# Novel Nanotubes from a Cationic Surfactant and an Anionic Stiff Aromatic Counter-Ion

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A novel class of nanotubes (NT) is reported which consists of two components, a cationic surfactant cetyltrimethylammoniumbromide (CTAB) and an anionic UV absorber, 2-phenylbenzimidazole-5-sulfonic acid (PBSA). When aqueous solutions of the components are mixed, a turbid low-viscosity solution is formed immediately. This solution is stable for several days. Then, within 1 day, the turbid samples are transformed into transparent, isotropic soft gels that contain thin single-walled tubuli (SWNT). The SWNT have been characterized by cryo-TEM micrographs. The NT have an extremely narrow size distribution of the outer (o.d.) and inner (i.d.) diameters. The tubes have an o.d. of $13 \pm 0.5$ nm and an i.d. of about 6 nm. Despite their small diameter, the NT are extremely stiff with a persistence length $l_p$ greater than several micrometers. It is assumed that the tubuli consist of bilayers of the cationic and anionic compounds with a one-to-one ratio. In solution, the tubuli seem to be stabilized by the adsorption of one of the excess amphiphilic compounds.

## Introduction

Typical aggregates that are formed in surfactant solutions are globular, threadlike, disclike micelles and vesicles.[1] All aggregates can actually be formed from one and the same surfactant by controlling the curvature of the micellar interface.[2] This is usually done by a change of thermodynamic parameters such as temperature, pressure, or salinity or by adding cosurfactants or other surfactants, in particular, when it comes to ionic surfactants.[3] We now have a good understanding of the shape of the micelles and the properties of micellar solutions. However, there is one more type of structure for which little is known, the single-walled tubuli (SWNT) or so-called nanotubules (NT). These structures are usually discovered by chance. Sometimes they are observed in combinations with uni- or multilamellar vesicles. They usually have diameters between 20 and 50 nm. At present, it is not known what controls their diameter and what are the conditions for their formation. An excellent summary of NT has recently been published by T. Shimizu et al.[4] The NT usually are fairly stiff with persistence lengths of hundreds of nanometers.

Most of the discovered NT are formed from a single amphiphilic compound and not from mixtures.[4,5] In most cases, the compounds were double-chain phospholipids. At present, there is no generally valid strategy available according to which NT can be prepared. In this work, we would like to report on novel single-walled nanotubes which we have discovered by chance and which are composed of two different amphipilic compounds, namely, from a cationic surfactant (CTAB) and a negatively charged amphiphilic, stiff molecule with an aromatic ring system, 2-phenylbenzimidazole-5-sulfonic acid (PBSA). We will briefly describe the preparation of the novel NT and characterize the NT by cryo-TEM measurements. We will also describe the rheological properties of the samples that contain NT. We hope that the novel NT will help to understand better the conditions under which NT are formed. For the present system, it is possible to control several parameters (chain length of the surfactant, mixing ratio of the components, ionic strength) of the solutions from which the NT are formed.

## Preparation of the Nanotubes

The original goal of this investigation was to study the different phases which are formed between the negatively charged aromatic compound 2-phenylbenzimidazole-5-sulfonic acid (PBSA, trade name Eusolex 232 from Merck; for the structure, see Figure 1) and the cationic surfactant CTAB. It was expected that the sequence of the phases would be similar for this system as for other catanionic systems of surfactants or of combinations of aromatic negatively charged counterions with cationic surfactants.[6,7] It has turned out, however, that this was not the case. First of all, the compound PBSA in its acidic form is not soluble in water, and the acid had to be titrated with NaOH to make the compound soluble. The titration curve is shown in Figure 1.

Obviously, the acidic proton of the compound does not dissociate in water but is located on the imine group of the compound. As the titration curve shows, the acidic form of PBSA has a $pK_s \approx 5.6$. In the neutralized form, the compound is soluble, and its solutions were used to mix with CTAB solutions. Samples which were prepared from the Na salt of 10 mM PBSA and 10 mM CTAB are shown in Figure 2.

