles, and therefore, there are aggregates of other morphology in the sample. We also studied the Sudan I solubilization in 10 mM CTAB–CR solutions, adding an appropriate amount of CR to 20 mM CTAB solutions saturated by probe. As can be seen from the Fig. 3b, the dye absorbance decrease is not sharp as in the above case, probably indicating that Sudan I is still preferring to lodge in the newly formed vesicle bilayer.

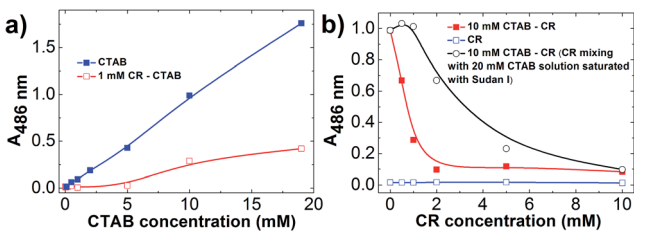

Fig. 3 (a) Dependences of absorbance of Sudan I at 486 nm on CTAB concentration in individual CTAB solution and in CR–CTAB mixture with fixed CR concentration of 1 mM, H_2O, 25 °C; (b) dependences of absorbance of Sudan I at 486 nm on CR concentration in individual CR solution and in CR–CTAB mixture with fixed CTAB concentration of 10 mM, H_2O, 25 °C.

Nevertheless, in this case the presence of an equimolar amount of CR leads to the complete destruction of the hydrophobic core of CTAB micelles, thereby releasing encapsulated hydrophobic substrate.

Solubilization of Sudan in 10 mM CTAB–CR solutions was also studied in the presence of Triton X-100. The results in Fig. S13 (ESI†) suggest that a very small change in absorbance of the Sudan I in 10 mM CTAB–0.5 CR solution occurs after the addition of Triton X-100 (20 mM). But in the case of 10 mM CTAB with 5 mM and 10 mM CR, a significant increase in probe absorbance was observed in the presence of Triton X-100, indicating that vesicles were disrupted in the presence of Triton X-100 and smaller structures such as mixed micelles were formed.[16] These results are consistent with estimates of the lipid order from anisotropy values for DPH and the size change from DLS.

One can envision that the micelles formed by CTAB encapsulate hydrophobic molecules within the hydrophobic moieties and release them in response to CR. With this in mind, the hydrophobic drug with fluorescent properties, BBI, was encapsulated in surfactant micelles, and free BBI was removed by filtration. The fluorescence emission spectrum of BBI solubilized in CTAB exhibits a maximum centered at 367 nm, while release of BBI from the interior of a micelle was accompanied by a decrease in fluorescence emission upon addition of CR (Fig. 4). It is known that fluorescence of hydrophobic probe is quenched in the presence of the dimethylaminomethylated resorcinarene due to the electron-donating amino groups.[19] In the acid medium (pH 2) the quenching by CR significantly decreases due to the protonation of the amino groups and the reduction of the process of photoinduced electron transfer to the excited state. To eliminate the possibility of BBI quenching in our case, we examined its fluorescence under acidic conditions. The fluorescence intensity of BBI in 10 mM CTAB solution at pH 2 is lower than at pH 7, probably due to a partial release of the protonated BBI form from the hydrophobic part of surfactant micelles. As in the case at pH 7, addition of CR decreases BBI fluorescence intensity, indicating the absence of the drug in mixed CR–CTAB aggregates. Thus, the BBI release from CTAB micelles can be followed through the fluorescence changes of drug. These data correlate well with the UV-spectroscopy data (Fig. S14 (ESI†)). If the BBI presence in micellar CTAB solution gives the absorption band, no spectral change was observed for mixed system CR–CTAB by addition of BBI. Such spectral changes indicate that the BBI is capable of binding the CTAB micelles, but does not bind to mixed aggregates formed in the presence of CR.

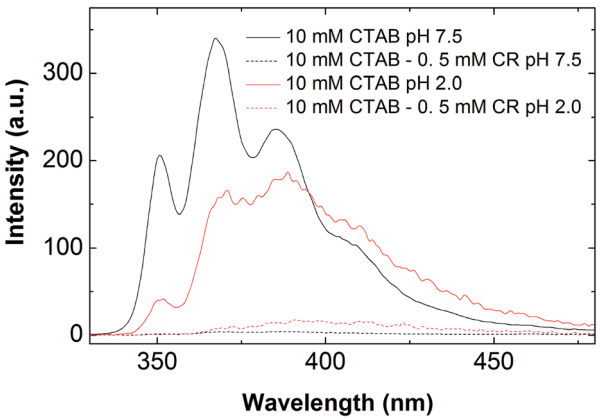

Fig. 4 Emission spectra of BBI measured in single 10 mM CTAB solutions (strong emission) and in mixed 10 mM CTAB–0.5 mM CR solutions (no emission) at pH 2.0 and 7.5, H_2O, 25 °C.

Summarising the results obtained from solubilization of Sudan I and BBI fluorescence, the modification of drug-loaded micelles by CR promotes the rapid and complete release of encapsulated drug. This phenomenon can be explained by considering that CR triggers the phase transition from CTAB micelles to mixed vesicles. The presence of CR in micellar CTAB solution results in the electrostatic attraction between oppositely charged lower rim of CR and head-group of CTAB. This may be followed by a counterion-induced vesicle formation which is typical for catanionic systems[13] and triggers the collapse of a micellar structure into the vesicles with concomitant release of the encapsulated hydrophobic drug. This result is of importance from the viewpoint of developing controlled-release formulations for water-insoluble drugs.

Conclusions

The results described here demonstrate that addition of oppositely charged calix[4]resorcinarene to surfactant micelles induced the collapse of the spherical micelles into vesicles. Remarkably, the small globular micelles were observed to transform into vesicles at the low amount of CR, which can be used to trigger the release of the encapsulated hydrophobic guest molecules. This stimuli-responsive supramolecular system might have potential application for selective drug delivery in tumor cells.

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