The mixtures appear at first to look similar to other catanionic mixtures.[6] For such combinations, one often observes the

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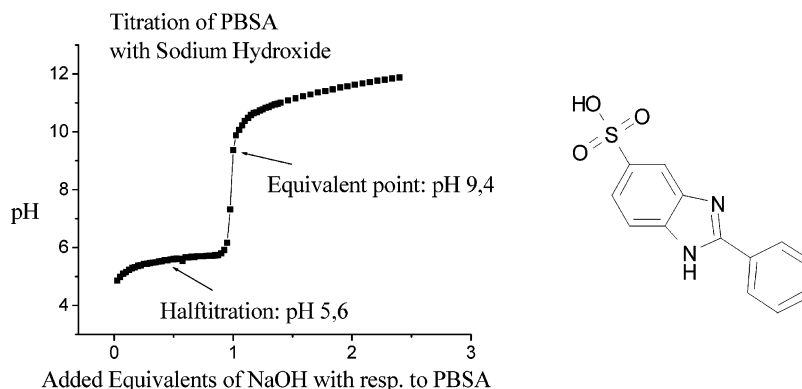|| University of Bayreuth, BZKG.

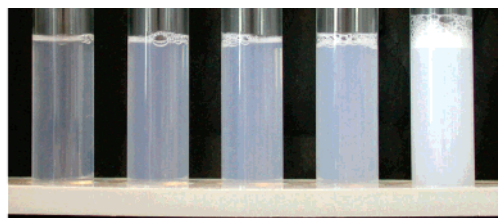**Figure 1.** Titration curve of PBSA and its molecular structure.



**Figure 2.** Photograph of freshly prepared mixtures of PBSA (Na salt) with CTAB at given molar ratios. Total concentration was 10 mM; $T$ = 22 °C.

formation of a precipitate at equimolar concentration but vesicles in mixtures which have an excess of one surfactant.[7] The vesicles form more or less instantaneously upon mixing of the surfactants. In such a situation, the vesicles are ionically charged from the excess surfactant, but the ionic charge is shielded by the salt that is formed from the counterions of the two ionic surfactants. As a consequence, there is little electrostatic interaction between the vesicles, and the vesicle solution has a low viscosity if the surfactant concentration is below 50 mM. The vesicle state that is reached in catanionic systems is very similar as the state that is reached in the present system. The phases are optically isotropic, of low viscosity, and are turbid, much more turbid than the solutions of both components.[8]

For catanionic mixtures, one usually observes a viscous sample when one component is added in small amounts to the other compound. The viscosity is the result of entangled wormlike micelles that are formed in the mixtures. In the present situation, this was not the case. The mixtures 9:1, 8:2, 7:3, and 6:4 (PBSA/CTAB) as shown in Figure 2 were all of low viscosity. All of the samples were turbid.

In this short investigation, we shall concentrate on the mixtures with excess PBSA, and we will not investigate in detail the 1:1 mixture and the mixtures with excess CTAB. These mixtures are also interesting, and the structures in these samples

and the properties of the samples will be described in a later, larger paper.[8] More experimental data, in particular, SAXS and cryo-TEM data, are already available on other mixtures, and the results thereof are consistent with the data reported in this manuscript.

The samples of this investigation, on standing still for a longer period of time (several days), become clear again and also viscous. Actually, the samples behave now like weak soft hydrogels.[9] The samples are optically isotropic and can be turned upside down for a short time without any noticeable flow. When the samples are tilted as in Figure 3, one notices a moving of the phase boundary and some birefringence in the area where the phase has been deformed by gravity. On return to the vertical position, the birefringence disappears again. When the gel-like phase is strongly shaken, it becomes much less viscous, and the viscosity does not recover to the value it has had before shaking even though it looks very much the same. It seems that the structure which had formed in the sample had been irreversibly destroyed or broken during shaking.

Figure 4 shows a sample that contains 16 mM PBSA (Na salt) and 4 mM CTAB right after the mixing process at 25° C and a sample with the same composition after ca. one month. The sample right after preparation is turbid, while the older sample is now transparent.

The viscosity of the freshly prepared solution is a Newtonian fluid with a viscosity close to water. In Figure 5a, a rheogram of a one-month-old sample with 80 mM PBSA (Na salt) and 20 M CTAB is shown after it had been cooled to 15° C and, in Figure 5b, after the temperature has been raised again to 25 °C. Figure 5a shows the typical signature of a viscoelastic fluid with a yield stress value. At low frequencies, both storage and loss moduli are independent of frequency, and $G'$ is about an order of magnitude larger than $G''$.

When the sample is strongly shaken, the viscoelastic properties are irreversibly destroyed. As the rheogram in Figure 5b
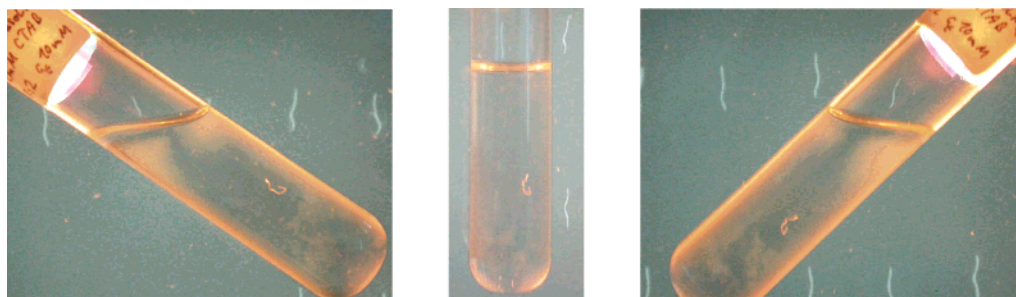


**Figure 3.** Photographs of a gelled mixture of PBSA (Na salt) with CTAB: molar ratio 8:2, total concentration 10 mM, tilted between crossed polarizers.

Letters

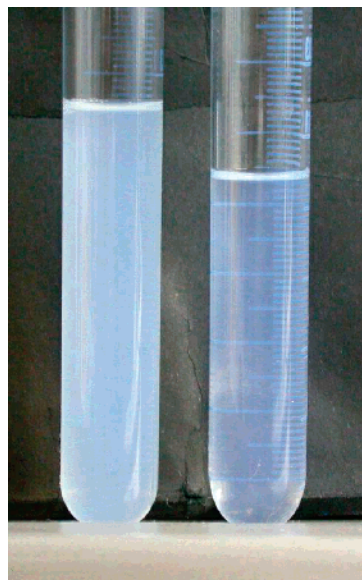*J. Phys. Chem. B, Vol. 110, No. 36, 2006* **17699**



**Figure 4.** Photographs of two samples, each containing 16 mM PBSA (Na salt) and 4 mM CTAB. Left: in direct light. Right: between crossed polarizers. In each photograph, the left sample is ca. 1 h, the right sample ca. 1 month old.
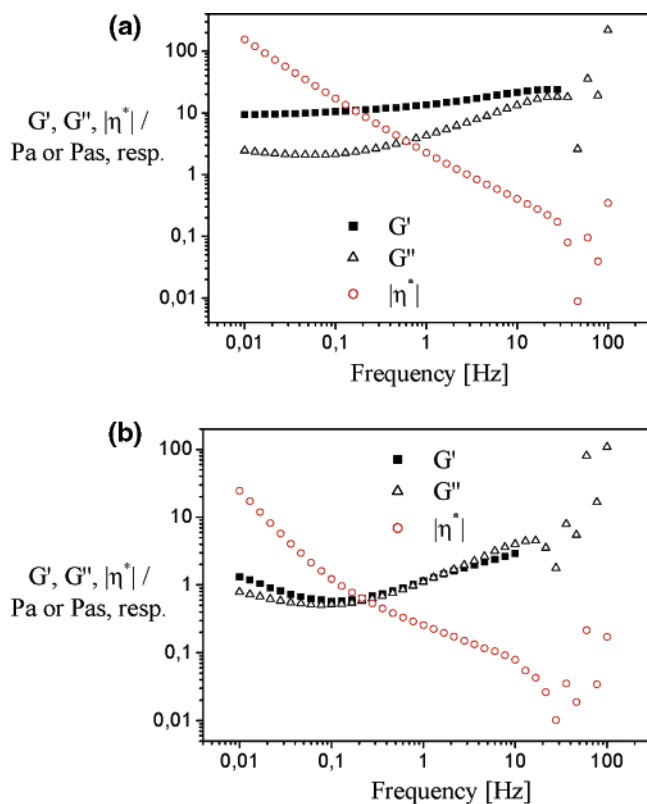


**Figure 5.** (a,b) Rheograms of a sample containing 80 mM PBSA (Na salt) and 20 mM CTAB: in (a) at 15 °C; in (b) at 22 °C.

shows, the shear modulus $G'$ also breaks down when the samples are heated above 20° C.

The turbidity of the samples right after preparation is an indication that large aggregates have been formed in the mixed samples. These aggregates cannot be large wormlike micelles, because samples with wormlike micelles are usually completely transparent and for CTAB micelles usually[10] viscous. Turbidity could also be the consequence of a coacervate phase. This, however, can also not be the case, because the turbid phases of the mixed samples are very stable and remain homogeneous even after long times. It is from this turbid state that new structures develop. The new structures must develop by a

nucleation mechanism when the temperatures of the samples are below a critical temperature. The turbid solutions can be undercooled for a long time. We have observed samples which for up to 10 days did not show any noticeable changes in turbidity and viscosity. On the 11th day, however, the samples were transparent and had gelled. Once the new structures are formed, they have a well-defined melting temperature. The situation is then very similar as for ionic surfactant solutions that are cooled below the Krafft temperature.

**Cryo-TEM Micrographs**

A micrograph was produced from a 10 mM solution of a 8:2 (PBSA/CTAB) mixture by the cryo-TEM method. Two micrographs with different magnification are shown in Figure 6a,b. All the micrographs show SWNT with an extremely small polydispersity in diameter and long lengths of many micrometers. The outer diameter is around 13 nm, and some of the tubuli are longer than 10 $\mu$m. The axial ratio is therefore larger than 1000. It is therefore likely that the structural relaxation times that can be determined from the rheograms are given by the rotation time constants of the tubuli. The tubuli are very stiff with a persistence length of several micrometers, as can be judged from the mean curvatures of the tubuli. In comparison to other tubuli which have been discovered in other lipid systems, the diameter of the present systems seem to be on the smaller side.[11,12]

In some of the micrographs, one can also notice a few vesicles (Figure 7). It is likely that these vesicles are leftover from the main micellar structures that were formed during the mixing process and were responsible for the turbidity of the samples.

**Formation Mechanism of the Tubuli**

At present, it is not clear why the tubuli are formed from the two amphiphilic compounds. On the basis of the available experimental information, we would like to discuss a possible mechanism for their formation. The appearance of the samples right after the mixing process, and the few vesicles that are visible in the cryo-TEM micrographs, can be used as evidence that vesicles are formed instantaneously during the mixing process. It is likely that in this respect the system behaves in the same way as other catanionic systems where the vesicle formation has been
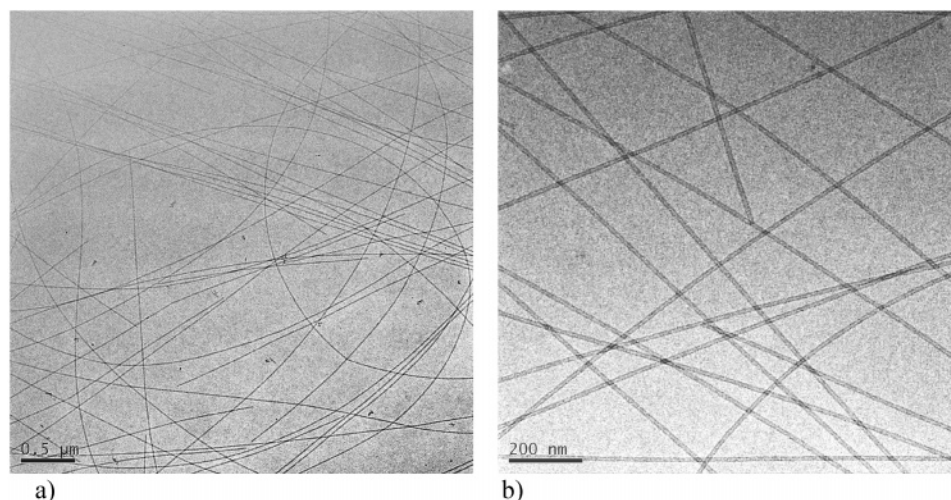
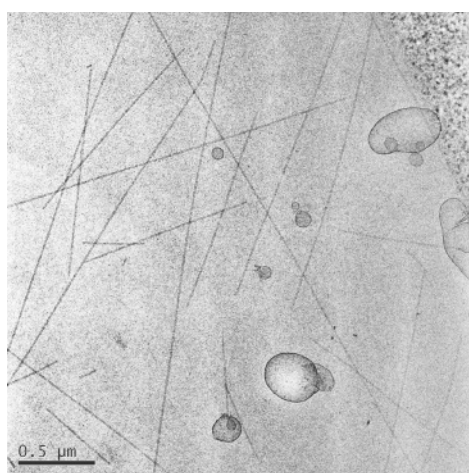**Figure 6.** (a,b) Cryo-TEM micrographs of a sample of 8 mM PBSA (Na salt) and 2 mM CTAB at different magnifications.



**Figure 7.** Cryo-TEM-micrograph of the sample of Figure 6 showing vesicles.



**Figure 8.** Sketch of the assumed way the amphiphiles arrange to form bilayers that make up the cylinder walls.

followed by time-resolved SANS measurements.[13] Within milliseconds, these systems form mixed-bilayer-type micelles which close to vesicles when the bilayer aggregates are large enough. The formation of the bilayers and the closing process of the bilayers to vesicles have different time constants. The vesicle formation is, however, complete in fractions of seconds.

In the present situation, it is likely that the composition of the vesicles is the same as the mole ratio of the two compounds in the solution and the two components are in the l.c. state. Nuclei of the NT with a 1:1 ratio of the two components are then formed in the bilayer of the vesicles and, when formed, grow rapidly into the NT, thereby using up all the material in one vesicle. The excess compound is present in an adsorbed state on the aggregates. The bilayer state in the 1:1 ratio of the two compounds is probably a semicrystalline interdigitated state like that sketched in Figure 8. The reason for the interdigitated state is the different length of CTAB and PBSA. The PBSA molecule is a stiff molecule that, unlike CTAB, cannot form kinks. It is mainly for this reason that the bending constant of the bilayer of the investigated systems is much higher than for other catanionic combinations which can form kinks. A nucleus formation is a rare event. However, when the nucleus is formed, it grows quickly and transforms all the bilayer material of one vesicle into a single tubulus which is thermodynamically more stable than the vesicles.

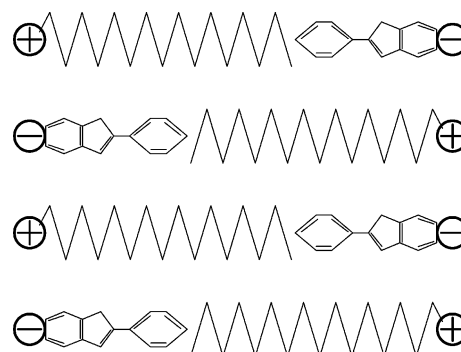Preliminary experimental evidence indicates that all tubuli have diameters which are independent of the mixing ratio of the samples. We surmise therefore that the diameters of the tubuli are determined by the bending constant of the one-to-one bilayer.

## Conclusions

The existence of single-walled nanotubes (SWNT) with an o.d. of 13.5 nm and a length of more than 10 $\mu$m is reported. The novel NT are formed from a cationic surfactant and the negatively charged stiff hydrophobic counterion, PBSA. Aqueous dispersions of the NT are stable and have viscoelastic properties. The wall of the NT seems to consist of a bilayer with a molar ratio of one of the two amphiphilic compounds.

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